FRIEDEL-CRAFTS ACETYLATION OF 1- AND 2-METHYLNAPHTHALENE

By

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FRIEDEL-CRAFTS ACETYLATION OF 1- AND 2-METHYLNAPHTHALENE

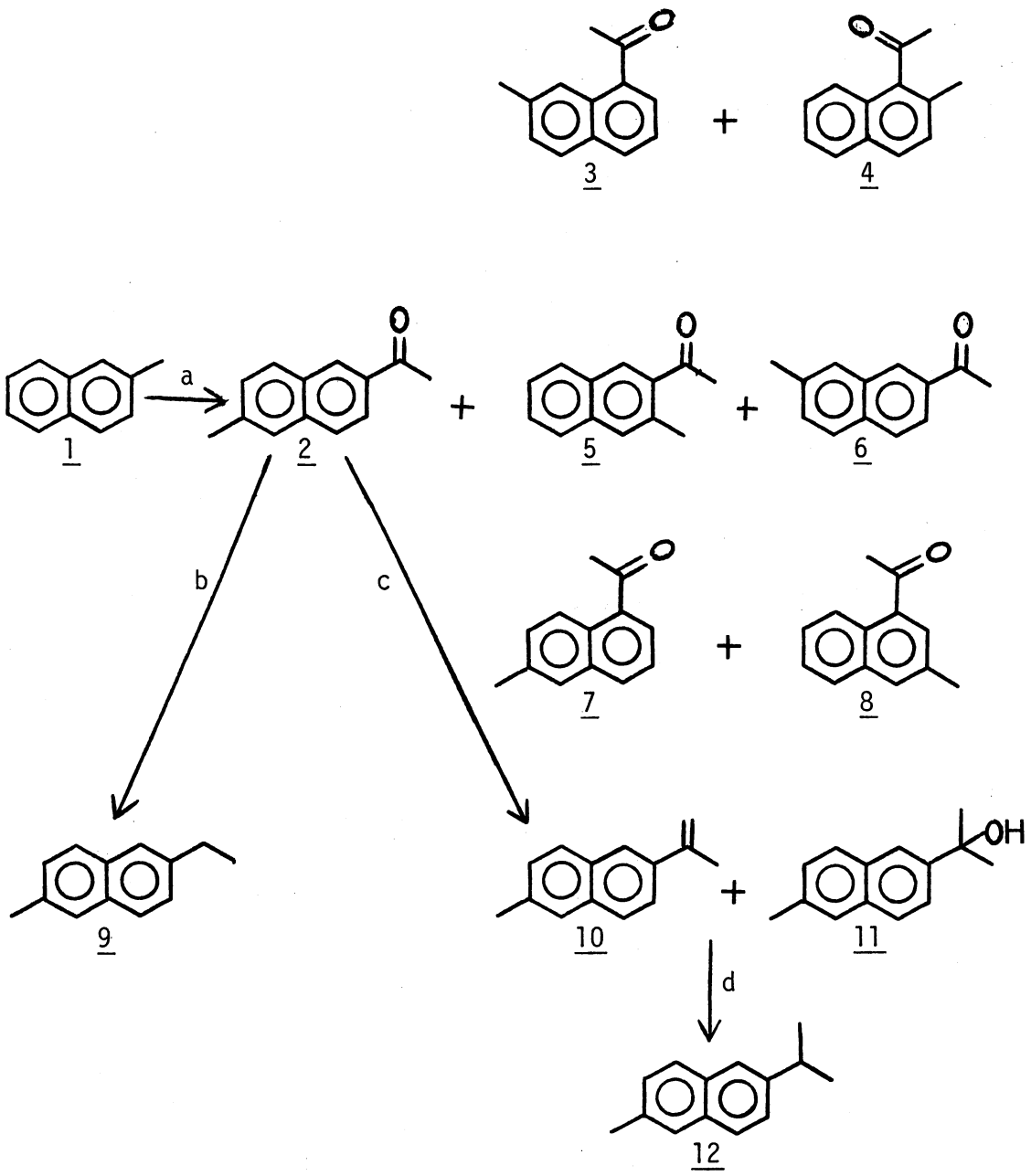
CHAPTER I

INTRODUCTION

One hundred years ago Friedel and Crafts published the first observation on the action of aluminum chloride in an organic reaction. This work resulted in numerous synthetic methods bearing their names.[1a] Friedel-Crafts reactions, as we know them today, have grown to perhaps the most versatile and frequently used synthetic tool in organic chemistry.[1a,b]

This study was undertaken to prepare pure samples of 9 and 12 for use in thermodynamic studies.[2] After considering methods for synthesizing these compounds, it was felt that acetylation, as shown in Figure 1 via the Friedel-Crafts reaction, and separation of the methylacetonaphthones would be the method of choice.

Several studies preceding this paper have dealt with Friedel-Crafts acetylation.[1b,3a,b,4,5,6,7,8,9] These studies have concentrated on variations of the aromatic nucleus, acyl component, the catalyst, or reactant ratios.[3b,10,11,12] There are few studies, if any, that take into account the methods of addition, controlling temperature versus time, and isomerization and diacetylation.



[a] CH_3COCl, $AlCl_3$, solvent, 5-10°C. [b] $NH_2NHCONH_2 \cdot HCl$, CH_3CO_2Na; KOH, $O(CH_2CH_2OH)_2$, Δ. [c] CH_3Li-LiBr, $(CH_3CH_2)_2O$; dil HCl, $NH_2NHC_6H_3(NO_2)_2$, $C_6H_5CH_3$, Δ; Column of neutral Al_2O_3, C_6H_{14}. [d] H_2, Pd/C, CH_3CO_2H, Δ.

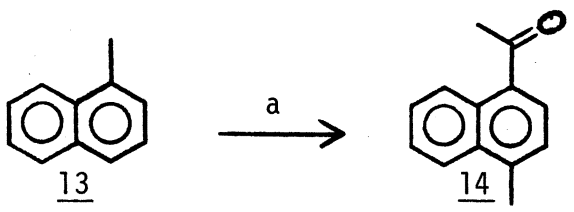
Figure 1. Synthesis of 2-Ethyl-6-methylnaphthalene (9) and 2-Isopropyl-6-methylnaphthalene (12).

CHAPTER II

HISTORICAL

Friedel-Crafts acetylation of monomethylnaphthalenes has been studied extensively.[3a,b,4,5,6,7,8,9,10,11,12]

Haworth and Marvin[9] reported that 1-methylnaphthalene (13) reacted in nitrobenzene solution in the presence of aluminum chloride with acetyl chloride to give 4-methyl-1-acetonaphthone (14). A similar



13 14

[a] CH_3COCl, $AlCl_3$, $C_6H_5NO_2$.

Figure 2. Acetylation of 1-Methylnaphthalene (13) to 4-Methyl-1-acetonaphthone (14).

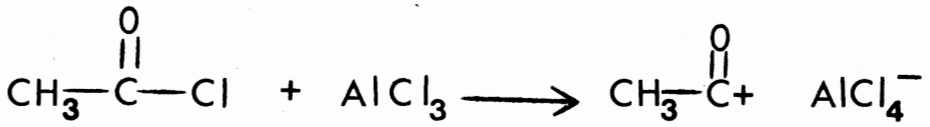
reaction using succinic anhydride gave β-(4-methyl-1-naphthoyl)propionic acid.

Aluminum chloride-catalyzed acylations of 2-substituted naphthalene generally occur at the 1-position.[8] Dziewoński and Brand[4] effected the acetylation in carbon disulfide at room temperature which constitutes a

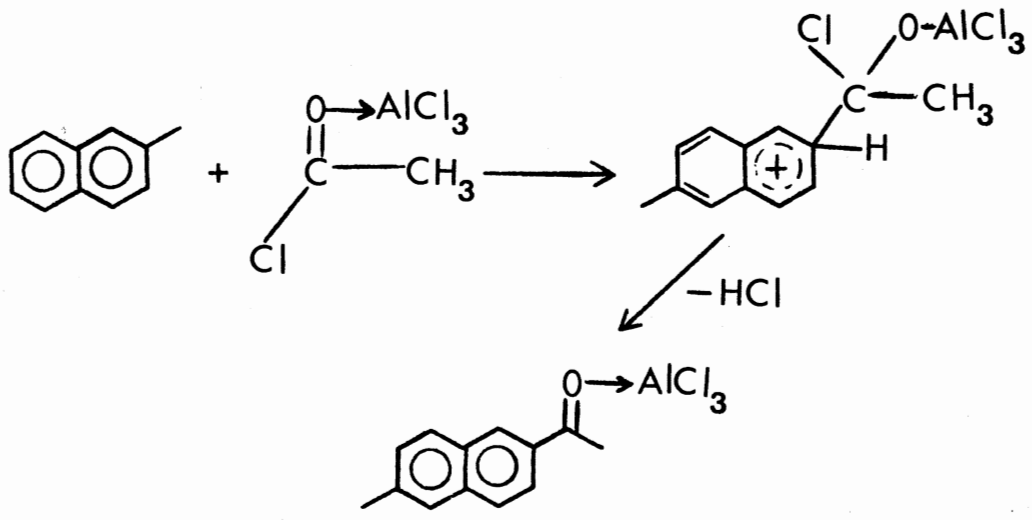
good method of preparing 6-methyl-2-acetonaphthone (2) and 7-methyl-1-acetonaphthone (3), separable by their oximes. They also incorporated the Elbs addition procedure which favors β-substitution.[8] Kon and Weller[5] repeated this reaction but obtained only the 6-isomer 2; they recommended nitrobenzene as solvent for a better overall yield of 2. 6-Methyl-2-acetonaphthone (2) was also obtained by a method which uses isopropenyl acetate as an acylating agent.[6] Wells and Alcorn[7] reported the formation in nitrobenzene, acetyl chloride, and aluminum chloride of 2 and 3 as the major components, together with some 2-methyl-1-acetonaphthone (4) and possibly 3-methyl-1-acetonaphthone (5). More recently Gore, Siddiquei, and Thorburn[3b] as well as Leahey and Prail[3b] obtained 7-methyl-1-acetonaphthone (3) from a Friedel-Crafts acetylation carried out in chloroform solution. These workers also reported the formation of 2, 3, and 4 by the action of acetyl perchlorate on the hydrocarbon 1 in benzene or nitromethane solution. Earlier work by Bonnier and Rinaudo[12] and Gore[3b] showed the Friedel-Crafts acetylation of 1 in various solvents. In the acetylation of 2-methylnaphthalene (1) reported by Rinaudo and Bonnier,[12] the β position was shown to be favored in nitrobenzene and the ∝ position in chloroform and carbon disulfide. The claimed order of reactivity is 1>8>6>>4>5>7. The relative rate constants for reaction at the various positions of 1 is lower than expected due to steric hindrance. In this work constant proportions of isomers 5, 6, 7, and 8 were reported, with 2 being formed in greater amounts than 4 in nitrobenzene solution, and in smaller amounts in the other two solvents. The isomers 6, 7, and 8 were not separable and the formation of 5 was only indicated, but not proven.[12] Gore[3b] reported the presence of seven isomers. The proportions of the isomers

formed is dependent upon the solvent and to a lesser extent on the addition procedure employed.[3b] The percentages of the individual isomers formed vary within wide limits: 2 (7-73%), 3 (9-59%), 4 (0.3-3.3%), 5 (0.8-14%), 6 (4-58%), 7 (0.4-2.0%), and 8 (0.8-5.5%).[3b] (Figure 1)

The mechanism of Friedel-Crafts acylation is not completely understood but at least two mechanisms probably operate, depending on the conditions.[13,14,15,16,17] In most cases, the attacking species is the acyl cation either free or an ion pair, formed as follows.[15]

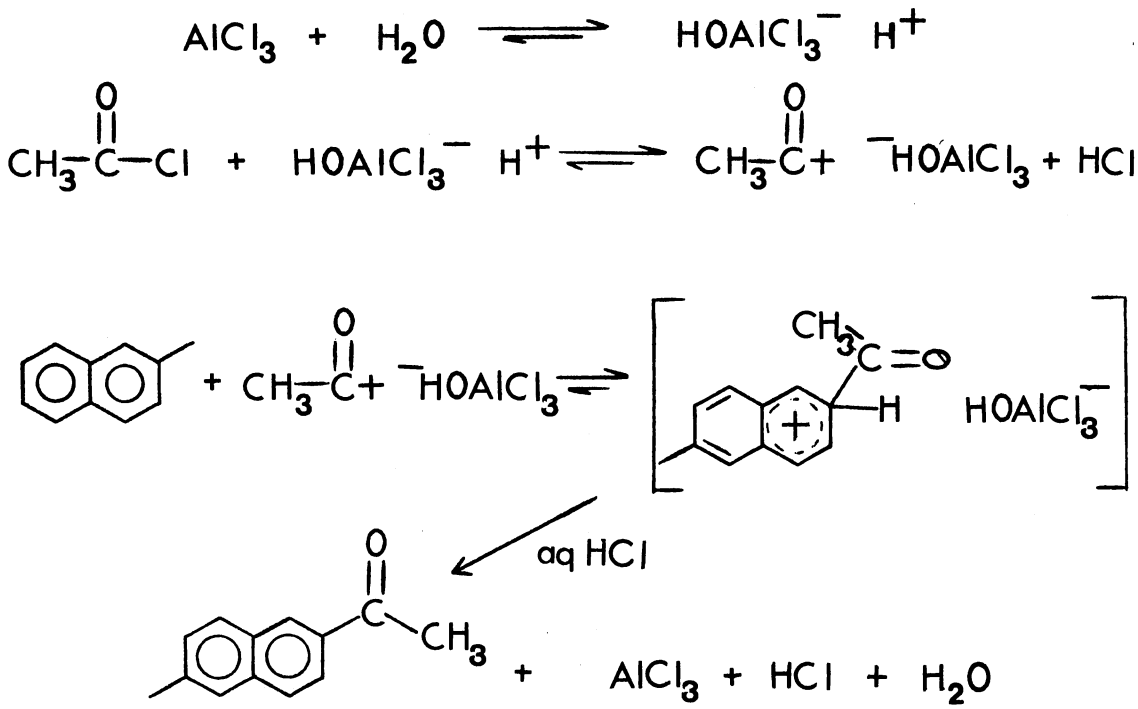


In the other mechanism, an acyl cation is not involved but the 1:1 complex attacks directly.[14]



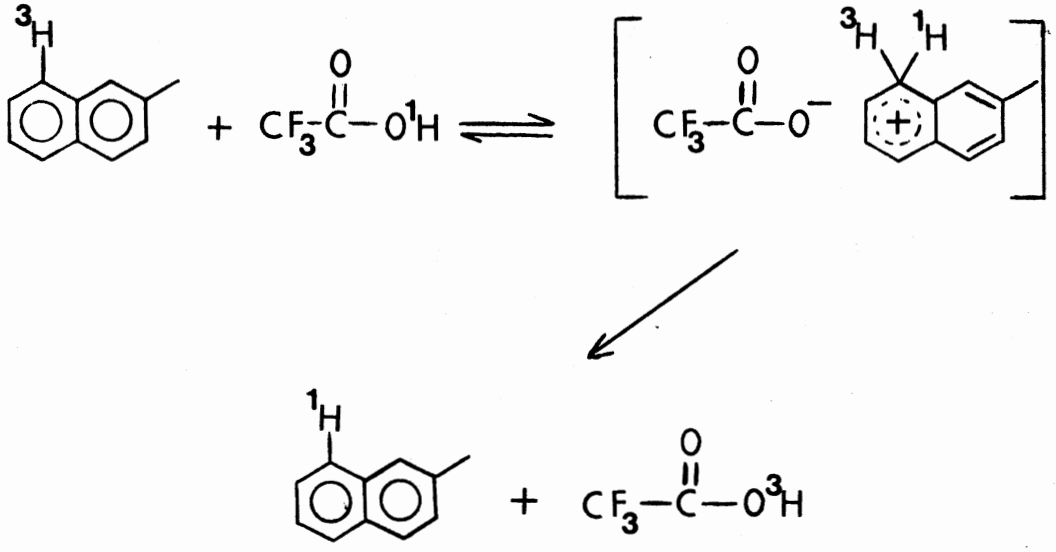
Free ion attack is more likely for sterically hindered acyl group.[14] The ion CH_3CO^+ has been detected (by IR spectroscopy) in the liquid complex formed from acetyl chloride and aluminum chloride and in a

polar solvent such as nitrobenzene; but in nonpolar solvents (chloroform) only the complex and not the free ion is present.[14,15] The ion CH_3CO^+ may also be produced from the presence of water. It should be recalled that, in general practice, perfectly anhydrous conditions for the Friedel-Crafts reaction are not obtained. Thus, another possible mechanism may be operating. The activation influence of water on aluminum halides has been explained[1b] by a result of hydrate formation which functions as a strong protonic acid.



Analysis of the influence of substituents on the ease of electrophilic substitution on the benzene ring has contributed to the present theories of substituent effects in organic chemistry.[18,19] The effects of methyl and methoxy-substituents attached to naphthalene have been measured for nitration of 1- and 2-methyl, and methoxynaphthalene in

several media.[18,19] Of interest were the results obtained for hydrogen-exchange of methyl-substituted 1- and 2-tritionaphthalenes in anhydrous trifluoroacetic acid. The advantages of this reaction in comparison with most electrophilic aromatic substitutions are that (a) there is no doubt about the position of reaction, and no analysis of isomeric products are involved, and (b) steric hindrance seems to be small or nonexistent.[18,19] However, the lack of steric effect creates difficulty in correlating detritiation with other electrophilic substitutions which involve reagents having a steric requirement.



The kinetics of these reactions in which hydrogen replaces tritium are followed by infrared or scintillation counting techniques.[18] These reactions are synthetically valueless and have therefore received less attention than they deserve. However, the detritiation data can be used to compare with the results of the acetylation of 1- and 2-methylnaphthalenes.

In Figure 3, the values of the first order rate constants are shown at the appropriate positions of the 1- or 2-methylnaphthalene. From these results one would predict that electrophilic substitution of 1-methylnaphthalene (13) should give products of substitution at a specific position in the following decreasing order: 4>>2>>5>8>7>3>6. Haworth and Marvin[9] reported that acetylation of 13 in the presence of aluminum chloride in nitrobenzene gave a high yield of 14.

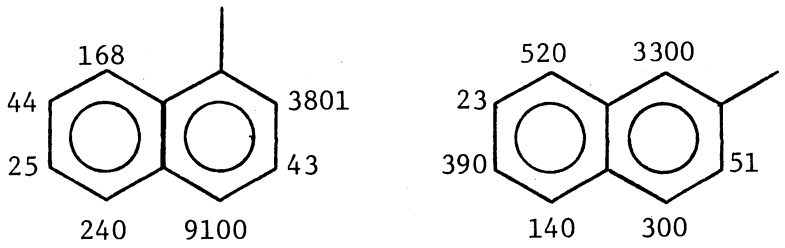


Figure 3. Values of $10^7 K$ (sec^{-1}) for Detritiation of 1- and 2-Methylnaphthalene at 70°C at the Position Indicated.[19]

For 2-methylnaphthalene (1), the order of reactivity of the various positions in detritiation is 1>>8>6>4>5>3>7.[19] In the absence of severe steric effects, this should be the order of decreasing proportion of the possible isomers formed in common electrophilic substitutions of 1, provided that the selectivity of the reagent is not too different from that of trifluoroacetic acid.[19]

In order to gain a better understanding of the concurrent and consecutive Friedel-Crafts type isomerization of the methylacetonaphthones, a study was carried out on the isomerization of isomeric

methylacetonaphthones by following the time-dependent isomerization using gas-liquid chromatography analysis.

In the more reactive 2-methoxynaphthalene system, slow rearrangement of α- to β-ketone could be effected;[10] the contribution of this reversible acylation, however, to the formation of the β-isomer in normal acylations was shown to be slight. It is held that acylation occurs rapidly and predominately at the most reactive aromatic position; where this position is also hindered, resonance stabilization is reduced, and deacylation proceeds, followed by resynthesis at the less hindered (and less reactive) position.[8] Thus, α-substitution is considered to be under kinetic control, and β-substitution under thermodynamic control.[8] Proof of the experimental importance of reversible acylation has been given for the acetylation of anthracene.[20]

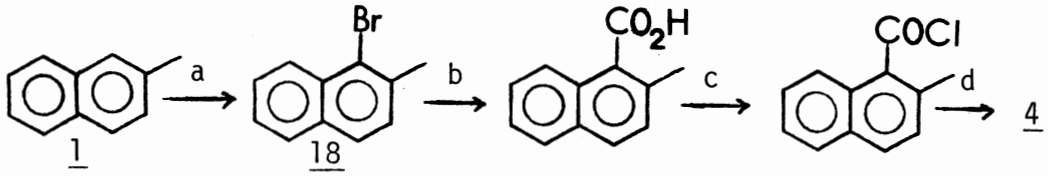
Reversibility was also tested in the acetylation of naphthalene. Instead of a rearrangement of 1- → 2-acetonaphthone, a product was formed in good yield which was identified as α-(1-chlorovinyl)-naphthalene, a derivative previously obtained by the action of phosphorous pentachloride on 1-acetonaphthone.[21,22]

It has recently been shown that reversibility is not a factor in the benzoylation of anthracene.[8] Therefore, we investigated the possibility of reversibility in the formation of 2, 3, 4, and 5. In particular, to establish whether the products of the Friedel-Crafts acetylation can be converted to other isomers under our Friedel-Crafts conditions.

Dziewoński and Brand[4] obtained, from their Friedel-Crafts reaction, a mixture of products from which both 6-methyl-2-acetonaphthone (2) and 7-methyl-1-acetonaphthone (3) were isolated by a tedious fractional

crystallization of their oximes; this process did not appear suitable for the preparation of larger quantities of 2 which was required for the preparation of 9 and 12. Kon and Weller[5] have, however, shown that substantially pure 2 is formed from 1 in the presence of nitrobenzene when 1 is condensed with acetyl chloride. We adopted their procedure to prepare a large quantity of 2 for subsequent reduction to 9 as well as methylation of 2 followed by reduction to 12.

Adams and Binder[23] reported that "the introduction of an acyl group into the alpha position of 1 is not possible by a Friedel-Crafts reaction," and so an indirect synthesis was sought. Gore[3b] obtained 4 (yield 50%) by treatment of the acid chloride ($SOCl_2$) of 2-methyl-1-naphthoic acid with an excess of methyl iodide as shown in Figure 4. 2-Methyl-1-acetonaphthone (4) exhibits a pale yellow color, bp 118-120°C at 0.35 mm Hg.



[a] Br_2-CCl_4, I_2. [b] Mg, dry $(CH_3CH_2)_2O$, (C_2H_5MgBr), C_6H_6, CO_2. [c] $SOCl_2$, 25°C. [d] CH_3I, $(CH_3CH_2)_2O$.

Figure 4. Synthesis of 2-Methyl-1-acetonaphthone (4).[3b]

Gore[3b] prepared 3-methyl-2-acetonaphthone (5) by treating a solution of the adduct of 1 with hexachlorocyclopentadiene in dichloromethane

with acetyl chloride and aluminum chloride in dichloromethane. The product was subjected to pyrolysis and crystallized to give light yellow 3-methyl-2-acetonaphthone (5), mp 76.5-77°C.[3b]

CHAPTER III

DISCUSSION AND RESULTS

Acetylation of 1-methylnaphthalene (13) in chloroform gave 14 as the major product. This may be attributed to steric requirements of the acetylating species. It should be recalled that hydrogen-exchange is apparently free of steric effects.[18,19] The agreement with the order (4>>2>5>8>7>3>6) in detritiation is poor, presumably because there is serious steric hindrance to acetylation for all except the 3-, 6-, and 7-positions. When this hindrance is taken into account, there is better agreement and dominance of 4-substitution is to be expected.

The recent acetylation studies along with this work on 2-methylnaphthalene are not in general agreement with the hydrogen-exchange experiments. It is observed that the acetylation reactions are also solvent dependent. These solvents fall into two main groups: Those with high dielectric constant which favor attack at the β position and low dielectric constant which favor attack at the α position.

Our results are in general agreement with those obtained by earlier workers with the exception of the minor isomers reported by Gore et al[3b] who pointed out that at 20°C the reaction shows a substantially lower yield of the 1-isomer and an increase in the minor isomers. Overall, under our conditions, 5-10°C temperature, the ratios of isomers were observed to decrease in the order 8>>6>1~3 in low dielectric constant solvents, and 6>>8>3~1 with solvent of high dielectric constant

(Table I). Variations in the order of addition, temperature, and solvent changes this order of dominance drastically (Table II).

In these reactions, the product is usually kinetically and not thermodynamically controlled.[24] In carrying out our Friedel-Crafts reaction, the reactions are usually stopped well before equilibrium is reached (compare the results obtained via normal Friedel-Crafts reaction with that of isomerization studies in Figure 5 and in Tables I and III); the reaction will be kinetically controlled since more of the faster-formed product will be present. Therefore, the possible intermediates that are formed are dependent not only on the thermodynamic stability of the products, but on the activation energy necessary to form each intermediate.[24] Because CH_3CO group is deactivating, the acetylation reaction stops cleanly after one group is introduced at 0-10°C, however at 25°C and after 18 h, diacetylation occurs. This may be due to deacetylation and re-acetylation to the thermodynamically more stable products as shown in Figure 5.[25] In acetylation a slight excess over 1 mole of catalyst per mole of reagent is required, since the first mole coordinates with the oxygen of the reagent.[25] Frequently this 1:1 complex is prepared, before the aromatic compound is added. Protonic acid (acetic acid) gives smooth acetylation in the presence of polyphosphoric acid at 80°C.[21]

If the reaction is permitted to approach equilibrium as shown in Figure 5, the predominant isomers formed should be β-substituted.[24] Under these conditions, the more sterically hindered α-substituted isomer forms first, this undergoes acyl group rearrangement to a less hindered α position and finally the acyl group resides at a β position. For example, the acetylation of 1 in nitroethane at 5-10°C, as shown in

TABLE I

RESULTS OBTAINED FROM FRIEDEL-CRAFTS REACTIONS VIA PERRIER PROCEDURE[8]

Solvent	% Isomeric Ketone			
	2	3	4	5
C_5H_{12}	13	63	5	19
CS_2	11	69	7	13
$CHCl_3$	13	65	11	11
C_6H_5Cl	9	73	7	11
CH_2Cl_2	7	76	6	11
$(CH_2)_2Cl_2$	6	70	6	18
$C_6H_5NO_2$	61	25	6	9
$CH_3CH_2NO_2$	68	19	4	9

Table I, gives a ratio of α:β (1.00:3.13) while at 45°C (Table II), the ratio becomes α:β (1.00:5.25). The α-isomers are thermodynamically less stable, because of steric interaction between the CH_3CO group and the hydrogen at the peri position as well as the CH_3 group at the 2-position. When 2-methylnaphthalene (1) was acetylated under normal Friedel-Crafts conditions, the ratios were as follows: In methylene chloride α (positions 1 and 8):β (Positions 3 and 6) (4.60:1.00) and in nitroethane α:β (1.00:3.30), but treatment of 2, 3, 4, and 5 with hydrogen chloride gas showed that only 4 rearranged, the other isomers were stable to rearrangement. 2-Methyl-1-acetonaphthone (4) eventually

gives an equilibrium mixture of ∝:β (3.10:1.00) in methylene chloride, and a ratio of ∝:β (2.50:1.00) in nitroethane. This result is in accord with the thermodynamic stabilities of the products.

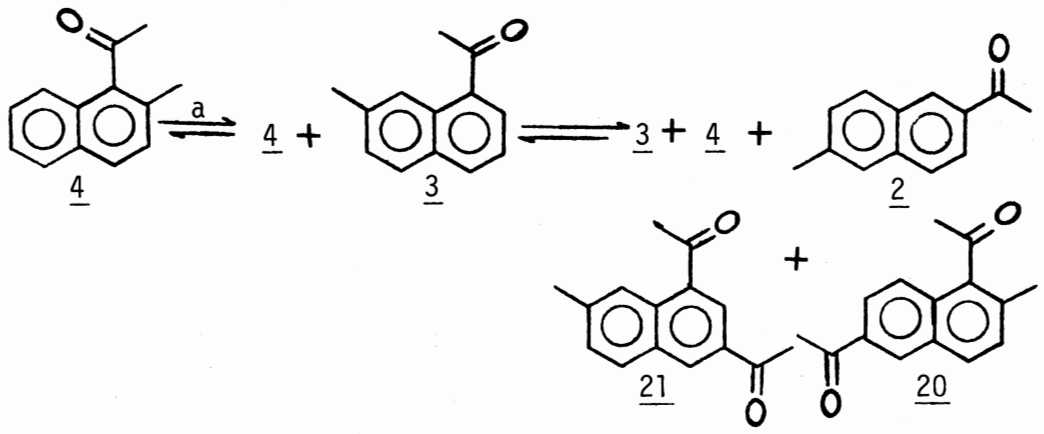
The present work clearly indicates that the gradual addition of the aluminum chloride-acetyl chloride complex to 1 must result in considerable β-substitution. For example, the Marino and Brown[13] procedure in methylene chloride gave ∝:β (4.90:1.00) and ∝:β (1.00:6.70) in nitroethane as compared to Perrier procedure,[8] where in methylene chloride, the ratio becomes (4.60:1.00), and in nitroethane ∝:β (1.00:3.30). These reactions clearly show solvent effect as pointed out in Table I.

TABLE II

VARIATION IN YIELD WITH CHANGE IN SOLVENT, TEMPERATURE AND ORDER OF ADDITION

	CH_2Cl_2		$CH_3CH_2NO_2$	
	5-10°C	35°C	5-10°C	45°C
2	7[a], 8[b]	2[a]	68[a], 80[b], 70[c]	81[a]
3	76[a], 31[b]	49[a]	19[a]. 9[b], 18[c]	14[a]
4	6[a], 52[b]	35[a]	4[a], 4[b], 3[c]	2[a]
5	11[a], 9[b]	14[a]	9[a], 7[b], 9[c]	3[a]

[a]% Yield, Perrier Procedure;[8] [b]% Yield, Marino and Brown Procedure;[13] [c]% Yield, Bouveault Procedure.[8]



[a] 1 CH_3COCl, 2 $AlCl_3$, HCl, CH_2Cl_2

Figure 5. Isomerization and Diacetylation of 2-Methyl-1-acetonaphthone (4).

We have studied in detail the Friedel-Crafts acetylation of 2-methylnaphthalene 1, using eight different solvents, and have observed that formation of products is profoundly influenced by the solvent. In this respect, 1 resembles other polyclic systems such as phenanthrane,[26] naphthalene,[8,16,21] substituted naphthalenes,[10,11] and anthracene.[3] Solvents ranging from dielectric constants of 2.64 to 35.87 were employed and the relationship of dielectric constants to product ratio are shown in Table I. A non-polar solvent such as carbon disulfide does not dissolve aluminum chloride or its acetyl chloride complex. Polar solvents (nitrobenzene) dissolve and solvate aluminum chloride, the acetyl chloride-aluminum chloride complex, and the aluminum chloride complex of the ketone products.[27] Solvents with intermediate polarities, such as methylene chloride, 1,2-dichloroethane, and chloroform do not dissolve aluminum chloride, but they readily dissolve the

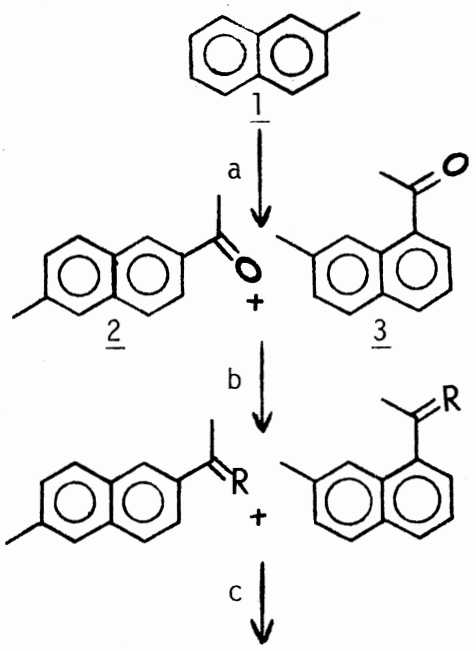
acetyl chloride-aluminum chloride complex; some of the ketone complexes are soluble. Many of the yield and substitution variations are due to the solubility differences of these complexes.[27]

In general, solvents which promote formation of 2-methyl-1-acetonaphthone (4) also favor another ∝-isomer, 7-methyl-1-acetonaphthone (3). The observed ∝ to β ratio decreases in solvent sequence: C_5H_{12}> C_6H_5Cl>$C_2H_4Cl_2$>CH_2Cl_2>$CHCl_3$>CS_2>CH_3NO_2>$C_6H_5NO_2$.[3b] This same sequence of "orientation by solvent has been found in the Friedel-Crafts acetylation of other mono-[11] and disubstituted[31] naphthalenes". Marino and Brown[13] acetylation in methylene chloride gives the highest yield of the 1-isomer 4 (52%), but the 8-isomer 3 is formed therein to the greatest extent. The 6-isomer 2 is formed in good yield in the Perrier[8] reaction carried out in a nitroalkane solvent or in an Elbs[8] reaction in carbon disulfide suspension.[3b] These several Friedel-Crafts acetylations can all be recommended for the preparation of the appropriate isomers.

In the present work, several of the reported acetylation products were carefully analyzed. Wherever possible, the component ketones 2, 3 and 4 were identified by isolation. In other cases, 4 and 5 were prepared by synthesis.

6-Methyl-2-acetonaphthone (2) and 7-methyl-1-acetonaphthone (3) were identified, as shown in Figure 6, by isolation of the isomers from the product obtained under a normal Friedel-Crafts reaction between 1 and acetyl chloride. The product was a semi-solid mixture, from which the desired solid 2 could be separated by filtration. A further amount was recovered in the form of the insoluble semicarbazone, mp 236-237°C (lit.,[5] mp 237°C). From the mother liquor was isolated,

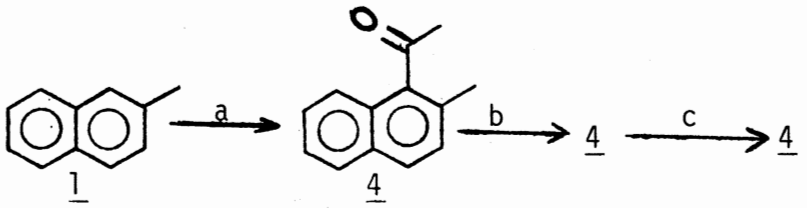
another, much more soluble semicarbazone which yielded the liquid ketone 3. This ketone formed a picrate, mp 104-106°C (lit.,[5] mp 106°C).



[a] CH_3COCl, $AlCl_3$, $CH_3CH_2NO_2$, 5-10°C. [b] $NH_2NHCONH_2 \cdot HCl$, CH_3CONa, H_2O, CH_3CH_2OH, Δ. [c] HCl, $(CH_3CH_2)_2O$. ($R=NNHCONH_2$)

Figure 6. Isolation and Separation of 6-Methyl-2-acetonaphthone (2) and 7-Methyl-1-acetonaphthone (3).

Contrary to the results of Adams and Binder[23] and other reports,[3b,4,5,7,12] it was found that 2-methylnaphthalene (1) was acetylated in the 1-position in better than 50% yield as shown in Table II. 2-Methyl-1-acetonaphthone (4) separated from the mother liquor via its picrate, mp 113-115°C, as shown in Figure 7. The yield of 2-methyl-1-acetonaphthone (4) present depends on the solvent and the mode of addi-

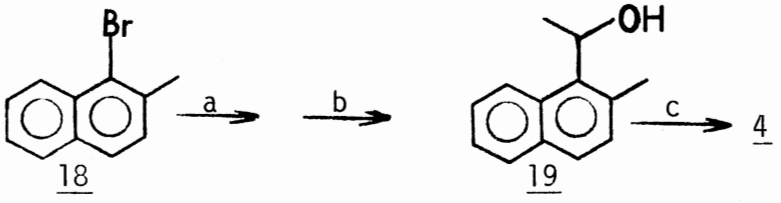


[a]CH_3COCl, $AlCl_3$, CH_2Cl_2, 5-10°C, (Marino and Brown Procedure[13])
[b]Picric acid. [c]NH_4OH, $(CH_3CH_2)_2O$.

Figure 7. Isolation and Separation of 2-Methyl-1-acetonaphthone (4).

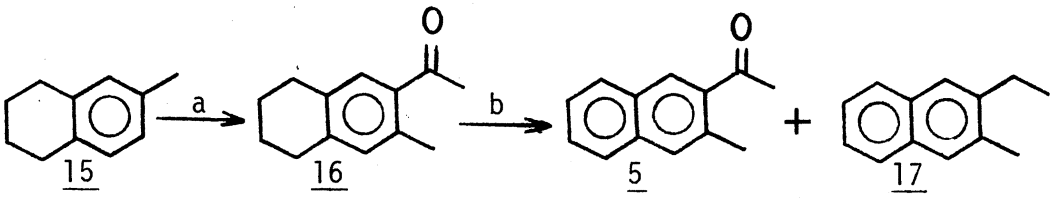
tion. Figure 8 shows our scheme for an alternate preparation of 4 which includes reaction of 1-bromo-2-methylnaphthalene (18) with acetaldehyde to give 19. Subsequent oxidation gave 4. Spectrometric determination, IR, NMR, and the mass spectrum show that 4 corresponds to that obtained from the Friedel-Crafts acetylations.

3-Methyl-2-acetonaphthone (5), mp 76-78°C, was obtained as shown in Figure 9 by acetylation of the tetralin 15 followed by dehydrogenation with sulfur. This dehydrogenation also yielded 17, picrate mp 128-129°C (lit.,[28] mp 129-130°C).



[a]Mg, $(CH_3CH_2)_2O$. [b]CH_3CHO; 10% NH_4Cl, H_2O. [c]CrO_3, H_2SO_4, H_2O, CH_3COCH_3.

Figure 8. Synthesis of 2-Methyl-1-acetonaphthone (4).



$^{a}CH_3COCl$, $AlCl_3$, $CH_3CH_2NO_2$, 5-10°C; $^{b}S_8$, 220°C.

Figure 9. Synthesis of 3-Methyl-2-acetonaphthone (5).

To assist in the analysis of the isomerization and rearrangement studies, mass fragmentography was used. This data was obtained via a CEC-110B high resolution mass spectrometer interfaced to a HP-5710A flame ionization gas chromatograph equipped with a 7' x 1/8" stainless steel SP-2100 column splitter, stainless steel variable jet separator, and stainless steel interface line.[29] The gas chromatography column was operated at 210°C. The mass spectrometer was set to alternately and repeatedly scan m/e 202, and 226 as the material eluted from the gas chromatography column.

Four of the ketones isolated from the various Friedel-Crafts reaction were used in this study. The solvents were chosen because of their dielectric constant and their low boiling point. It was felt that these conditions would give a representation of events in the reaction mixture.

When treated in methylene chloride solution, with acetyl chloride and aluminum chloride (in sufficient amount to complex with both of the reactants), under a dry HCl atmosphere, only 2-methyl-1-acetonaphthone (4) showed a very drastic change as compared to the other ketones. 2-

Methyl-1-acetonaphthone (4) gave a mixture containing unchanged 4 (6.7%), two diacetylated products which were not isolated but believed to be 20 (20%), and 21 (5%), as well as the expected rearrangement to 2 (18.3%) and 3 (50%). 3-Methyl-2-acetonaphthone (5) did not undergo isomerization whereas 6-methyl-2-acetonaphthone (2) gave one diacetylated product and 7-methyl-1-acetonaphthone (3) gave two diacetylated products.

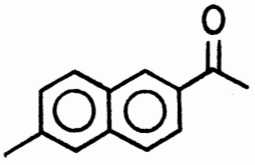
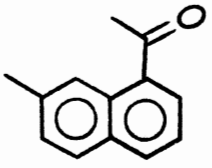
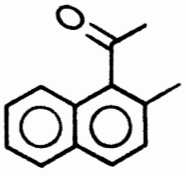
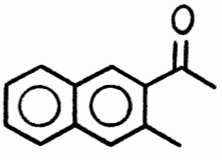
When treated in nitroethane solution with acetyl chloride and aluminum chloride, under a dry HCl atmosphere, similar results were obtained. In all reactions carried out under these conditions, there were trace amount of diacetylated products. The ketones 2, 3 and 5, were all relatively stable forming in approximately 99% yield. However, ketone 4 gave a mixture containing unchanged 4 (55%), the expected rearranged ketones, 2 (27%), and 3 (12%) as well as two diacetylated products (7%).

These results do not coincide with those obtained under normal Friedel-Crafts reactions. The data in Table III were obtained after 18 h. Under normal conditions of Friedel-Crafts reactions, the reactants remain in contact for approximately 2 h. Under these conditions, there is no formation of diacetylated products, and only 4 undergoes isomerization. After 3 h in methylene chloride, 4 isomerizes to 3 (9%) and after 3 h in nitroethane, 4 isomerizes to 2 (3%).

It is clear that reversible acetylation does not play a major part in our studies and it is significant that no diketone is formed during the first 3 h in this isomerization study. This suggests that the reaction is also time dependent. The data are summarized in Table III.

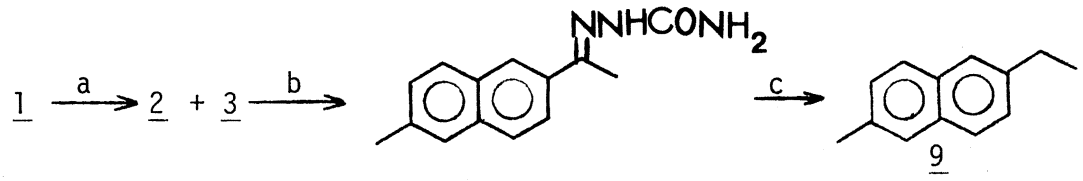
TABLE III

REARRANGEMENT OF 6-METHYL-2-ACETONAPHTHONE (2), 7-METHYL-1-ACETONAPHTHONE (3), 2-METHYL-1-ACETONAPHTHONE (4) AND 3-METHYL-2-ACETONAPHTHONE (5) IN METHYLENE CHLORIDE AND IN NITROETHANE

Starting Material	% Rearranged —Monoacetylated Ketone—				% m/e 202	% m/e 226
	2	3	4	5		
	95[a],99[b]	-	-	-	-	16, 5[a]
	-	90[a],99[b]	-	-	-	16, 5[a] 17, 5[a]
	18[a],27[b]	50[a],12[b]	7[a],55[b]	-	-	16 & 17, 25[a]
	-	-	-	100[a],99[b]	-	trace

[a]% composition in methylene chloride. [b]% composition in nitroethane.

Kon and Weller[5] reported that reduction of 2 in alcohol with amalgamated zinc, water and hydrochloric acid gives 9, mp 44-45°C. An attempt to prepare hydrocarbon 9 by treating the semicarbazone of 2 with sodium in benzyl alcohol at 180-190°C was unsucessful.[5] However, treatment of the semicarbazone of 2 with potassium hydroxide, diethylene glycol, at reflux, yielded 9 (84%). 2-Ethyl-6-methylnaphthalene (9) was synthesized as shown in Figure 10. Acetylation of 1 and separation of isomers through crystallization yielded 2. In addition to 3, three other minor peaks were observed in the gas chromatography of the crude product. The ketone 2 was converted to the semicarbazone derivative which was purified by leaching with hot 95% ethyl alcohol and then directly subjected to reduction in the presence of potassium hydroxide

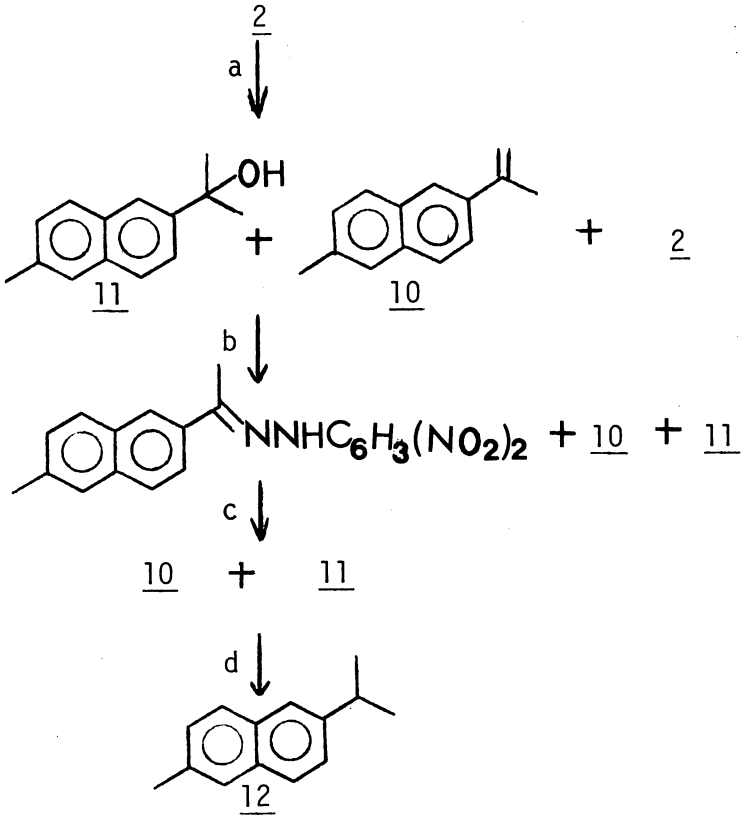


[a] CH_3COCl, $AlCl_3$, $CH_3CH_2NO_2$, 0-5°C. [b] $NH_2NHCONH_2 \cdot HCl$, CH_3CO_2Na. [c] KOH, $O(CH_2CH_2OH_2)$, Δ.

Figure 10. Synthesis of 2-Ethyl-6-methylnaphthalene (9).

in refluxing diethylene glycol. This reduction resulted in 9, mp 42.5-43.5°C. 2-Isopropyl-6-methylnaphthalene (12), as shown in Figure 11, was obtained by treating 2 with methyl lithium to give a mixture of 2,

10, and 11 (99%). Treatment of this mixture with 2,4-dinitrophenylhydrazine-hydrochloride and separation of the 2,4-dinitrophenylhydrazone via a column of neutral alumina gave a mixture of 10 and 11. Hydrogenolysis/hydrogenation of the mixture 10 and 11 gave 2-isopropyl-6-methylnaphthalene (12), mp 36-37°C.[30]



[a]CH_3Li-LiBr, $(CH_3CH_2)_2O$; dil HCl, H_2O. [b]$NH_2NHC_6H_3(NO_2)_2$, $C_6H_5CH_3$, Δ. [c]Column of neutral Al_2O_3, C_6H_{14}. [d]H_2, Pd/C, CH_3CO_2H, Δ.

Figure 11. Synthesis of 2-Isopropyl-6-methylnaphthalene (12).

CHAPTER IV

EXPERIMENTAL

Pre-Experimental Procedure for all Friedel-Crafts Reactions. After setting up the apparatus, it was heated and purged with a stream of nitrogen for 5 min. The nitrogen inlet adapter was then disconnected and replaced with a drying tube.

Friedel-Crafts Acetylations: General Procedure. The reactants, 2-methylnaphthalene (1) or 1-methylnaphthalene (13), acetyl chloride, and anhydrous aluminum chloride were combined with solvent in one of the following procedures: A. Perrier Procedure.[8] Methylnaphthalene, 1 or 13, was added as the last reactant to a stirred mixture of acetyl chloride and aluminum chloride catalyst. B. Elbs Procedure.[8] The catalyst was added last. C. Bouveault Procedure.[8] Acetyl chloride was added last. D. Marino and Brown Procedure.[13] Preformed acetyl chloride-aluminum chloride complex in a solvent was added to 1 or 13 in the same solvent. E. Scharwin Procedure.[32] A solution of acetyl chloride and the 1 or 13 in a solvent was added to a slurry of aluminum chloride in the same solvent.

In each procedure, the mixture was maintained at a given temperature. The final reactant was added with the aid of a small volume of the solvent, usually during 20 min, and stirring was maintained. The mixture was then treated as described under the 'post-experimental procedure.'

Post-Experimental Procedure for all Friedel-Crafts Reactions:

After the completion of the reaction, the crude product was isolated by addition of crushed ice and 6N hydrochloric acid and separation of the organic layer. Additional solvent or ether was added as necessary to extract the crude product. The extract was then washed with water, dilute hydrochloric acid, water, sodium chloride or sodium bicarbonate solution, and water, respectively. The extract was dried ($MgSO_4$), filtered through Dicalite, and concentrated under vacuum or steam-distilled when nitrobenzene was used. If necessary, the product was distilled (Kugelrohr; 110-114°C, 0.3 mm Hg) before attempting gas chromatography analysis.[33]

Acetylation of 1-Methylnaphthalene (13) with Acetyl Chloride-Aluminum Chloride in Chloroform to 4-Methyl-1-acetonaphthone (14). To a 500 mL, 3-necked, round-bottomed flask was added chloroform (161 mL) and aluminum chloride (22.5 g, 0.17 mol). As the mixture was being mechanically stirred at 10°C, acetyl chloride (13.3 g, 0.17 mol) was added dropwise over a period of 5 min. A solution of 13 (12.1 g, 0.085 mol) in chloroform (16.2 mL) was added dropwise over 20 min. The ice bath was removed and the mixture was continuously stirred at room temperature (20 min). At the end of this period, the reaction mixture was 'worked-up', distilled at 100-120°C (0.9 mm Hg) to give 15.5 g (99%) of product. Gas chromatography revealed only one peak. The ketone was then recrystallized from methanol to give 13 g of 14: mp 37-39°C; bp 100°C (0.9 mm Hg), (lit.,[9] bp 174-175°C, 15 mm Hg); mass spectrum (70 eV) m/e (rel intensity) 185 (M^++1, 7), 184 (M^+, 36), 170 (13), 169 (100), 141(57), 115 (22); ^1H NMR (CCl_4) δ 2.44 (s, CH_3), 2.50 (s, $COCH_3$), 7.00-7.85 (m, ArH), 8.80-8.89 (d, 8-H); IR (KBr) 1680 cm^{-1} (CO).

Acetylation of 2-Methylnaphthalene (1) with Acetyl Chloride-Aluminum Chloride in 1,2-Dichloroethane. A. To a stirred mixture of acetyl chloride (42.9 g, 0.55 mol) and aluminum chloride (72.8 g, 0.55 mol) in 1,2-dichloroethane (200 mL) kept at 10-20°C, was added a solution of 1 (39.3 g, 0.28 mol) in 1,2-dichloroethane (100 mL) over 20 min. With the initial drop of 1, the color of the solution changed from brown to green. A green solid formed on the wall of the flask where the addition of the reagent to the flask was taking place (this was improved in the later experiments by using an extended adapter which enabled direct addition of reagent to the solution). At the end of the addition of 1, the cooling bath was removed. The solution was allowed to warm to room temperature and then stirred for 30 min; with a resulting color change to orange. At the end of this period, the reaction mixture was processed as described in the 'post-experimental procedure'; distilled at 110-115°C (0.3 mm Hg) with the later portions being collected at 144°C, to give 49.0 g (97%) of a mixture shown by glc studies to be: 2:3:4:5 (1:14.6:1.3:2.6) and two unknown ketones (1.2%).

B. The above experiment was repeated with the following changes: To a stirred solution of 1,2-dichloroethane (276 mL) at 5°C, was added aluminum chloride (39.0 g, 0.29 mol) over a period of 5 min to maintain the temperature. The acetyl chloride (22.6 g, 0.29 mol) was added dropwise over a period of 5 min at 5-10°C. 2-Methylnaphthalene (1) (41.2 g, 0.29 mol) in 1,2-dichloroethane (56 mL) was added dropwise to the mixture (20 min). After the addition of 1, the ice bath was removed and the mixture was mechanically stirred for an additional 20 min. The final reaction temperature was 29°C. The product was isolated as

described in the 'post-experimental procedure'. After distillation, 48.3 g (90%) of mixed methylacetonaphthones were recovered. The composition was: 2:3:4:5 (1.2:8.3:1:2.1).

C. To a stirred mixture of acetyl chloride (22.6 g, 0.29 mol) and aluminum chloride (38.4 g, 0.29 mol) in 1,2-dichloroethane (276 mL) were added, at 0-10°C over 20 min, a solution of 1 (21.8 g, 0.15 mol) in 1,2-dichloroethane (29 mL). The reaction mixture was then stirred at room temperature for 20 min. The 'post-experimental procedure' was used for further processing. After distillation, the total weight of the product was 26.6 g (97%). The composition was 2:3:4:5 (1.3:11.9:1:3.7).

Acetylation of 2-Methylnaphthalene (1) with Acetyl Chloride-Aluminum Chloride in Nitroethane. A. Nitroethane (200 mL) and anhydrous aluminum chloride (33.8 g, 0.25 mol) were stirred continuously at 0°C while 19.5 mL of acetyl chloride (2.14 g, 0.27 mol) was added over a period of 5 min. After an additional solution of nitroethane (5 mL) was added, a solution of 1 (32.3 g, 0.23 mol) dissolved in nitroethane (20 mL) was added dropwise (10 min), with the initial drops changing the complex to dark green. A semi-solid mixture was obtained after 20 min. The reaction was stirred at 0°C for an additional 4 h. After the completion of the reaction, the crude product was worked up as described in the 'post-experimental procedure'. Kugelrohr distillation gave 38.9 g (93%) of a dark brown semi-solid consisting of: 2:3:4:5 (17.2:4.3:1:1.9).

B. To a stirred solution of nitroethane (276 mL), at 0°C, was added aluminum chloride (38.7 g, 0.29 mol). Acetyl chloride (22.6 g, 0.29 mol) was added dropwise (5 min) to the stirred reaction mixture.

This solution was allowed to react at 0-5°C for an additional 20 min. 2-Methylnaphthalene (1) (21.2 g, 0.15 mol) in nitroethane (29 mL) was added dropwise for a period of 20 min. During the course of the addition, the temperature changed from 5 to 10°C. After the addition of 1, the addition funnel was rinsed with nitroethane (5 mL), the ice bath was removed, and stirring was continued for an additional 20 min. The final reaction temperature was 15°C. The reaction was 'worked-up' and the product mixture was distilled at 75-140°C (0.02-0.28 mm Hg) to give 26.0 g (96.5%) of the mixed ketones consisting of: 2:3:4:5 (9.5:4.7:1:1.8).

C. To a stirred solution of nitroethane (284 mL), at 10°C, was added aluminum chloride (41.1 g, 0.30 mol) at a rate to maintain the stated temperature. Acetyl chloride (22.2 g, 0.29 mol) was added dropwise (5 min). 2-Methylnaphthalene (1) (21.9 g, 0.15 mol) in nitroethane (30 mL) was added dropwise (20 min). After the addition of 1, the addition funnel was rinsed with nitroethane (5 mL), the ice bath was removed, and stirring was continued for 20 min. The final reaction temperature was 15°C. The 'post-experimental procedure' was used. Distillation gave 28.0 g (96.5%) of the mixed ketones consisting of: 2:3:4:5 (55.4:9.4:1:5.6).

Isolation of 6-Methyl-2-acetonaphthone (2) and 7-Methyl-1-acetonaphthone (3). The pasty solid obtained from the above reaction B was filtered to give 2 (5.2 g) which was found to be about 82% pure by glc. The filtrate (33.2 g) was converted to the semicarbazone, filtered, recrystallized from 95% ethanol, and then shaken with ether and 10% hydrochloric acid until the semicarbazone dissolved. The ether layer was dried ($MgSO_4$), filtered, and concentrated to give 21.2 g (64%) of

pure 2, mp 66-67°C, (lit.,[3b] 69-70°C); mass spectrum (70 eV) m/e (rel intensity) 184 (M^+, 32), 170 (100), 169 (63), 141 (38), 115 (14), 18 (9); ^{1}H NMR (CCl_4) δ 2.47 (s, CH_3), 2.54 (s, $COCH_3$), 7.18-7.90 (m, ArH), 8.03 (s, 5-H), 7.65 (s, 1-H); IR (KBr) 1686 cm^{-1} (CO), (lit.,[3b] 1675 cm^{-1}).

The filtrate from the distillate was enriched in 3. The picrate of 3 was prepared and recrystallized from ethanol to give mp 104-106°C, (lit.,[5] mp 106°C). The picrate was cleaved by shaking with ammonium hydroxide and ether. The dried ($MgSO_4$) ether solution was concentrated to give pure 3 (10.0 g), bp 140°C (0.02 mm Hg), (lit.,[5] 150-154°C, 1.5 mm Hg); mass spectrum (70 eV) m/e (rel intensity) 186 (M^++2, 1.2), 185 (M^++1, 15), 184 (M^+, 100), 169 (3), 141 (0.8), 42 (0.5); ^{1}H NMR (CCl_4) δ 2.36 (s, CH_3), 2.45 (s, $COCH_3$), 7.02-7.70 (s, ArH), 8.60 (s, 1-H); IR (film) 1670 cm^{-1} (CO), (lit.,[3b] 1675 cm^{-1}).

Acetylation of 2-Methylnaphthalene (1) using Polyphosphoric Acid. A. Polyphosphoric acid (200 mL) was added to a 3-necked, 500 mL flask and with stirring, heated to 80°C. At this temperature, a solution of 1 (14.4 g, 0.10 mol) in acetic acid (9.0 g, 0.20 mol) was added. With the addition of this mixture to the flask, there was a change from colorless to black. Heating was continued for 2 h. The cooled mixture of crude product was added directly to a beaker containing approximately 750 g of ice. The crude black tar changed to a light brown milky solution with a layer of oil. After 2 h, the mixture was extracted with ether and the extract was dried ($MgSO_4$). A glc analysis showed: 1:2:3:4:5 (1:trace:22.1:25.6:14.4). The crude product was then filtered through Dicalite, concentrated, and distilled at 100-140°C (0.4 mm Hg) to give 14.6 g (72.2%) of the mixed ketones.

B. Repetition of A but increasing the reaction time by 1 h gave 14.7 g (72.3%) in the same ratio of products.

Acetylation of 2-Methylnaphthalene (1) with Aluminum Chloride-Acetyl Chloride in Chloroform. A. To a stirred solution of chloroform (250 mL) at 0°C, was added aluminum chloride (34.9 g, 0.26 mol) and acetyl chloride (20.4 g, 0.26 mol) during 5 min. A solution of 1 (18.6 g, 0.13 mol) in chloroform (50 mL) was added to the mixture over 20 min. During the addition, the solution changed from colorless to green and then to yellow. After the addition of 1, the ice bath was removed and stirring was continued at room temperature for an additional 20 min. The mixture was then worked-up as described in 'post experimental procedure.' The product was distilled to give 21.5 g (89%) of the methylacetonaphthones: 2:3:4:5 (1:6.4:1.4:1) and two minor isomers (2%).

B. To a stirred solution of chloroform (276 mL) and aluminum chloride (22.6 g, 0.29 mol) was added acetyl chloride (22.6 g, 0.29 mol). After addition, the mixture was allowed to stir for 5 min. 2-Methylnaphthalene (1) (31.2 g, 0.22 mol) in chloroform (56 mL) was then added dropwise over a period of 20 min. The temperature at this time was 22°C. After the addition of 1, the ice bath was removed and stirring was continued for 20 min. The final reaction temperature was 25°C. The product distilled at 110-114°C (0.3 mm Hg) to give 36.2 g (89.4%) of mixed methylacetonaphthones: 2:3:4:5 (1.4:7.3:1:1.3).

Acetylation of 2-Methylnaphthalene (1) with Acetyl Chloride-Aluminum Chloride in Dichloromethane. A. To a chilled solution of dichloromethane (272 mL) was added aluminum chloride (38.0 g, 0.29 mol); the colorless solution changed to a cloudy white suspension. Acetyl chloride (22.3 g, 0.29 mol) was added dropwise (5 min) to the mechani-

cally stirred mixture with a resulting color change to brown. 2-Methylnaphthalene (1) (20.3 g, 0.14 mol) in dichloromethane (28.8 mL) was added dropwise (20 min) with the temperature remaining at 10°C; the solution changed from brown to yellow. The addition funnel was rinsed with 5 mL of dichloromethane, the ice bath was removed, and stirring was continued for 20 min. The final reaction temperature was 15°C. The reaction yielded 20.0 g (77%; some mechanical loss) of methylacetonaphthones: 2:3:4:5 (1.3:11.9:1:2.7).

B. A solution of 1 (21.0 g, 0.15 mol) in dichloromethane (29 mL) was added to a solution of aluminum chloride (41.2 g, 0.30 mol) and acetyl chloride (24.2 g, 0.31 mol) in dichloromethane (295 mL) at 10°C. After the addition of 1, the ice bath was removed and stirring continued for 20 min. The final reaction temperature was 15°C. This reaction gave 26.2 g (92%) of the methylacetonaphthone mixture: 2:3:4:5 (1:15.1:1.1:1.2).

Acetylation of 2-Methylnaphthalene (1) With Aluminum Chloride-Acetyl Chloride in Chlorobenzene. A. Acetyl chloride (21.0 g, 0.27 mol) was added dropwise during 5 min to a stirred solution of chlorobenzene (266 mL) and aluminum chloride (37.9 g, 0.28 mol); this resulted in a yellow solution. 2-Methylnaphthalene (1) (19.7 g, 0.14 mol) in chlorobenzene (29 mL) was added dropwise over a period of 20 min at 10°C. The addition funnel was rinsed with chlorobenzene, the ice bath was removed and stirring was continued for 20 min. The reaction was then 'worked-up' as described earlier, to give 18.8 g (72.4%) of the mixed ketones: 2:3:4:5 (1.2:10.1:1:1.4).

B. Aluminum chloride (37.6 g, 0.28 mol) was added to chlorobenzene (268 mL) at 10°C, to give a cloudy white suspension. Acetyl

chloride (21.9 g, 0.28 mol) was then added dropwise which resulted in a colorless solution. A solution of 1 (20.0 g, 0.14 mol) in chlorobenzene (27 mL) was added dropwise (20 min) at 5°C. The ice bath was removed and stirring was continued for 20 min at room temperature. This reaction gave 13.1 g (51%) of: 2:3:4:5 (1.3:10.7:1:1.9).

Acetylation of 2-Methylnaphthalene (1) with Acetyl Chloride-Aluminum Chloride in Nitrobenzene. A. Acetyl chloride (24.5 g, 0.32 mol) was added dropwise (5 min) to a stirred mixture of aluminum chloride (41.9 g, 0.32 mol) at 5°C. To this yellow mixture, a solution of 1 (22.3 g, 0.16 mol) in nitrobenzene (30 mL) was added (20 min); the temperature remaining at 5°C. The solution color changed to red. The ice bath was removed and stirring was continued for 20 min. The reaction was 'worked-up' in the usual manner to give 26.5 g (92%) of methylacetonaphthones consisting of: 2:3:4:5 (16.2:6.2:1:2.2).

B. To a stirred solution of nitrobenzene (270 mL) and aluminum chloride (37.8 g, 0.28 mol) at 5°C, was added acetyl chloride (22.2 g, 0.28 mol) over a period of 5 min. 2-Methylnaphthalene 1 (20.2 g, 0.14 mol) in nitrobenzene (27 mL) was added over a period of 20 min. At the end of the addition of 1, the ice bath was removed, and the mixture was allowed to stir for 20 min at room temperature. After the usual 'work-up' and distillation, 24.6 g (94%) of ketone mixture consisting of: 2:3:4:5 (11.3:5.1:1:1.8) was obtained.

Acetylation of 2-Methylnaphthalene (1) with Aluminum Chloride-Acetyl Chloride in Pentane. Pentane (236 mL) was added to the chilled reaction flask. The aluminum chloride (33.1 g, 0.25 mol) was added while the mixture was mechanically stirred (20 min). Aluminum chloride is insoluble and a cloudy white suspension resulted. Acetyl chloride

(19.4 g, 0.25 mol) was added dropwise for 5 min. A solution of 1 (17.7 g, 0.13 mol) in pentane (24 mL) was added dropwise (20 min). Hydrogen chloride was given off in greater quantity than previously observed. After the addition of 1, the ice bath was removed and the reaction mixture allowed to stir for 20 min. The 'post-experimental procedure' was carried out and 21.0 g (92%) of methylacetonaphthone mixture was obtained. The composition was 2:3:4:5 (3.3:14.9:1:4.5).

Acetylation of 2-Methylnaphthalene (1) With Acetyl Chloride-Aluminum Chloride in Carbon Disulfide. A. To a stirred solution of carbon disulfide (283 mL) and aluminum chloride (39.6 g, 0.30 mol) which is insoluble in carbon disulfide, was added acetyl chloride (23.4 g, 0.20 mol) over 5 min. A solution of 1 (21.1 g, 0.15 mol) in carbon disulfide (28.6 mL) was added over a period of 20 min. The initial drop containing 1, changed the solution from colorless to green and with continued addition the solution eventually changed to yellow. The ice bath was removed, and the mixture was stirred for 20 min. The reaction was then 'worked-up'. This time the carbon disulfide solution was allowed to evaporate at room temperature for two days. The crude product was combined with ether, washed with H_2O, NaCl, H_2O, and then dried ($MgSO_4$). After distillation 24.7 g (92%) of methylacetonaphthones mixture was recovered consisting of: 2:3:4:5 (1.8:12.2:1:2.5).

B. A second experiment was carried out in similar manner with the following changes: To a stirred solution of carbon disulfide (298.5 mL), was added aluminum chloride (41.7 g, 0.31 mol). Acetyl chloride (24.5 g, 0.31 mol) was added dropwise (20 min) with no resulting temperature change (5°C). A solution of 1 (22.3 g, 0.16 mol) in carbon disulfide (30.1 mL) was added dropwise (20 min). At the end of the

addition of 1, the ice bath was removed and the reaction continued at room temperature for 20 min. The reaction was then processed as described in the previous reaction A. The reaction gave 26.3 g (91%) of methylacetonaphthones in the ratio of 2:3:4:5 (1.4:8.7:1:1.5).

Acetylation of 2-Methylnaphthalene (1) - Bouveault Procedure[8]. To a stirred solution of 1 (18.6 g, 0.13 mol) and nitroethane (254 mL) at 5°C, was added aluminum chloride (34.9 g, 0.26 mol). This resulted in an increase to 10°C. To this mixture was added acetyl chloride (21.0 g, 0.26 mol) dropwise at a rate to ensure that the total addition took place in 20 min. The ice bath was then removed and the reaction continued at room temperature (20 min). The reaction was then 'worked-up' in the usual manner, to give 21.3 g (88%) of the ketone mixture 1:2:3:4:5 (1.2:23.3:6.1:1:2.9).

Acetylation of 2-Methylnaphthalene (1). Perrier Procedure[8] at 30-50°C. A. To a stirred solution of nitroethane (268.5 mL) at 30°C was added aluminum chloride (37.7 g, 0.28 mol) over 20 min with a corresponding temperature rise from 30 to 45°C. There was no color change. Acetyl chloride (20 g, 0.26 mol) was added with a resulting color change to green. The temperature was allowed to drop to 40°C before 1 (20.0 g, 0.14 mol) in nitroethane (27 mL) was added (20 min). The color changed to a black 'tar' and the temperature rose to 50°C. This temperature was maintained for 10 min and then the reaction was allowed to cool. The reaction was worked-up as described in the 'post-experimental procedure'; however, with the presence of tar, this work-up was much more tedious than those reactions carried out between 0-15°C. This reaction gave 11.2 g (43%) consisting of: 2:3:4:5 (36.7: 6.2:1:1.6).

B. To a stirred solution of methylene chloride (263 mL) at 35°C was added aluminum chloride (36.8 g, 0.28 mol) over a period of 10 min; the reaction changed from colorless to peach. Acetyl chloride (21.6 g, 0.28 mol) was added dropwise for 5 min with a color change from peach to brown. A solution of 1 (19.6 g, 0.14 mol) in methylene chloride (27.5 mL) was added (20 min). After the addition of 1, the solution was allowed to cool to room temperature before 'work-up'. A 20.4 g (88%) sample of the mixed ketones was recovered which showed an isomer ratio: 2:3:4:5 (1:24.5:17.5:7).

Acetylation of 2-Methylnaphthalene (1) - Marino and Brown Procedure.[13] A. The complex was formed by combining 18.8 mL of acetyl chloride (20.6 g, 0.26 mol) and aluminum chloride (35.5 g, 0.27 mol) in nitroethane (251.4 mL). This complex was added to a solution of 1 (18.7 g, 0.13 mol) in nitroethane (25.4 mL) with the reaction being maintained at 7°C for 40 min. The ice bath was removed and the reaction was stirred an additional 15 min. After this period, the reaction was processed in the usual manner to give 15.1 g (62.2%) of mixed ketones consisting of: 1:2:3:4:5 (trace:22.1:2.4:1:1.7).

B. To a solution of 1 (18.3 g, 0.13 mol) in methylene chloride (25.0 mL) at 5°C which was mechanically stirred, was added the preformed complex of aluminum chloride (34.3 g, 0.26 mol) and acetyl chloride (20.2 g, 0.26 mol) in methylene chloride (251 mL). The temperature changed from 5 to 10°C. At the end of 40 min, the reaction was 'worked-up' to give 22.6 g (98) of mixed ketones consisting of: 2:3:4:5 (1:3.8:6.5:1.2).

The Isolation of 2-Methyl-1-acetonaphthone (4) from B. A beaker containing 30 mL of 95% ethyl alcohol and picric acid (19.14 g) was

heated. In a separate vessel, the mixture of ketone from B (14.0 g) was dissolved in 5 mL of hot 95% ethanol and heated. The solutions were mixed, heated, and then allowed to cool. After cooling, the crystals were filtered, with the mother liquor being recovered and stored. The dried crystals were then recrystallized numerous times to give a melting point of 113-115°C. The picrate was then extracted with concentrated ammonium hydroxide and ether. The ether layer containing 4 was then washed with water, dried ($MgSO_4$), filtered, concentrated and distilled at 100-110°C, 0.5 mm Hg, (Lit.,[3b] bp 110°C, 3 mm Hg) to give 3.8 g of 4 (25%) which according to glc was 97.5% pure; ^1H NMR (CCl_4) δ 2.22 (s, CH_3), 2.36 (s, $COCH_3$), 6.96-7.65 (m, ArH); IR (KBr) 1687 cm^{-1} (CO), (lit.,[3b] 1690 cm^{-1}).

Acetylation of 1,2,3,4-Tetrahydro-6-methylnaphthalene (15) to Prepare 3-Methyl-2-acetonaphthone (5). To a stirred solution of nitroethane (142.2 mL) at 5°C, was added aluminum chloride (19.9 g, 0.15 mol) with a resulting temperature increase to 21°C. Acetyl chloride (11.7 g, 0.15 mol) was added dropwise (5 min). A solution of 15 (10.9 g, 0.075 mol) in nitroethane (14.4 mL) was then added (20 min). The ice bath was removed and the reaction was stirred at room temperature (20 min). The reaction was 'worked-up' as described earlier. The crude product was then distilled with 16 being collected at 95-115°C, 0.15 mm Hg, (lit.,[22] bp 156-157°C, 11 mm Hg). This distillation gave 13.1 g (93.4%) consisting of 16 (86.4%), 15 (10.8%) and two minor products contributing 2.8%. The solid crystals were separated and recrystallized numerous times with petroleum ether to give 16, mp 29-32°C. The structure was verified by IR, NMR, and mass spectrum.

To a 25 mL, round-bottomed, 1-necked flask was added 16 (1.6 g) and sulphur (0.5 g). The mixture was heated in a molten wax bath at 220°C until the evolution of H_2S cleared. The reaction was 'worked-up' and the crude product was distilled with 5 being collected at 90-100°C (0.5 mm Hg). The ketone 5 was recrystallized with petroleum ether to give: mp 76-78°C, (lit.,[3b] mp 76.5-77.5°C); mass spectrum (70 eV) m/e (rel intensity) 184 (M^+, 55), 170 (15), 169 (100), 141 (67), 139 (12), 114 (22); ^1H NMR (CCl_4) δ 2.23 (s, CH_3), 2.28 (s, $COCH_3$), 7.20-7.69 (m, ArH), 7.89 (s, 8-H); IR (KBr) 1670 cm^{-1} (CO), (lit.,[3b] 1673 cm^{-1}), 2-Ethyl-3-methylnaphthalene (17) was a minor product of this reaction and was isolated via its picrate which gave yellow needles, mp 128-129°C (lit.,[22] mp 129-130°C).

Preparation of 2-Methyl-1-acetonaphthone (4) via the Grignard Reaction. A mixture of 2.7 g of Mg (0.11 g atom mol) and 1-bromo-2-methylnaphthalene (18) (22.1 g, 0.1 mol) was added to a 300 mL round-bottomed flask equipped with a Dry Ice condenser. The reaction was initiated by addition of ethylmagnesium bromide and gentle warming. After the reaction started, acetaldehyde (4.8 g, 0.11 mol) was added dropwise by way of the Dry Ice condenser. After the addition, the reaction was continued until the formation of a white semi-liquid was observed. Dilute hydrochloric acid and water were added in sufficient quantities to decompose the salt complex which was formed. The ether-alcohol layer was separated and then extracted with 5% aqueous sodium hydroxide and water respectively. After 'work-up', the product separated and gradually crystallized. Recrystallization from petroleum ether and benzene gave 17.7 g of 19, mp 84-87°C; mass spectrum (70 eV) m/e (rel intensity) 186 (M^+, 56), 171 (81), 153 (26), 143 (100), 128

(55), 43 (23), 20 (32); ^{1}H NMR (CCl_4) δ 1.32-1.38 (d, CH_3), 2.26 (s, $ArCH_3$), 3.06 (s, OH), 5.22-5.42 (m, CH), 5.92-6.62 (m, ArH), 8.12-8.26 (s, peri-H); IR (KBr) Vmax 3268 cm^{-1} and 1053 cm^{-1} (OH).

A solution of 19 dissolved in acetone was titrated with a solution of chromic acid and sulfuric acid (stoichiometric amount) in H_2O. The alcohol was oxidized to 4 (10.12 g) (93%). Injection of the oxidized product with that obtained from the Friedel-Crafts reaction revealed they were identical (first peak of the reaction products). Spectra (IR, NMR, and mass) corresponded to that obtained from the isolation of 4 from the Friedel-Crafts acetylations.

Attempted Rearrangement of 7-Methyl-1-acetonaphthone (3). A. In Methylene Chloride. Dry hydrogen chloride was passed into a stirred solution of aluminum chloride (1.335 g, 0.01 mol) and acetyl chloride (0.38 g, 0.005 mol) in methylene chloride (9.25 mL). 7-Methyl-1-acetonaphthone (3) (1 g, 0.005 mol) dissolved in methylene chloride (1.05 mL) was then added, the mixture was cooled in an ice bath for 30 min, and then allowed to warm to room temperature. With the addition of 3 to the complex, a heterogeneous orange mixture resulted. Samples taken at 1 and 3 h revealed no change in the reaction mixture. At the end of 18 h, two diacetylated products appeared; the composition was: 3:20:21 (18:1:1).

B. In Nitroethane. Reaction A was repeated with the following changes: With the addition of the ketone to the complex, a heterogeneous green mixture resulted. Samples taken at 1 and 3 h revealed no change, 3 (100%). After 18 h there was a trace of a diacetylated product.

Attempted Rearrangement of 2-Methyl-1-acetonaphthone (4). A. In Methylene Chloride. To a mixture of acetyl chloride (0.38 g, 0.005 mol) and aluminum chloride (1.335 g, 0.01 mol) in methylene chloride (9.52 mL), which was stirred under dry hydrogen chloride atmosphere, was added 1.05 mL of methylene chloride containing 2-methyl-1-acetonaphthone (4) (1 g, 0.005 mol). Within a few seconds, a homogeneous brown solution resulted. The mixture was stirred at room temperature for 18 h. After 1 h, there was some rearrangement to 3 (4%, 1 h), 3 (9%, 3 h) and after 18 h the ratio was 2:3:4 (2.7:7.5:1) and the diacetylated products were 20:21 (4:1).

B. In Nitroethane. Reaction A was repeated with the following changes: With the initial addition of the ketone, the complex gave a homogeneous brown solution. After 1 h there was 2:4 (1:32.3), after 3 h these ratios remained the same, however, at the end of 18 h 2:3:4 (2.3:1:4.6) and the diacetylated products 20 and 21 gave a combined ratio of (7%).

Attempted Rearrangement of 3-Methyl-2-acetonaphthone (5). A. In Methylene Chloride. To a stirred mixture of acetyl chloride (0.38 g, 0.005 mol) and aluminum chloride (1.335 g, 0.01 mol) in methylene chloride (9.52 mL) under dry hydrogen chloride atmosphere, was added 3-methyl-2-acetonaphthone (5) (1 g, 0.005 mol) in methylene chloride (1.05 mL). With the addition of this ketone to the complex, a heterogeneous light green mixture resulted. Analysis at 1, 3, and 18 h showed there was no change.

B. In Nitroethane. Repeating A in nitroethane solvent gave no noticeable change after 18 h with the exception of less than 1% of the diacetylated products.

Attempted Rearrangement of 6-Methyl-2-acetonaphthone (2). A. In Methylene Chloride. Dry hydrogen chloride was passed into a stirred solution of aluminum chloride (1.335 g, 0.01 mol) and acetyl chloride (0.38 g, 0.005 mol) in methylene chloride (9.52 mL). 6-Methyl-2-acetonaphthone (2) (1 g, 0.005 mol) dissolved in methylene chloride (1.05 mL) was then added, the mixture was cooled for 30 min, and then warmed to room temperature. The initial color was green. After 1 and 3 h there were no changes. After 18 h a single diacetylated product (5%) and 2 (95%) were observed.

B. In Nitroethane. In nitroethane, the addition of 2 to the complex gave a homogeneous brown solution. After 3 h there was no change. However, after 18 h there was a trace of the diacetylated products.

Acetylation of 2-Methylnaphthalene (1) to 6-Methyl-2-acetonaphthone (2). This reaction was a repeat of a similar previous acetylation in nitroethane with the exceptions of the quantities used. In this reaction, (1200 g, 9 mol) of aluminum chloride, (702 g, 9 mol) of acetyl chloride, and 1 (643 g, 4.5 mol) were combined in nitroethane (8.2 L). This resulted in 801.8 g (96%) of mixed methylacetonaphthones. The ketone mixture (182 g) was combined with 95% ethanol (425 mL) and added to a warm mixture containing semicarbazide·HCl (114 g), sodium acetate (60 g), H_2O (135 mL), and ethanol (575 mL). This mixture was allowed to stir continuously for 2 h, filtered, and washed with hot alcohol to yield 196 g of semicarbazone, mp 234-235°C. This semicarbazone (100 g) was leached once more with 95% hot ethanol leaving 95 g of semicarbazone, mp 236-237°C (Lit.,[5] 237°C).

Preparation of 2-Ethyl-6-methylnaphthalene (9) from the Semicarbazone of (2). A mixture of 2-methyl-6-acetonaphthone semicarbazone

(48 g, 0.20 mol), potassium hydroxide (28 g) and diethylene glycol (300 mL) were heated to reflux (230°C) in a metal flask equipped with a Dean-Stark trap. The hydrocarbon 9 slowly collected in the trap and the contents were drained periodically. A total of 32.8 g of hydrocarbon and diethylene glycol were collected which was diluted with H_2O and extracted with hexane. The hexane solution was dried and distilled to yield 28.4 g (84% yield) of 2-ethyl-6-methylnaphthalene (9). The crude hydrocarbon 9 from the hydrazine reduction was collected in two fractions as a distillate during the reaction; the first cut being purest. The second cut showed two minor impurity peaks; this cut was not used for further synthesis.

Purification of 2-Ethyl-6-methylnaphthalene (9). Distilled 9 (31 g) was added to a solution of picric acid (55 g) in 170 mL of 95% ethanol. The solution was heated and the crude picrate (mp 106-107°C) was filtered after cooling. Recrystallization from 95% ethanol yielded a picrate which melted at 107.5-108.5°C (Lit.,[5] 109°C). This picrate was cleaned with a basic alumina column using hexane as elutant. The hexane solvent was removed and hydrocarbon 9 was recrystallized from methanol (25 mL), filtered, and finally distilled using the Kugelrohr apparatus. This procedure yielded 2-ethyl-6-methylnaphthalene (9) (21 g). Carbon dioxide recovery from combustion and from the benzoic acid calibration experiments revealed that 9 was greater than 99.98% pure; mp 42.5-43.5°C (Lit.,[5] 44-45°C); mass spectrum (70 eV) m/e (rel intensity) 170 (M^+, 16), 155 (32), 32 (23), 28 (100), 18 (27), 17 (6); ^1H NMR (CCl_4) δ 1.08-1.13 (m, CH_3), 2.09 (s, CH_3), 2.27-2.38 (m, CH_2), 7.02-7.28 (m, ArH); IR (KBr) 2960 cm^{-1}.

A. Reaction of Methyl Lithium with 6-Methyl-2-acetonaphthone (2). To a stirred solution of anhydrous diethyl ether in a 1 L round-bottomed flask, was added methyl lithium - lithium bromide (31.7 mL of a 2.05 M solution). The initial reaction temperature was 30°C. 6-Methyl-2-acetonaphthone (2) (10 g, 0.054 mol) in anhydrous diethyl ether (5 mL) was added dropwise to the methyl lithium solution. After the addition of ketone 2, the mixture was heated at reflux for 50 min. Next, 5% hydrochloric acid (10 mL) and water was added dropwise into the reaction flask to quench the reaction and dissolve the complex that formed. The mixture was then placed in a separatory funnel and extracted with ether, washed with water, aqueous sodium bicarbonate, and again with water. The extract was dried ($MgSO_4$), filtered through Dicalite, and concentrated. Distillation under vacuum 105°C (0.35 mm Hg) gave 10.8 g (99%) of crude product. Gas chromatography showed 11 (95%), 2 (4.5%), and 10 (0.5%).

Reaction of 2,4-Dinitrophenylhydrazine-hydrochloride with the Product Mixture of A. To 2.7 g of the mixture containing 2(6-Methyl-2-naphthyl)2-propanol (11, 95%), 6-methyl-2-acetonaphthone (2, 4.5%) and 2-methyl-6-isopropenylnaphthalene (10, 0.5%), was added toluene (50 mL). The mixture was heated to azeotrope any water that may be present, (excessive heat may cause dehydration). Since there was according to glc, 4.5% of 2, it was calculated that there were approximately 2 (7.0×10^{-4} mol) present in the mixture. The mixture was then allowed to cool to room temperature before 2-4-dinitrophenylhydrazine-hydrochloride (1.78 g) was added. After addition, the mixture was heated to boiling, cooled, and the 2-4-dinitrophenylhydrazone was separated from the alcohol 11 and the alkene 10 by passing the mixture through a

chromatography column of neutral alumina. The crude mixture gave a gas chromatogram showing the presence of the test-alcohol 11 (99.3%) and 2-methyl-6-isopropenylnaphthalene 10 (0.7%); there was no ketone present. The yield was 1.5 g (84%).

Isolation of 2-Methyl-6-isopropenylnaphthalene (10). Recrystallization of the mixture of 11 (99.3%) and 10 (0.7%) from 2-propanol was attempted. However, this recrystallization causes some dehydration to 10 which separates as a solid. This solid gave a sharp melting point of 61-62°C. 2-Methyl-6-isopropenylnaphthalene (10) (0.3 g) was then distilled under vacuum with the (0.25 g, 84%) of distillate being collected at 109-114°C (0.14 mm Hg). The percent composition was 10 (99.8%) and 11 (0.2%). The melting point was unchanged. Mass spectrum (70 eV) m/e (rel intensity) 184 (M^++2, 5.5), 183 (M^++1, 16), 182 (M^+, 100), 169 (.8); ^{1}H NMR (CCl_4) δ 2.24 (s, C = C-CH), 2.48 (s, ArCH), 5.08 (s, C = C-CH), 5.43 (s, C = C-CH), 7.14-7.89 (m, Ar-H); IR (KBr) 2924 cm^{-1}.

Isolation of 2(6-Methyl-2-naphthyl)2-propanol (11). The mixture obtained in A was recrystallized from diethyl ether. The mixture (4 g) was dissolved in a few milliliters of ether to give 2.95 g of 11 approximately 99% pure; mp 53-54°C; mass spectrum (70 eV) m/e (rel intensity) 200 (M^+, 20), 186 (6), 182 (7), 141 (11), 115 (8) and 43 (100); ^{1}H NMR (CCl_4) δ 1.50 (s, CH_3), 2.44 (s, Ar-CH), 2.76 (s, OH), 7.06-7.70(m, Ar-H), in D_2O no absorption at 2.76 (s, OD); IR (KBr) 3378 cm^{-1} (OH), 1133 cm^{-1} (CO).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.03; H, 8.07.

Hydrogenation/Hydrogenolysis of a 2(6-Methyl-2-naphthyl)2-propanol (11) (99.3%) and 2-Methyl-6-isopropenylnaphthalene (10) 0.7%) Mixture. To a 100 mL hydrogenation flask was added 1.70 g of the mixture containing the above percentages of compounds and 5% Pd/C (0.296 g). These reagents, in a hydrogen atmosphere, were allowed to react in acetic acid (50 mL). After consuming 495 mL of hydrogen, the reaction was filtered through Dicalite, stripped of acetic acid, taken up in diethyl ether and then washed with water, sodium bicarbonate, and water, respectively. The organic mixture was then dried ($MgSO_4$), filtered through Dicalite and concentrated to a crude product (1.5 g 88%). Gas chromatography studies showed 11 and 2-ethyl-6-methylnaphthalene (9), 2-methyl-6-isopropenylnaphthalene (10), 2-isopropyl-6-methylnaphthalene (12), and reduced ring products. This mixture was then passed through a column of silica gel with the aid of isohexane as the solvent. Gas chromatography showed the removal of 11 and 10 and some of the reduced ring products. The yield, after passing through silica gel, was 1.3 g.

To 10 ml of hot 95% ethanol was added 2.24 g of picric acid and 1.3 g of the hydrocarbon mixture of 2-isopropyl-6-methylnaphthalene (12) and 2-ethyl-6-methylnaphthalene (9) in ethanol (3 mL). A light red color formed immediately; with orange crystals forming after 1 h. Recrystallization from ethanol gave a picrate, mp 91-91.5°C. Hydrolysis of the picrate gave 0.9 g of the hydrocarbon mixture. Gas chromatography revealed 12 (99.9%) and 2-ethyl-6-methylnaphthalene (9) (0.1%) mp 36-37°C; mass spectrum (70 eV) m/e (rel intensity) 184 (M^+, 42), 182 (16), 170 (17), 169 (100), 154 (30), 141 (27), 32 (21); ^1H NMR (CCl_4) δ 1.26-1.36 (d, CH_3), 2.45 (s, ArCH), 2.8-3.14 (m, CH), 7.08-7.60 (m, ArH); IR (KBr) 2924 cm^{-1}.

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29. The author wishes to thank Dr. G. W. Keen of the Continental Oil Company at Ponca City, Oklahoma, for providing and interpreting the gas chromatography - mass fragmentography spectra.

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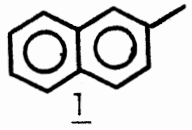
33. GLC analyses of the isomeric ketones were done with a Hewlett-Packard 5750B instrument using an 8-ft x 0.25 in. copper tubing column of 4% UCW-98 on 80-120 mesh Chromosorb A (50%) and Chromosorb G (50%) at 220°C.

APPENDIX

GLOSSARY OF STRUCTURES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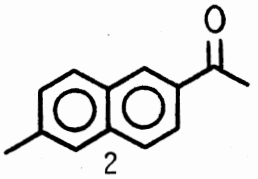

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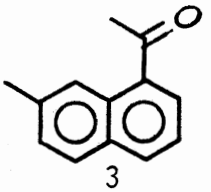

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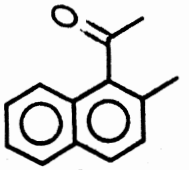

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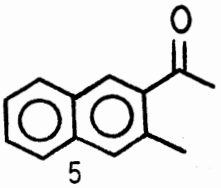

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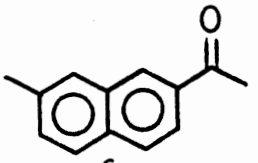

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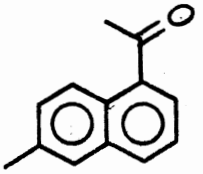

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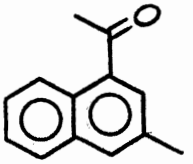

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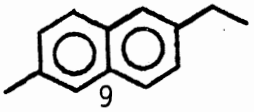
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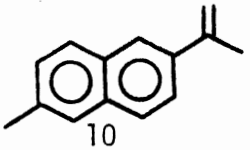
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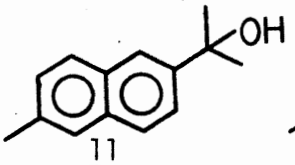

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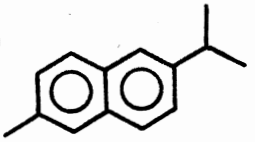
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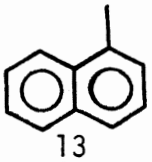
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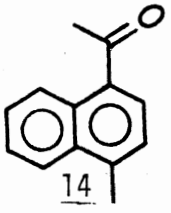

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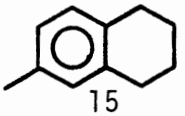
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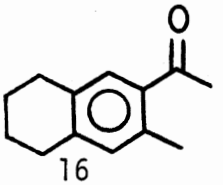

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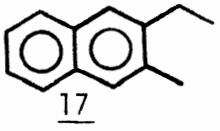
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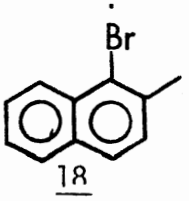

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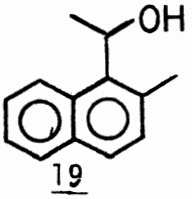

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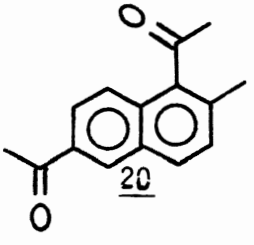

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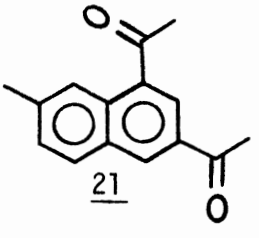

21

VITA[2]

Hubert Emmanuel Storr

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Master of Science

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Education: Graduated from Saint Augustine's High School, Nassau, Bahamas, in 1972; received the Bachelor of Science degree from Langston University, Langston, Oklahoma in July, 1975, with a major in biology and a minor in chemistry; completed requirements for the Master of Science at Oklahoma State University in July, 1978.

Professional Experience: Undergraduate Teaching Assistant, Langston University, 1974-75; Graduate Teaching Assistant, Oklahoma State University, 1975-77; Graduate Research Assistant, Energy Research and Development Administration, Oklahoma State University, 1976; Graduate Teaching Assistant, Sunoco Summer Fellowship, Oklahoma State University, 1976; Graduate Research Assistant, Environmental Protection Agency, Oklahoma State University, 1976-77; Graduate Teaching Assistant and Dow Chemicals Summer Fellowship, Oklahoma State University, 1976; Graduate Research Assistant, Energy Research and Development Administration, Oklahoma State University, 1977-78; Member of Beta Kappa Chi and Phi Lambda Upsilon.