

THE ACETYLATION OF NAPHTHALENE AND THE FORMATION  
OF (CHLOROVINYL)NAPHTHALENES THEREIN

By

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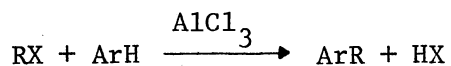
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## CHAPTER I

### INTRODUCTION

In 1877 Charles Friedel and James Crafts<sup>1</sup> reported alkylation in the presence of  $\text{AlCl}_3$ . They found that alkyl chlorides could react with benzene in the presence of  $\text{AlCl}_3$ .

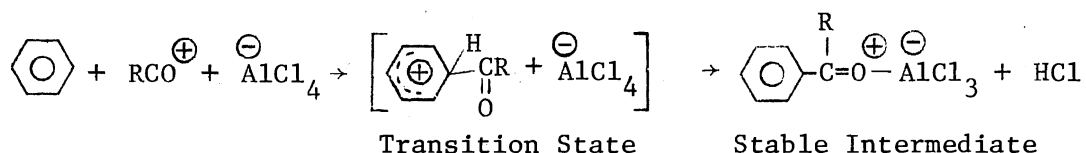


Earlier work by Zincke<sup>2</sup> reported the formation of diphenylmethane during an attempted Wurtz synthesis of  $\beta$ -phenylpropionic acid. Benzyl chloride reacted with the benzene solvent in the presence of a metallic catalyst.

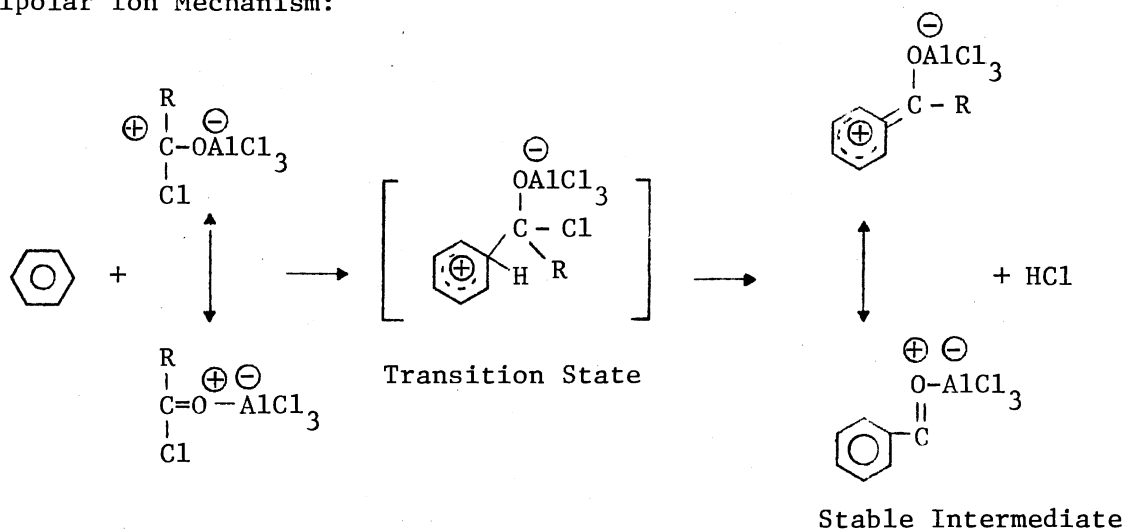
Thousands of Friedel-Crafts acylation reaction studies have been reported.<sup>3</sup> These studies have dealt with variations of the aromatic nucleus, acyl component, the catalyst, order of addition of reactants, temperature, solvent and reactant ratios. Product analysis procedures have concentrated on reaction yield and the positions of substitution. There have been few studies of reaction by-products and impurities in spite of reported yields of desired product as low as 15 percent. Many of these studies predated gas chromatography, nmr spectrometry, and mass spectrometry. Present-day concerns about contamination of the environment and industrial safety have augmented the importance of reaction by-products.

Two types of Friedel-Crafts acylation mechanisms have been proposed.<sup>4</sup> These may be called an ion pair mechanism and a dipolar ion mechanism. Normal acylations are presumed to proceed via the

Ion Pair Mechanism:



Dipolar Ion Mechanism:



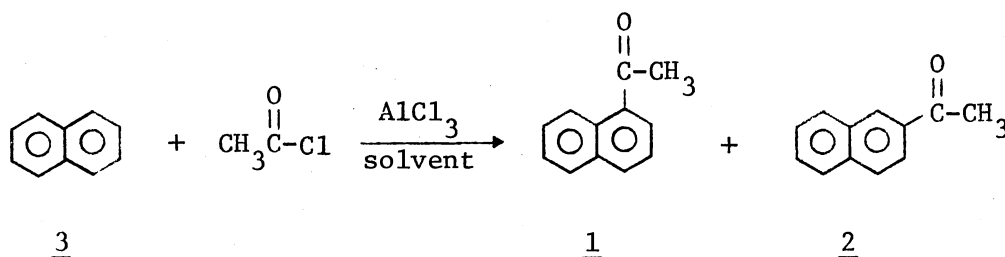
dipolar ion mechanism. The ion pair mechanism seems to be more important in sterically hindered reactions.

A variety of solvents have been used for Friedel-Crafts acylation reactions.<sup>5</sup> A nonpolar solvent such as carbon disulfide fails to dissolve aluminum chloride or its acyl halide complex whereas a polar solvent (nitrobenzene) dissolves and solvates aluminum chloride, the acyl halide-aluminum chloride complex, and the aluminum chloride complex of the ketone products. Solvents with intermediate polarities,



such as methylene chloride, 1,2-dichloroethane and chloroform, do not dissolve aluminum chloride, but they readily dissolve the acyl halide-aluminum chloride complex. Some of the ketone complexes are soluble. Many of the variations in yield and orientation are due to the varied solubilities of these complexes.

The Friedel-Crafts acetylation of naphthalene has been extensively reported.<sup>6</sup> Two isomeric ketones, 1-acetonaphthone (1) and 2-acetonaphthone (2), can be prepared by the reaction of naphthalene (3) with acetyl chloride and aluminum chloride. The solvent effect on



naphthalene acylation has been studied intensively.<sup>5</sup> The 1/2 product substitution ratio is solvent-dependent and a reversible acylation process has been proposed<sup>6</sup> to explain this solvent dependence. The aluminum chloride-ketone complex is insoluble in solvents such as methylene chloride, ethylene dichloride, or chloroform. The 1-acetonaphthone-aluminum chloride complex can form rapidly and precipitate from the solution to prevent further reaction. However in the polar solvent, nitrobenzene, the complex is soluble. The 1-isomer can deacylate, and the slower 2-acylation reaction may then occur. The Givaudon Corporation markets, under the unregistered trademark "Oranger Liquid," a mixture of about 95:5, 1:2.<sup>7</sup>

## Mass Fragmentography

The use of a combination of a gas chromatograph and a mass spectrometer (GCMS) to analyze complex mixtures was first reported by Gohlke,<sup>8</sup> who combined a time-of-flight mass spectrometer with a gas chromatograph. Lindeman and Annis<sup>9</sup> used a combination of a gas chromatograph and a Consolidated Electrodynamics Corporation (CEC) Model 21-103C mass spectrometer to analyze complex hydrocarbon mixtures. The 21-103C can be used to monitor a single peak or to scan a narrow mass range repeatedly. Lindeman and Annis used this capability to deconvolute complex chromatograph peaks.

Sweeley, Elliott, Fries and Ryhage<sup>10</sup> used a prototype of the LKB mass spectrometer coupled to a gas chromatograph to analyze glucose and glucose-d<sub>7</sub> mixtures and to analyze for trimethylsilyl ethers of dihydroepiandrosterone and epiandrosterone. Hammer, Holmstedt and Ryhage<sup>11</sup> used a similar system to analyze for chlorpromazine metabolites. They used an accelerating voltage alternater unit to record the intensities of three mass numbers and named the technique "mass fragmentography."

Hammer and Hessling<sup>12</sup> utilized a multiple ion detector (MID) in combination with a peak-matching technique designed for a low resolution LKB-based GCMS system. They recognized the potential of a high resolution system but had non available to them. Watson, Pelster, Sweetman, and Frolich<sup>13</sup> used an LKB system to analyze for prostaglandins by the MID technique.

Frew and Isenhour<sup>14</sup> used an AEI-902 double-focusing high resolution mass spectrometer in combination with a computer and peak-matching circuitry to determine isotope ratios. Chapman, Compson, Done, Merren and Tennant<sup>15</sup> used an AEI system to analyze for trace levels of steroids by an MID technique. Albrecht, Plattner, Hagerman, Markey and Murphy<sup>16</sup> reported the use of an MS-12 high resolution system with rapid peak switching circuitry to measure xenon isotope ratios.

Strong and Atkinson<sup>17</sup> used "quadrupole mass fragmentography" to analyze for lidocaine and its metabolites. Their Finnigan 3000 GCMS system with a 240-01 automatic peak selector and a four-pen recorder was used to monitor the m/e 58, 86 and 120 peaks.

Several mass fragmentography studies using GCMS-computer systems have been reported. These utilized Hitachi RMU-6L,<sup>18</sup> Finnigan-3000,<sup>19</sup> DuPont 21-491,<sup>20</sup> LKB-9000,<sup>21,22</sup> and UTI-100C<sup>23</sup> systems. Despite numerous CEC-110B mass spectrometer systems in use, there has been no reported mass fragmentography utilizing this versatile high resolution instrument, which is capable of mass fragmentography with a resolution of 1 part in 20,000. In the present study, the m/e 188.039 and 190.036 signals of the (chlorovinyl)naphthalenes present in the reaction products were fed to a 2-pen recorder as these materials were eluted from a gas chromatography column.

Figure 1 shows the GC-MF trace from K&K 1-acetonaphthone. Figure 2 shows the trace from K&K 1-acetonaphthone which has been spiked with 0.5% 1-(1-chlorovinyl)naphthalene. Figure 3 shows the trace from K&K 1-acetonaphthone which has been spiked with 0.5% 1-(1-chlorovinyl)-naphthalene and 0.5% 2-(1-chlorovinyl)naphthalene. Similar data for Eastman 1-acetonaphthone (Figure 4), Aldrich 1-acetonaphthone

(Figure 5), Oranger Liquid (Figure 6), and reaction products (Figures 7-10) have been obtained. All figures are presented in Appendix B.

## CHAPTER II

### RESULTS AND DISCUSSION

#### Acetylation of Naphthalene with Acetyl Chloride in Chloroform

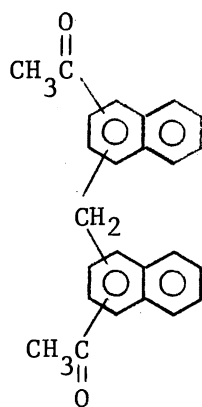
A study of the Friedel-Crafts acetylation of naphthalene was prompted by a need to isolate a considerable quantity of pure 1. Bassilios, Makar and Salem<sup>24</sup> had reported the preparation of 99 percent 1 in 90 percent yield by adding 0.25 mol of 3 in  $\text{CHCl}_3$  to a chloroform solution of 0.5 mol of the aluminum chloride-acetyl chloride complex. The purity and the yield of 1 were determined by Baddeley's picrate melting point procedure.<sup>25</sup>

The procedure of Bassilios et al.<sup>26</sup> was used to prepare 1, but the expected purity of 98% was not achieved. A GC analysis indicated a purity of 91-94 percent instead.

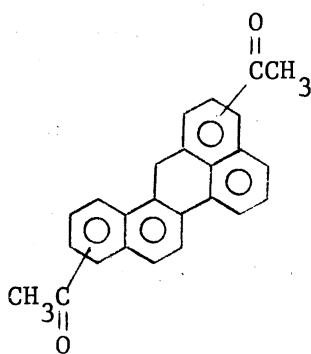
The chromatographic analysis indicated the presence of not only 1 and 2 but a component which had been separated by Bansal<sup>27</sup> and tentatively identified by Flanagan<sup>28</sup> to be 1-(1-chlorovinyl)naphthalene (4).

The most striking thing about the acylation in chloroform is the green color of the reaction mixture. The undistilled liquid product was green, and a dark green precipitate remained in the reaction flask. This material fouled the filtration funnel. The dark green

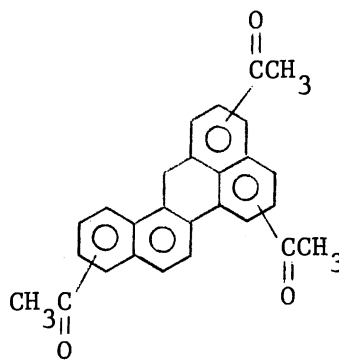
semi-solid was analyzed via a probe distillation analysis with a mass spectrometer. Spectra were obtained at various probe temperatures. At 80°, the mass spectrum had peaks corresponding to the acetonephthones and the (chlorovinyl)naphthalenes. The acetonephthones were the major components until the probe temperature reached 255°. At 250°, peaks at  $m/e$  352, 350 and 392 indicated the presence of alkylation product of the types represented by 6, 7, and 8. Since position isomers are not readily distinguishable by mass spectrometry, the positions of attachment were not determined.



6  
 $M^+ = 352$



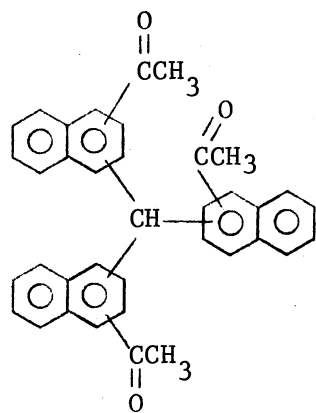
7  
 $M^+ = 350$



8  
 $M^+ = 392$

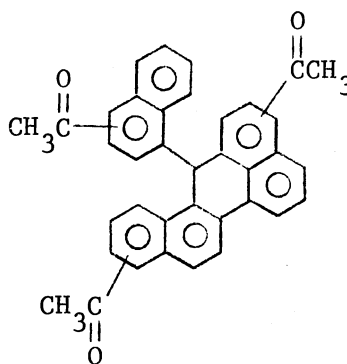
At 250°, the mass spectrum had peaks corresponding to 7 and 8. At 300°, the spectrum had peaks from 7, 8 and 9. At 325°, 340° and 350°, the spectra had intense peaks from 9 and smaller peaks from 10.

A solution of 3 in  $\text{CHCl}_3$  was added to a suspension of  $\text{AlCl}_3$  in  $\text{CHCl}_3$ . Acetyl chloride was added and a green rubbery material was isolated. The ether soluble portion was analyzed via a mass spectral probe distillation. The major components identified by



$$\underline{9}$$

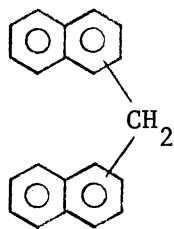
$$M^+ = 520$$



$$\underline{10}$$

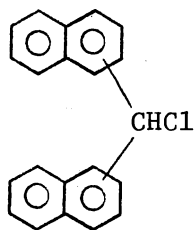
$$M^+ = 518$$

their molecular ion peaks, were dinaphthylmethane (11) and chlorodinaaphthylmethane (12). Small amounts of perylene (13), naphthophen- alenes (14), and ethoxydinaphthylmethane (15) were also observed.



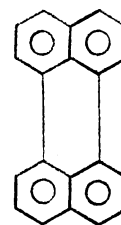
$$\underline{11}$$

$$M^+ = 268$$



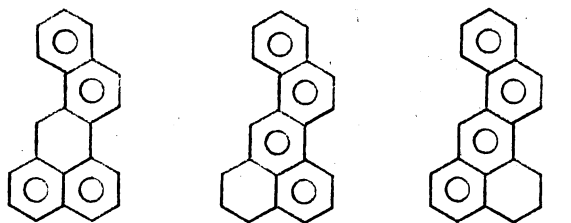
$$\underline{12}$$

$$M^+ = 302$$



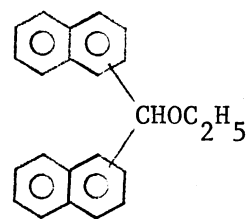
$$\underline{13}$$

$$M^+ = 252$$



$$\underline{14}$$

$$M^+ = 266$$



$$\underline{15}$$

$$M^+ = 312$$

Heavier material was present which did not produce mass spectra. Only a small portion of the sample vaporized.

Analysis of Reaction Mixtures to Show the  
Formation of 4 and 5

The GC-mass fragmentography method was applied in order to determine the concentration of 4 and 5 in reaction mixtures.

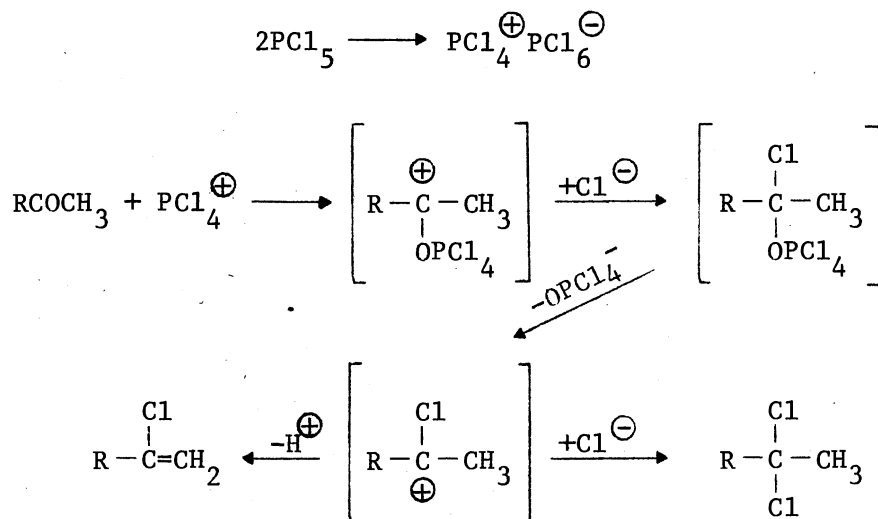
A GC-mass fragmentography procedure is used to monitor specific mass spectral peak intensities as material is eluted from a GC column. In this case, the mass spectrometer was set up so that it alternately and repeatedly scanned the molecular ion peaks ( $m/e$  188.039 and 190.036) of (chlorovinyl)naphthalenes. Figure 3 shows a GC-mass fragmentography trace of K&K acetonephthalones spiked with 0.5% of 4 and 0.5% of 5.

There is an evident increase in the mass fragmentography (MF) signals during the time that 4 was eluted. The  $m/e$  188 and 190 peaks are in a ratio of 3:1 because these correspond to the natural abundances of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  nuclides.

The MF signals increase a second time in the area where 1 and 2 were eluted from the chromatograph. These two signals are due to 5. Thus, the GC-MF method not only provides a method for the identification and quantitative determination of 4, but it shows the presence of the previously undetected 5. The retention times were confirmed by the synthesis of 4 and 5.

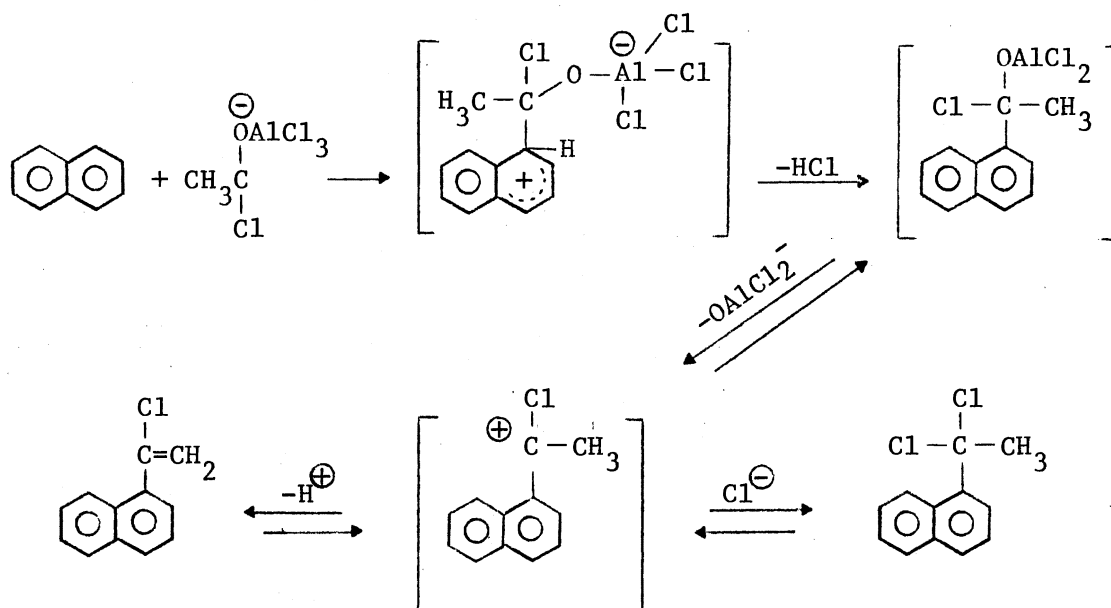
Newman et al.<sup>29,30</sup> studied the mechanism of the reaction of  $\text{PCl}_5$  with ketones. They proposed the following mechanism:



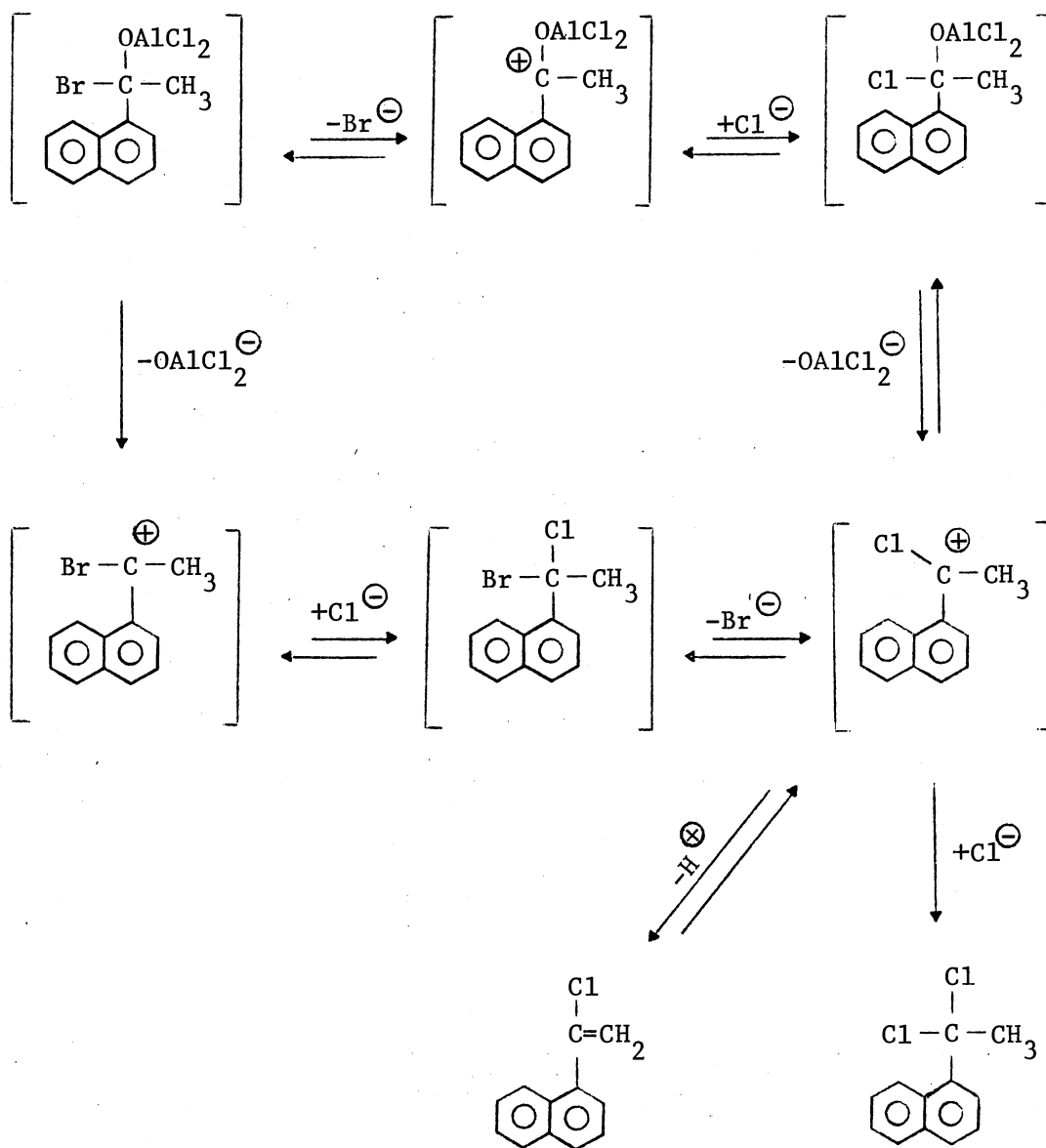


Their evidence indicates that the dichloride was *not* formed by an SN2 displacement of  $\text{OPCl}_4^-$  by chloride ion. They believed that the chloro-carbonium ion was the most significant species in the reaction of ketones with  $\text{PCl}_5$ .

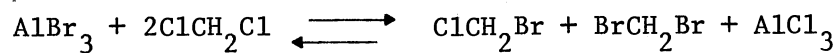
The formation of 4 from the reaction of 3 with the aluminum chloride-acetyl chloride complex may result from the same intermediate chlorocarbonium ion.



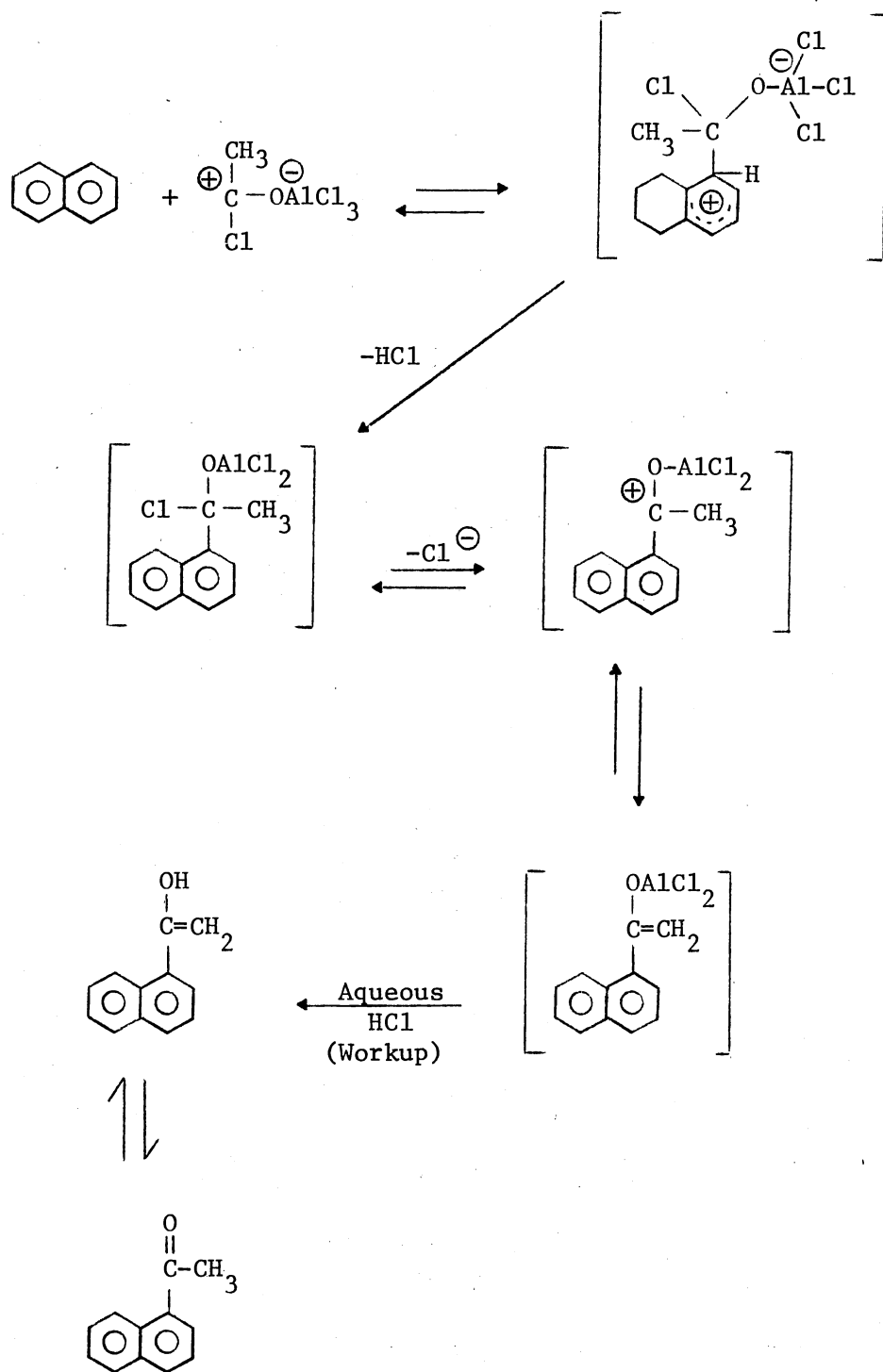
An additional step is required to explain the formation of 4 and 5 from the acetyl bromide intermediate.



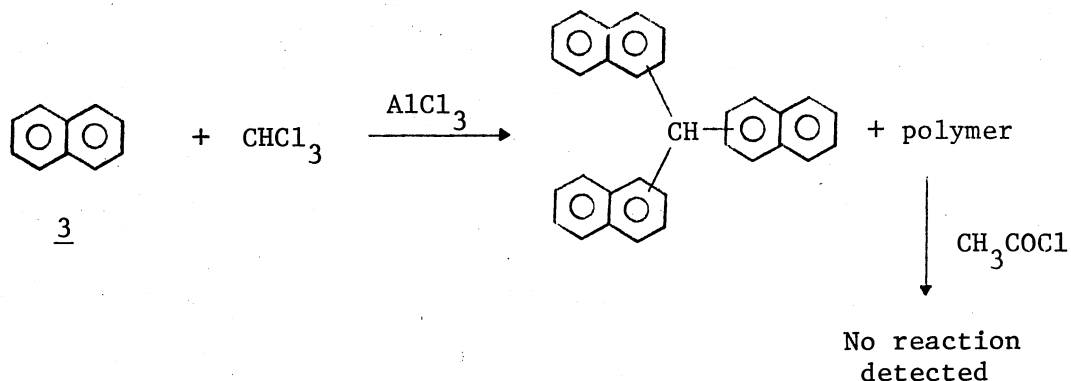
Either the chlorinated solvent or  $\text{AlCl}_3$  can serve as a source of chloride ions. This was especially obvious when  $\text{AlBr}_3$  was used as a catalyst; bromochloromethane and methylene bromide were observed.



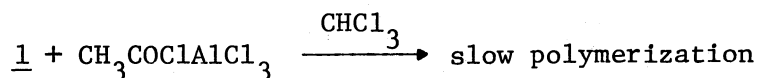
It is interesting to explore ionic intermediates leading to the formation of 1 and 2.



Several polymeric products were observed. When 3 and  $\text{CHCl}_3$  were contacted with  $\text{AlCl}_3$ , the expected alkylation products were formed, but subsequent addition of acetyl chloride caused little reaction, apparently because of the insolubility of the polymer produced by the alkylation of naphthalene with chloroform.

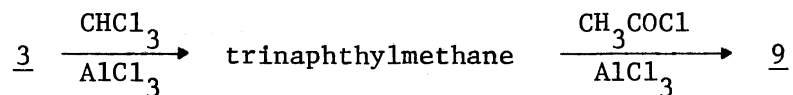


The trinaphthylmethane was apparently trapped in the insoluble polymer, preventing further reaction. Traces of trinaphthylmethane were observed in the probe distillation mass spectra. When a chloroform solution of 1 was added to chloroform solution of the  $\text{AlCl}_3\text{-CH}_3\text{COCl}$  complex, a dark color developed. Gas chromatography analysis after 1 hour at  $30^\circ\text{C}$  indicated that 1 had not reacted appreciably. Possibly this is because of the stabilizing effect of the electron-withdrawing acetyl group.

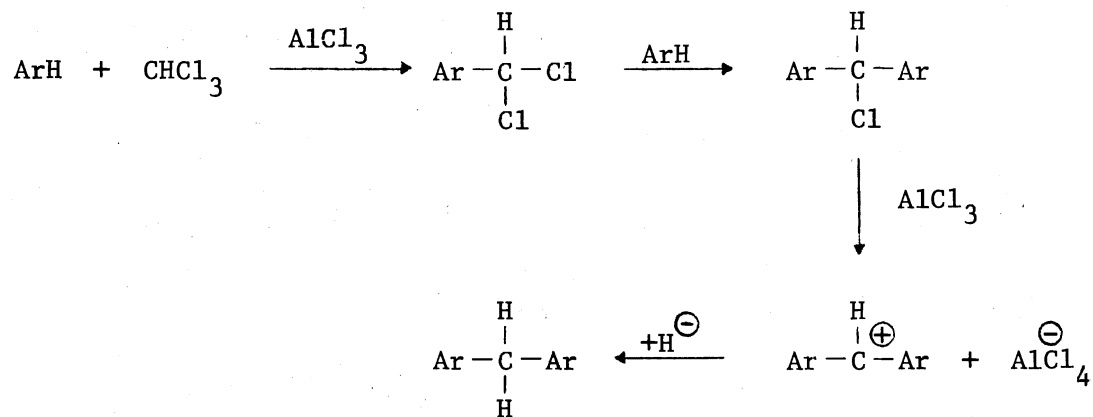


The addition of a  $\text{CHCl}_3$  solution of 3 to a  $\text{CHCl}_3$  solution of the  $\text{CH}_3\text{COClAlCl}_3$  complex formed an acetylated polymer. In this case, the

trinaphthylmethane was probably acetylated before it was trapped in insoluble polymeric material.



The dinaphthylmethane products were probably formed by hydride transfer as shown below.

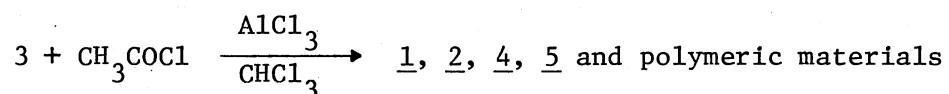


The alkylation-acylation products contained numerous position isomers.

## CHAPTER III

### EXPERIMENTAL

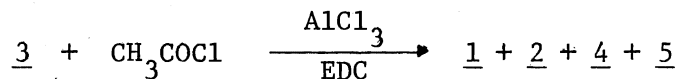
#### Acetylation of Naphthalene with Acetyl Chloride- Aluminum Chloride in Chloroform



A 1000-ml, 3-necked, round-bottom flask was equipped with a Teflon paddle stirrer, addition funnel and gas vent tube. It was mounted in a plastic basin containing ice water. Chloroform (200 ml) and anhydrous aluminum chloride (150 g) were stirred continuously while 81 ml of acetyl chloride (89.4 g) was added over a period of 5 minutes.

A solution of naphthalene (68 g) in chloroform (200 ml) was added over a period of 15 minutes. During this time the color of the reaction mixture changed from yellow to blue-green to black. The reaction mixture was warmed to 30°C and stirred for 30 minutes. The reaction mixture was poured into a stirred mixture of ice and concentrated HCl. The chloroform layer was separated, filtered through Dicalite and concentrated to yield a dark green semi-solid product, GK-I.

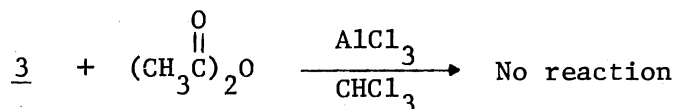
Acetylation of Naphthalene with Acetyl  
Chloride-Aluminum Chloride in  
1,2-Dichloroethane (EDC)



The acetylation reaction was repeated with EDC as a solvent in place of  $\text{CHCl}_3$ . The reaction yield of 1:2 (93.5:6.5) was 98 percent. A GC-MF analysis indicated the presence of 1.1 percent of 4 and 0.2 percent of 5. The green solid was not formed.

A 500-ml, 3-necked, round-bottomed flask, equipped with a Teflon paddle stirrer, addition funnel, and gas vent tube, was mounted in a plastic basin of ice water. 1,2-Dichloroethane (100 ml) and aluminum chloride (70 g) were stirred continuously while 40.5 g of acetyl chloride was added over a period of 5 minutes. The funnel was rinsed with 20 ml of ethylene dichloride. A solution of naphthalene (34 g) in EDC (100 ml) was added over a period of 15 minutes. The color turned bright yellow around the dropping funnel where some solid material formed (or collected). The solution was yellow-brown at first, then bright yellow and opaque. The solution was warmed to 30°C and stirred for 30 minutes, whereupon it turned orange. The reaction mixture was worked up as before and the EDC layer was concentrated to yield 44 g of a product, GK-II.

The Attempted Acetylation of Naphthalene with  
Acetic Anhydride-Aluminum Chloride  
in Chloroform

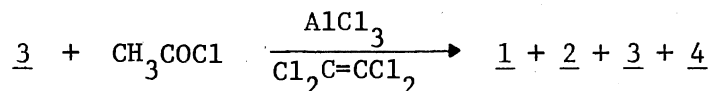


An attempt was made to react naphthalene with acetic anhydride in chloroform under standard reaction conditions, but the acetic anhydride-aluminum chloride complex was apparently insoluble. No reaction occurred. Crystalline naphthalene was recovered.

Aluminum chloride (75 g) was placed in a 500 ml, round-bottomed flask equipped as before. The flask was cooled in ice and 100 ml of chloroform was added. The suspension was stirred continuously while 52 ml of acetic anhydride was added over a period of 5 minutes. A white solid with the appearance of a partially melted ice cube appeared in the solution and persisted throughout the low-temperature portion of this experiment. Naphthalene (34 g) in chloroform (100 ml) was added over a period of 15 minutes, during which time the reaction mixture changed from yellow to brownish-yellow. The reaction mixture was warmed to 30°C and stirred for 30 minutes, during which time the reaction mixture progressively became dark green in color. The reaction mixture was worked up as in the acetyl chloride run and treated as before. The chloroform layer was separated, filtered through Dicalite and concentrated to yield a light brown solution from which white crystals were separated. The white crystals were naphthalene.



The Acetylation of Naphthalene with Acetyl  
 Chloride-Aluminum Chloride in  
 Tetrachloroethylene

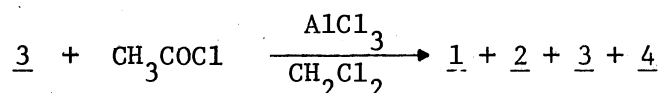


The acetylation in tetrachloroethylene produced a 90 percent yield of 1:2 (85:15). A GC-MF analysis indicated 1.0 percent 4 and 0.65 percent 5. No green product formed.

A 500-ml, 3-necked, round-bottomed flask was equipped and chilled as usual. Tetrachloroethylene (100 ml) and aluminum chloride (70 g) in the flask were stirred continuously while 40.5 g of acetyl chloride was added over a period of 5 minutes. The addition funnel was rinsed with 20 ml of ethylene dichloride. A solution of naphthalene (34 g) in tetrachloroethylene (100 ml) was added over a period of 15 minutes. The solution, first yellow-brown, changed to bright yellow and then became opaque. The solution was warmed to 30°C and stirred for 30 minutes, whereupon it turned orange. The reaction mixture was hydrolyzed and otherwise treated as usual to yield 43 g of product, GK-III. The yield was 96 percent.

The Acetylation of Naphthalene with Acetyl  
Chloride-Aluminum Chloride in  
Methylene Chloride

Acetylation of 3 in Dichloromethane

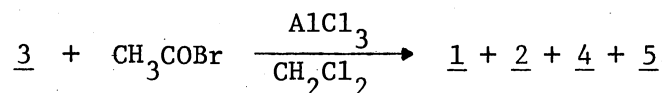


The acetylation reaction in dichloromethane produced 1 and 2 in a 97:3 ratio. A GC-MF analysis indicated 0.9 percent of 4 and 0.15 percent of 5. No green product formed.

A 500-ml, 3-necked, round-bottomed flask was equipped with a Teflon paddle stirrer, a gas vent tube and an addition funnel which had been modified so the added solution would drop directly into the solution rather than down the side of the flask. The apparatus was cooled in ice water, and a methylene chloride (100 ml) suspension of aluminum chloride (75 g) in the flask was continuously stirred while acetyl chloride (40.5 g) was added over a period of 5 minutes. The addition funnel was rinsed with 10 ml of  $\text{CH}_2\text{Cl}_2$ .

A solution of naphthalene (34 g) in  $\text{CH}_2\text{Cl}_2$  (100 ml) was added over a period of 15 minutes, during which the reaction mixture changed from opaque white to yellow. The temperature was increased to 27°C, and the mixture was stirred for 30 minutes, the color deepening to orange. The reaction mixture was worked up to yield GK-IV in 93% yield.

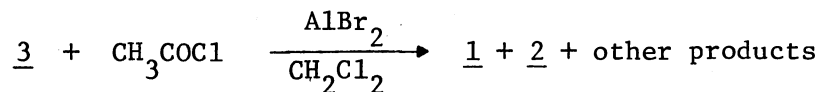
The Acetylation of Naphthalene with Acetyl  
Bromide-Aluminum Chloride in  
Methylene Chloride



The acetylation of 3 with acetyl bromide and aluminum chloride produced 1:2 (96:4) in 92 percent yield.

To a 500-ml, 3-necked flask equipped and chilled as before was added 75 g of  $\text{AlCl}_3$  (0.56 mol) in 100 ml of  $\text{CH}_2\text{Cl}_2$ , which was stirred continuously while 42 ml (0.56 mol) of acetyl bromide was added dropwise. A solution of 34 g of naphthalene (0.25 mol) in 100 ml of  $\text{CH}_2\text{Cl}_2$  was added over a period of 15 minutes. The color changes from light brown to bright, opaque orange. Fumes were observed. A green color was observed near the  $\text{AlCl}_3$  deposits on the upper half of the flask that were not in contact with the solvent. The temperature was raised to  $30^\circ\text{C}$ , and the stirring was continued for 30 minutes. The reaction mixture was treated as usual to yield GK-V.

The Acetylation of Naphthalene with Acetyl  
Chloride-Aluminum Bromide in  
Methylene Chloride



The acetylation of naphthalene with aluminum bromide-acetyl chloride in methylene chloride produced 1:2 (83:17) in 89 percent

yield. The impurities in the crude reaction product included 4, 5, (bromovinyl)naphthalenes (16 and 17) bromochloromethane, dibromomethane, and 6. A trace of (1,1-dichloroethyl)naphthalene was observed.

To a 500-ml, 3-necked flask equipped as usual was added 100 g  $\text{AlBr}_3$  (0.37 mol) in about 100 ml of  $\text{CH}_2\text{Cl}_2$ . The solid aluminum bromide was received in a sealed tube. The tube was crushed with pliers in a 1000-ml beaker, and the  $\text{AlBr}_3$  was dissolved in the solvent. Aluminum bromide is much more soluble than aluminum chloride. To this solution was added 26.3 ml of acetyl chloride (0.37 mol). A solution of 23.68 g of naphthalene in 100 ml of  $\text{CH}_2\text{Cl}_2$  was added over a period of 15 minutes. Fumes were evolved, and a pale green color developed. The mixture was warmed to  $30^\circ\text{C}$  and stirred for 30 minutes, then worked up as usual to yield GK-VI.

#### The Reaction of Oranger Liquid and Phosphorus Pentachloride

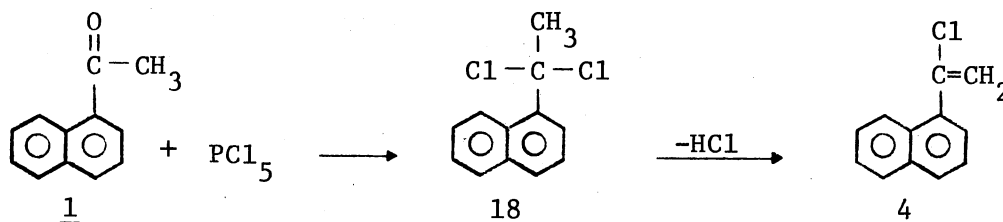
A solution of 34 g of Oranger liquid in 100 ml of  $\text{CH}_2\text{Cl}_2$  was added to a suspension of 45.7 g of  $\text{PCl}_5$  in 200 ml of  $\text{CH}_2\text{Cl}_2$  in the usual 3-necked, 500-ml flask equipped with a Teflon-paddle stirrer, a nitrogen inlet tube and a vented dropping funnel. Evolution of  $\text{HCl}$  was indicated by pH paper, but no immediate color change occurred. After all the ketone had been added, the solution was lime-green. The separatory funnel was replaced with a condenser and the solution was stirred for one hour. A 5-ml aliquot was drawn from the solution, added to ice water, the  $\text{CH}_2\text{Cl}_2$  layer separated, and the water layer extracted again with 5 ml of  $\text{CH}_2\text{Cl}_2$ . The total extract was washed

with  $\text{H}_2\text{O}$ , filtered through glass wool and concentrated. The mass spectrum indicated 22 percent ketone remaining.

A similar workup of a sample taken after 2 hours indicated 8 percent ketone remaining. A plot of  $\log [(1\text{-ketone})/\text{product ketone}]$  vs. time indicated that the reaction would be complete after 5 hours. A workup of the remaining reaction mixture after 5 hours yielded 55 g of reaction product, GK-VII.

In a variation of the above experiment the reaction mixture was stirred for 72 hours at room temperature. Sodium bicarbonate was added until the pH reached 7. The bicarbonate-organic mixture was stirred for 24 hours after some  $\text{CCl}_4$  had been added because some of the  $\text{CH}_2\text{Cl}_2$  was lost during the long reaction. The organic layer was removed and concentrated to yield GK-VIII.

#### The Reaction of 1 with Phosphorus Pentachloride

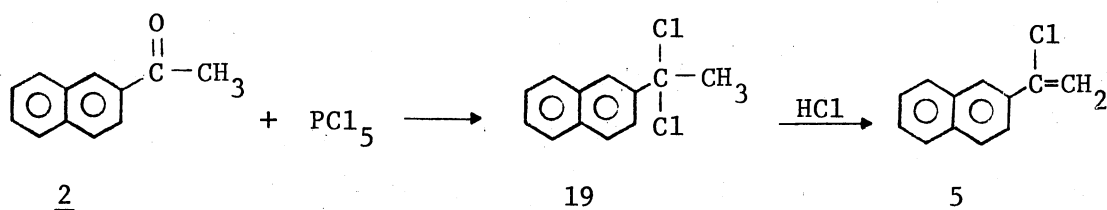


The reaction of 1 with  $\text{PCl}_5$  produced the dichloride 18. The dichloride gradually loses  $\text{HCl}$  upon storage to produce 4. The dichloride was indicated by nmr analysis, but it was not isolated in a pure state.

Into a 500-ml, 3-necked flask equipped with a Teflon-paddle stirrer and a water-cooled condenser, and containing 45.7 g of  $\text{PCl}_5$  in 100 ml of  $\text{CH}_2\text{Cl}_2$ , was added 34 g of 1 in 100 ml of  $\text{CH}_2\text{Cl}_2$ . The reaction mixture turned lime-green, and the temperature increased to

36°C. After 20 hours, the reaction mixture was pale green. Water (50 ml) was added through the dropping funnel, and 100 g of  $\text{NaHCO}_3$  was added very carefully with a spatula in small amounts. Extensive foaming occurred. The mixture was stirred for 4 hours (slowly at first), the layers were separated, and the organic layer was concentrated to yield 44 g of product, GK-IX.

The Reaction of 2 with Phosphorus Pentachloride



The reaction of 2 with  $\text{PCl}_5$  produced the dichloride 19 which also lost  $\text{HCl}$  to yield 5.

This reaction was conducted almost exactly as for 1. Workup as for 1 yielded 43 g of GK XI.

The Reaction of Oranger Liquid  
with Aluminum Chloride

To 20 g of  $\text{AlCl}_3$  suspended in 150 ml of  $\text{CCl}_4$  was added 20 g of oranger liquid<sup>7</sup> in 50 ml of  $\text{CCl}_4$ . The solution immediately turned brown. Stirring was continued for 24 hours at room temperature. The reaction mixture was poured into ice and  $\text{HCl}$ . The organic layer was separated and concentrated to yield GK-XII.

### The Stability of 4

In order to test the stability of 4, it was reacted with several reagents. A methylene chloride solution of 4 showed no change upon stirring with aqueous  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$  and  $\text{HCl}$ . The addition of anhydrous  $\text{AlCl}_3$  to a methylene chloride solution of 4 immediately yields a black flocculent polymer.

### The GC Analysis of Mixtures of 1 and 2

Each of the acetylation reactions produced a mixture of 1 and 2. In order to determine the 1:2 ratio, a gas chromatography method was developed. A 2.5% solution in acetone was separated on a 14' x 1/8" UCW 98 column at 200° isothermal. A typical trace is shown in Figure 12 (see Appendix B). Table I shows the results from the GC analysis of selected reaction products.

### The GC-Mass Fragmentography (GC-MF) Analysis of 4 and 5 in Reaction Products

The GC trace shows that 4 is resolved from 1 and 2 on a UCW 98 column, but 5 is not detected because it is co-eluted with 2.

The Consolidated Electrodynamics Corporation (CEC) model 110B high resolution mass spectrometer was used for the mass fragment detector. The magnetic field was adjusted to focus the m/e 188 peak. The mass measurement chassis was utilized to alternately scan the m/e 188 and 190 regions. Thus, the mass spectrometer was set up to detect only those compounds which yield peaks at m/e 188 or 190. The

TABLE I  
THE GC ANALYSIS OF MIXTURES OF 1 and 2

| Product                     | 1:2 Ratio |
|-----------------------------|-----------|
| GK-II                       | 93.5:6.5  |
| GK-III                      | 85.2:14.8 |
| GK-IV                       | 97:3      |
| GK-V                        | 96:4      |
| GK-VI                       | 83:17     |
| Oranger Liquid <sup>7</sup> | 96:4      |
| Eastman 1-Acetonaphthone    | 95:5      |
| Aldrich 1-Acetonaphthone    | 76:24     |
| K&K 1-Acetonaphthone        | 96:4      |

intensity ratio provides further confirmation; both 4 and 5 produce m/e 188 and 190 peaks in a ratio of 3:1. The mass spectrometer was interfaced to a Hewlett-Packard model 5100A gas chromatograph via a variable jet separator.

Figures 1 to 11 (Appendix B) show typical GC-MF traces. The signal from the flame ionization detector is shown as a classical GC trace. The MF signals are shown as a series of vertical lines in the regions where 4 and 5 were eluted. The quantitative data are summarized in Table II.



TABLE II  
THE GC-MF ANALYSIS OF SELECTED SAMPLES  
FOR 4 and 5

| Sample                      | % <u>4</u> | % <u>5</u> |
|-----------------------------|------------|------------|
| GK-IX <sup>a</sup>          | 98%        | 0          |
| GK-X <sup>b</sup>           | 0          | 98%        |
| GK-II                       | 1.1%       | 0.2%       |
| GK-III                      | 1.0%       | 0.65%      |
| GK-IV                       | 0.9%       | 0.15%      |
| GK-V                        | 0.2%       | 0.05%      |
| GK-VI                       | 0.7%       | 0.1%       |
| Oranger Liquid <sup>7</sup> | 0.8%       | 0.2%       |
| Eastment 1-Acetonaphthone   | < 0.05%    | < 0.05     |
| Aldrich 1-Acetonaphthone    | < 0.1      | < 0.1      |
| K&K 1-Acetonaphthone        | < 0.05     | < 0.05     |

<sup>a</sup>1-(1-chlorovinyl)naphthalene standard

<sup>b</sup>2-(1-chlorovinyl)naphthalene standard

### Probe Distillation Mass Spectrometry Procedure

Mass spectrometry data for several reaction products were obtained via probe distillation mass spectrometry. Samples were loaded into 10 mm x 1 mm glass capillaries which were packed with 1 mm x 1 mm quartz wool plugs and the loaded into the CEC-110B high resolution mass spectrometer via the direct inlet probe. Data were recorded at 25° intervals via the Super Nova-based computer system as the sample temperature was programmed from 100° to 300°C.

The unpublished work of Bansal<sup>27</sup> is so closely related to the present study that a summary is appropriate to illustrate the contrast in yields.

#### Experiment No. 1

A solution of 1.6 mol of 3 in  $\text{CHCl}_3$  was added to a  $\text{CHCl}_3$  solution of 3.2 mol of acetyl chloride and 3.3 mol of aluminum chloride. After 30 minutes at 30°C, a dark oil was isolated. GLC analysis indicated 1:2 (90.7:9.3) in 70 percent yield.

#### Experiment No. 2

This was a repeat of Experiment No. 1. A green reaction mixture was noted. GLC analysis indicated 1:2 (93:7) in 95 percent yield.

#### Experiment No. 3

A repeat of Experiment No. 1 produced an 86 percent yield after distillation.

Experiment No. 4

A repeat of Experiment No. 1 produced an 81 percent yield of 1:2, 94:6.

Experiment No. 5

A commercial sample of 1 was purified by recrystallization of the picrate from 95 percent ethanol. This provided pure 1.

Experiment No. 6

A 1:2 mixture from experiment 1-4 was purified by recrystallization of the picrate from 95 percent ethanol. Pure 1 was isolated. An impurity which was concentrated in the mother liquors was separated by preparative GLC and analyzed by nmr and mass spectrometry. The mass spectral analysis indicated a molecular weight of 188 and showed the presence of one chlorine atom. This data, combined with the nmr data, indicated (chlorovinyl)naphthalene (4).

Experiment No. 7

A commercial sample<sup>7</sup> of 1 was purified by recrystallization from ethanol. The mother liquors were twice treated with 2,4-DNP reagent and steam distilled to produce m-dinitrobenzene and a (chlorovinyl)-naphthalene mixture (probably 4 and 5).

Experiment No. 8

A crude reaction product containing 1, 2, 3, and 4 was refluxed with concentrated  $\text{Na}_2\text{CO}_3$  solution. GLC analysis showed no change.

Experiment No. 9

$\text{AlCl}_3$  was added to a  $\text{CHCl}_3$  solution of 1 and  $\text{CH}_3\text{COCl}$ . A green color was observed, but GLC analysis showed no change. An intense green color was observed when  $\text{HCl}$  was bubbled through the mixture, but no observed change in the GLC trace was noted. The reaction mixture was warmed from  $20^\circ$  to  $30^\circ$  and stirred for about 2 hours. GLC analysis indicated no change. The reaction was quenched, the chloroform solution was concentrated, and a green, ether-insoluble solid was isolated.

Experiment No. 10

This was a repeat of Experiment No. 9, except 2 was used instead of 1. A green solid was isolated.

Experiment No. 11

$\text{AlCl}_3$  was added to a  $\text{CHCl}_3$  solution of 2. A green color was observed, but 2 was recovered after the  $\text{AlCl}_3$ -ketone complex was decomposed with water. The green color disappeared.

Experiment No. 12

This was a repeat of Experiment No. 11, except 1 was used in

in place of 2. A green color was observed, but the color disappeared when the complex was decomposed with water. Ketone 1 was recovered unchanged.

#### Experiment No. 13

A solution of 3 in  $\text{CHCl}_3$  was added to a suspension of  $\text{AlCl}_3$  in  $\text{CHCl}_3$ . An intense blue color was observed. Acetyl chloride was added. A green rubbery product was isolated. Note that this was an inverse addition.

#### Experiment No. 14

This experiment was the same as Experiment No. 1, except that the amount of  $\text{CHCl}_3$  was tripled. The yield was 93 percent. The product was 1:2:4 (84:16:0.2) in 85 percent yield.

#### Experiment No. 15

This experiment used 1/2 the amount of  $\text{CHCl}_3$  used in Experiment No. 1. The 1:2 ratio was 93:7. Some 4 was observed. A green solid was isolated.

#### Experiment No. 16

This experiment used two times the usual amount of  $\text{CHCl}_3$  (20 mol). The product was 1:2 (92:8) in 92 percent yield. A green solid was also isolated.

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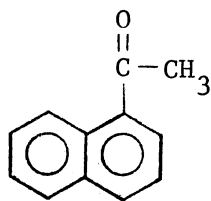
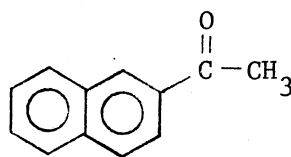
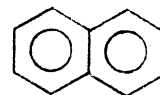
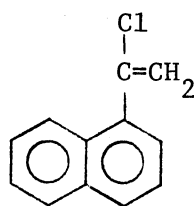
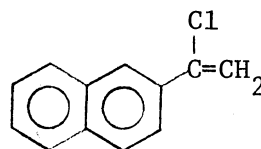
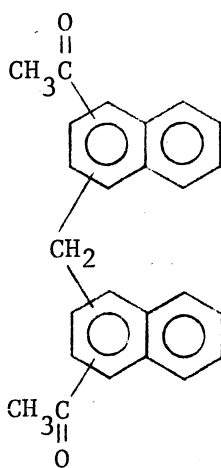
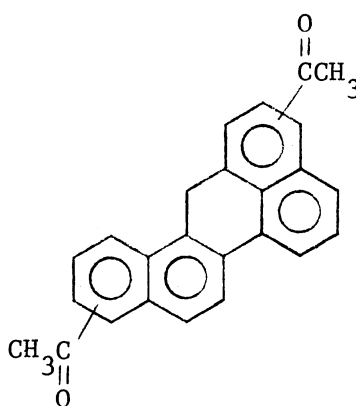
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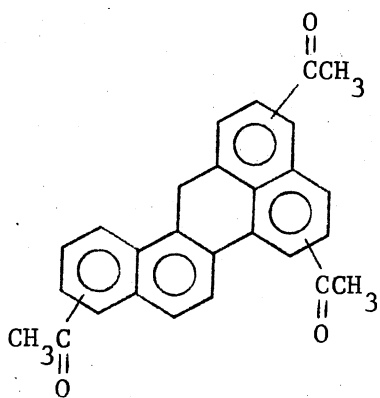
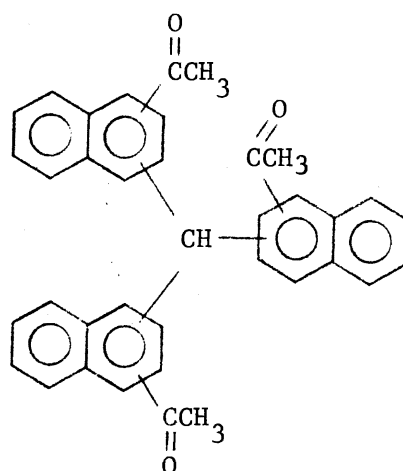
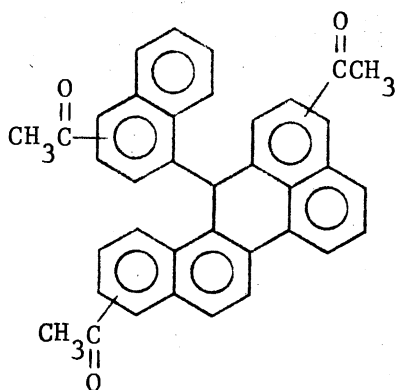
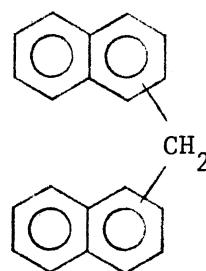
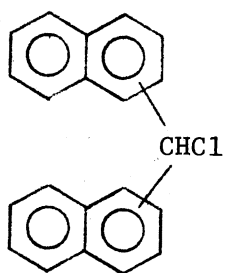
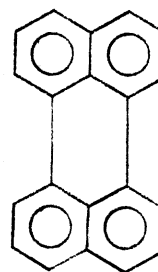
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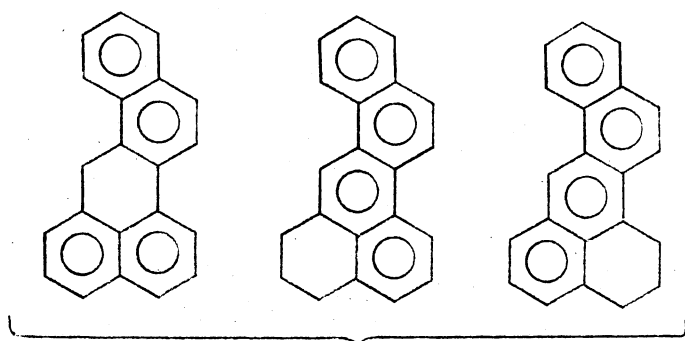
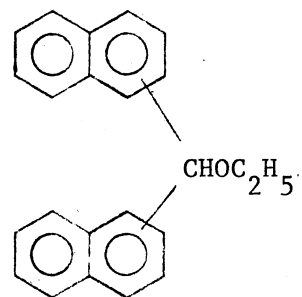
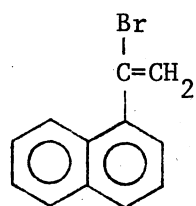
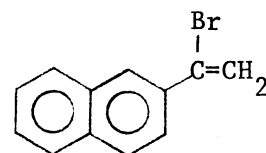
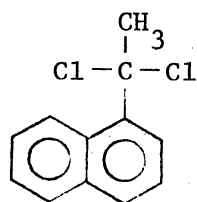
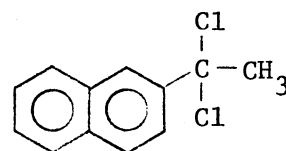
APPENDIX A

GLOSSARY OF STRUCTURES



1234567

8910111213

141516171819

APPENDIX B

MASS FRAGMENTOGRAPHY AND GAS  
CHROMATOGRAPHY TRACES

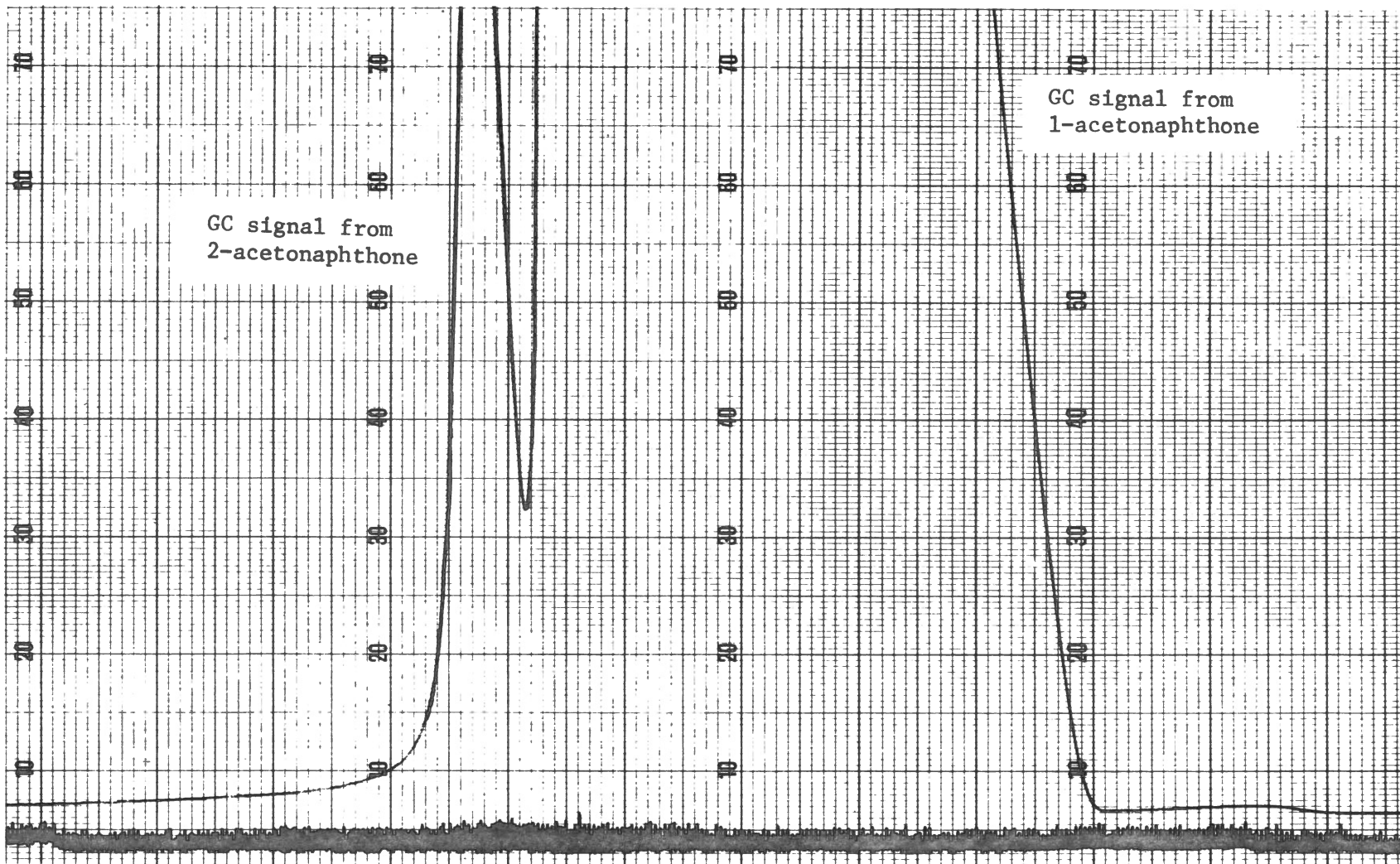


Figure 1. The GC-MF Trace from K&K 1-Acetonaphthone

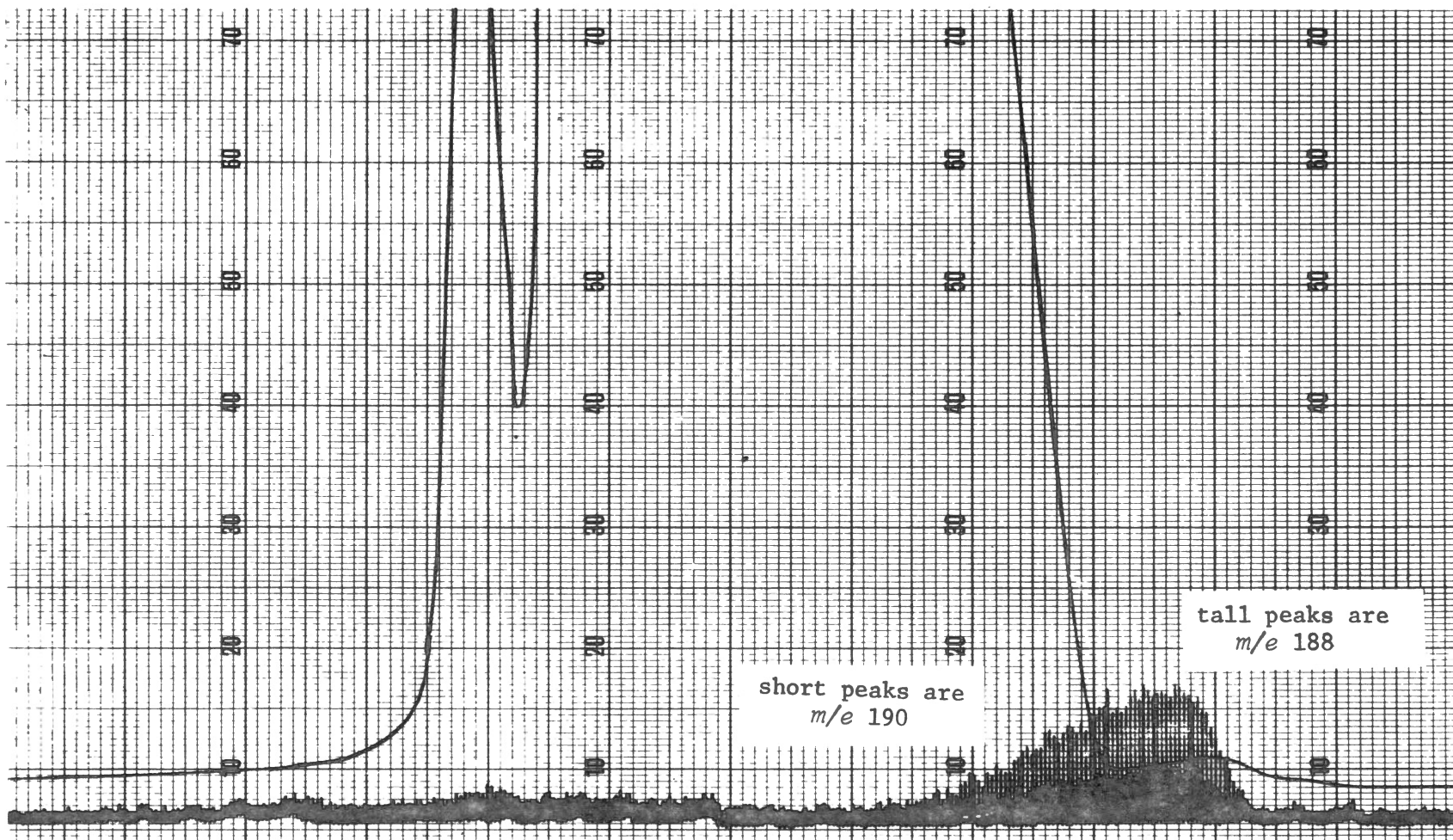


Figure 2. The GC-MF Trace from K&K 1-Acetonaphthone Plus 0.5% 1-(1-Chlorovinyl)naphthalene

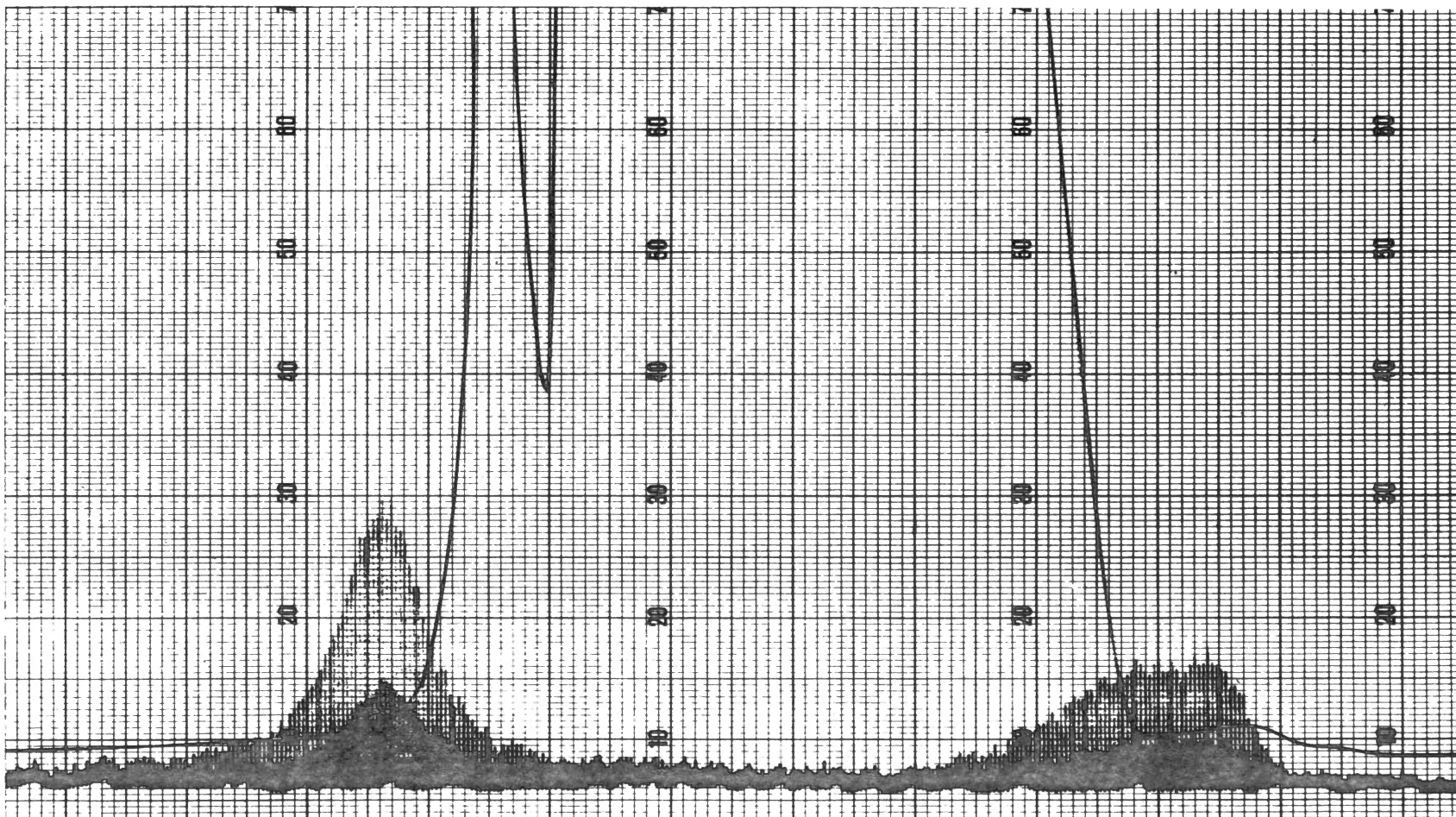


Figure 3. The GC-MF Trace from K&K 1-Acetonaphthone Plus 0.5% 1-(1-Chlorovinyl)naphthalene and 0.5% 2-(1-Chlorovinyl)naphthalene

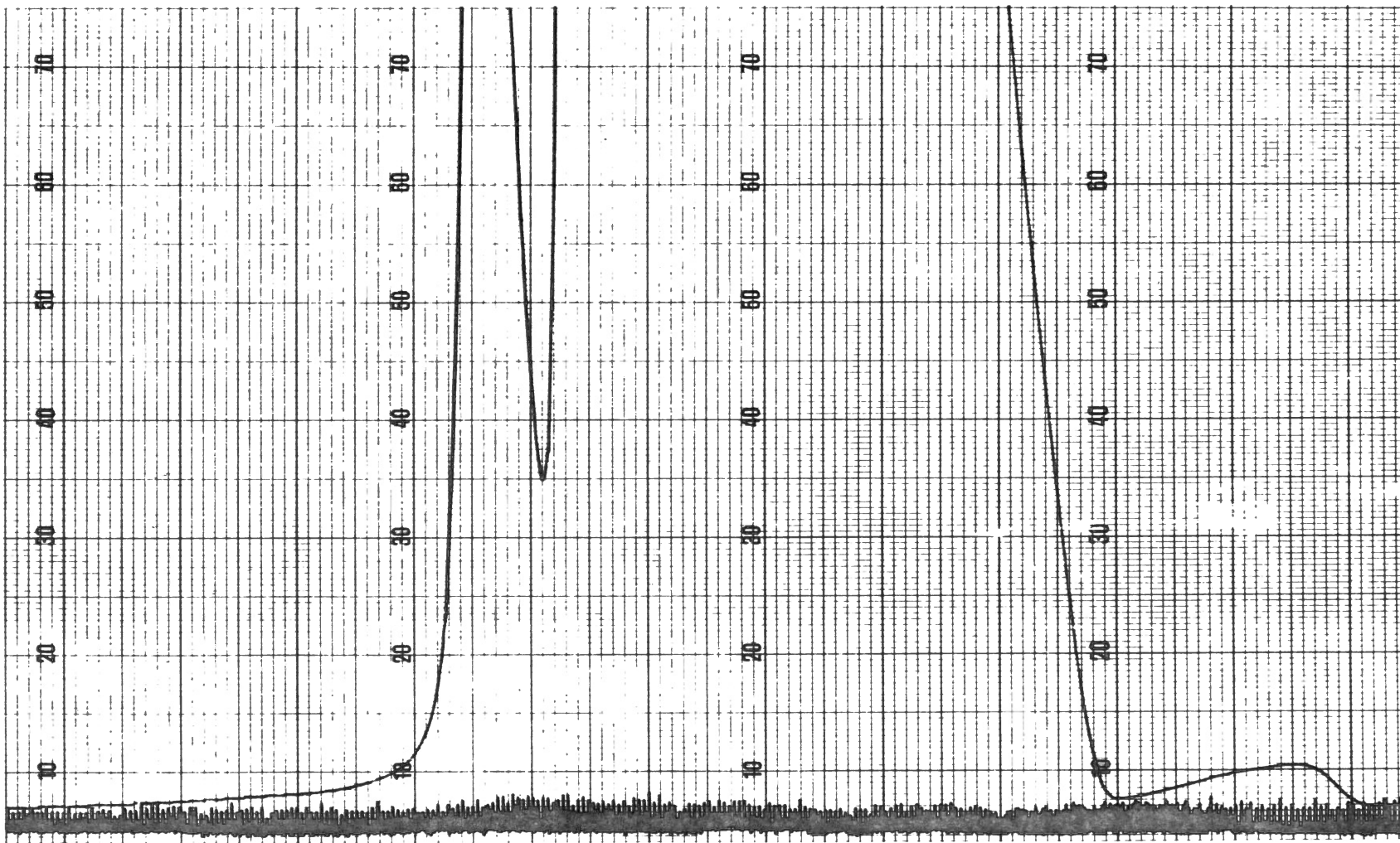


Figure 4. GC-MF Trace From Eastman 1-Acetonaphthone



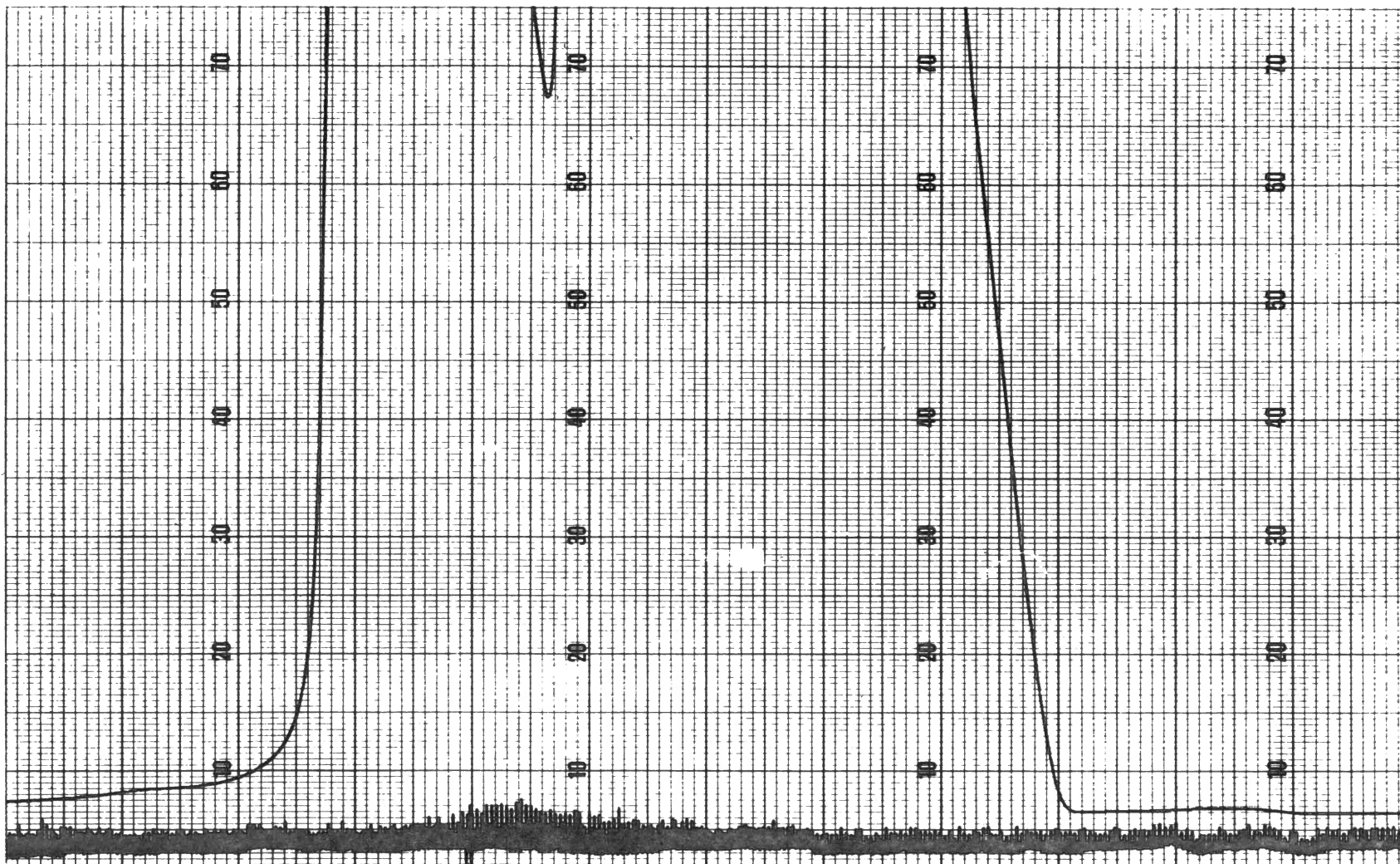


Figure 5. The GC-MF Trace From Aldrich 1-Acetonaphthone

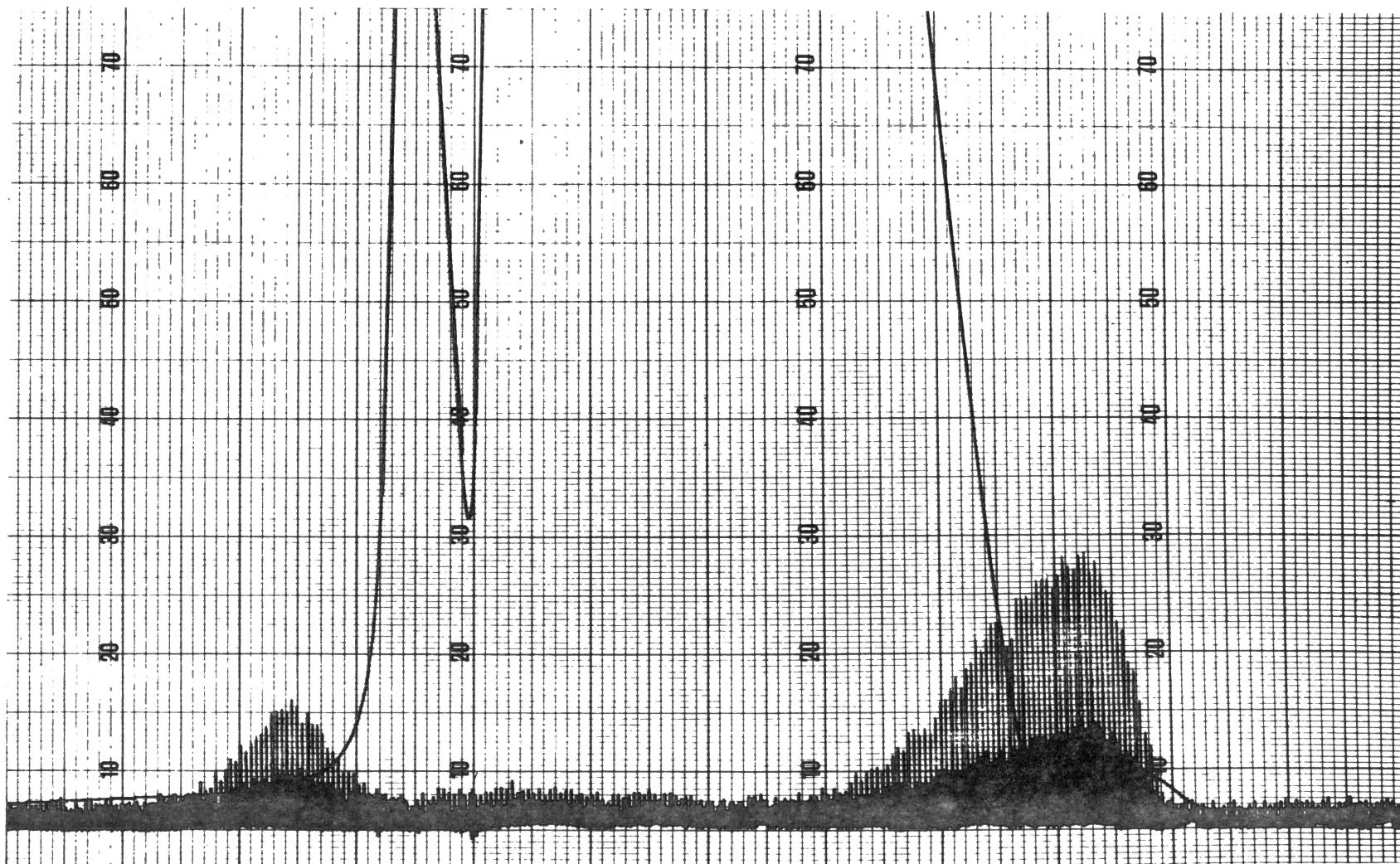


Figure 6. The GC-MF Trace from Oranger Liquid

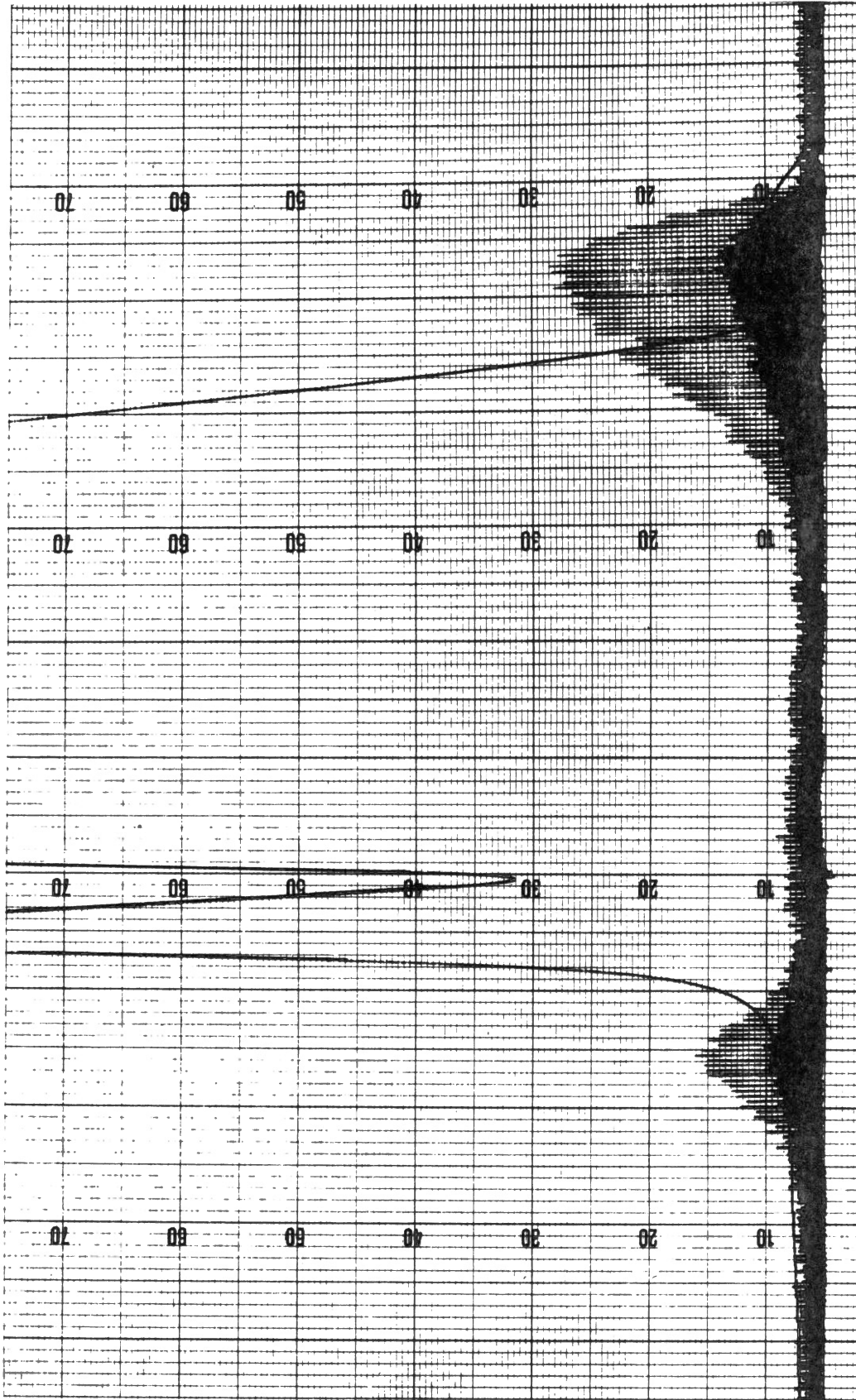


Figure 7. The GC-MF Trace From GK-II

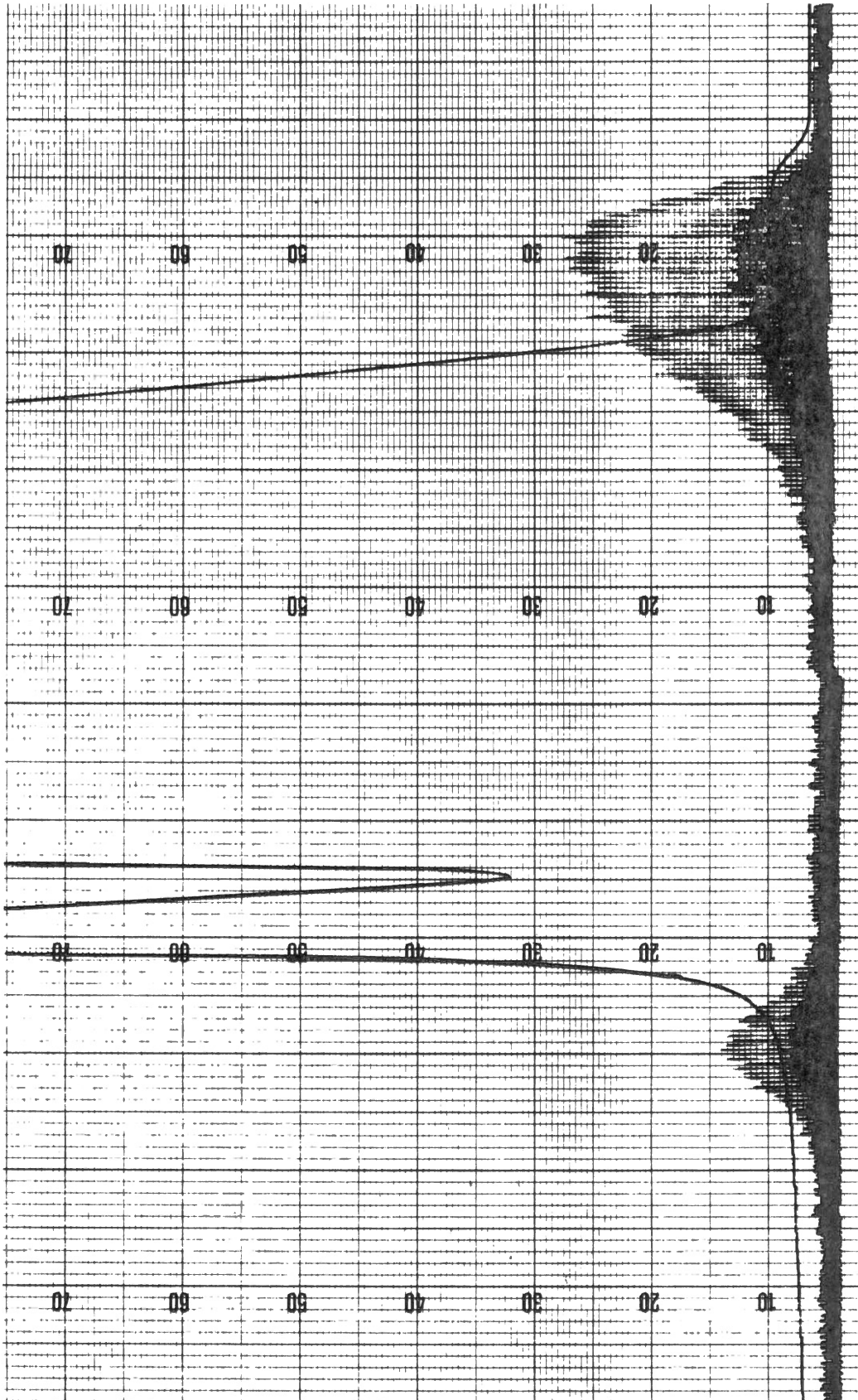


Figure 8. The GC-MF Trace From CK-III

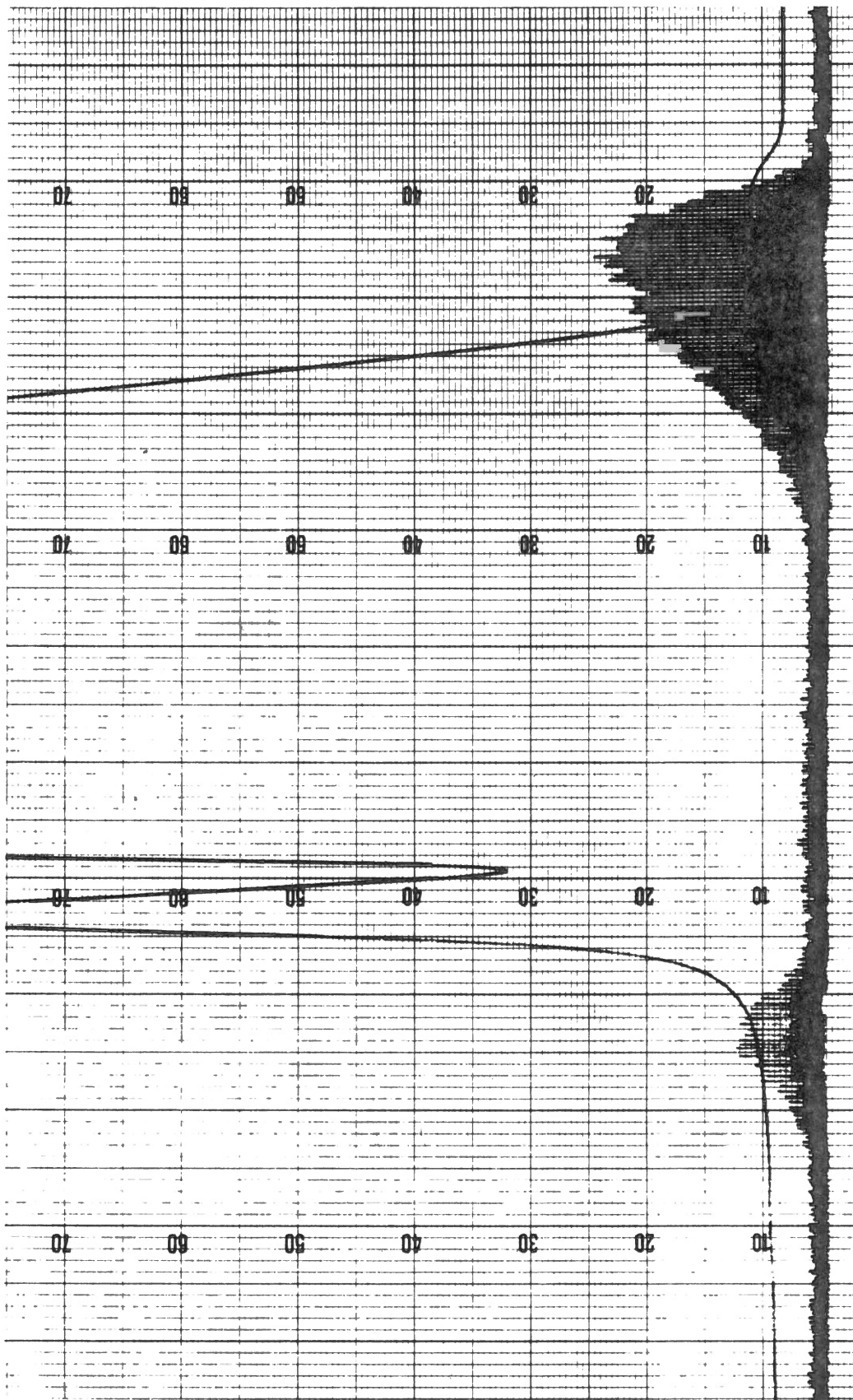


Figure 9. The GC-MF Trace From GK-IV

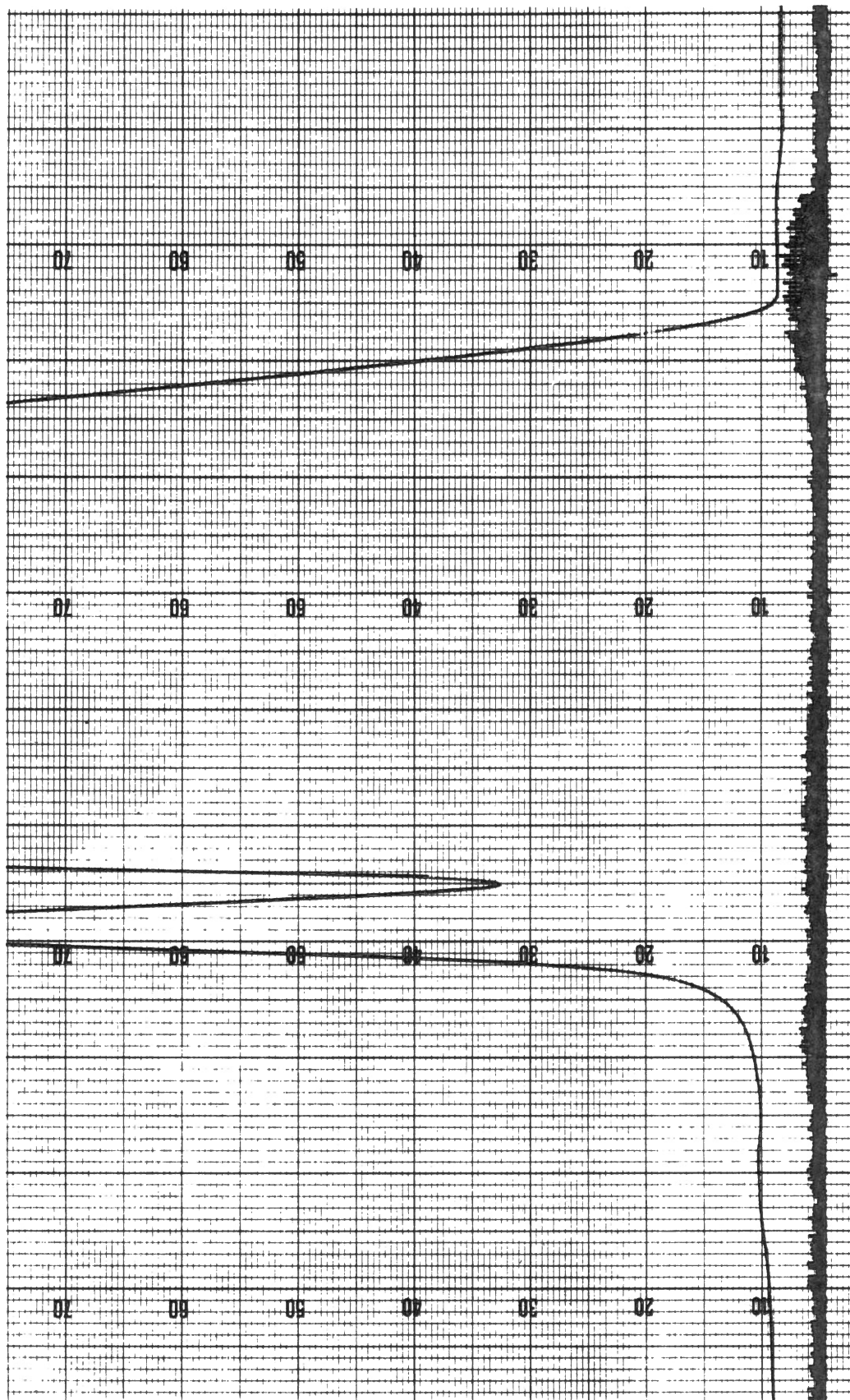


Figure 10. The GC-MF Trace From GK-V

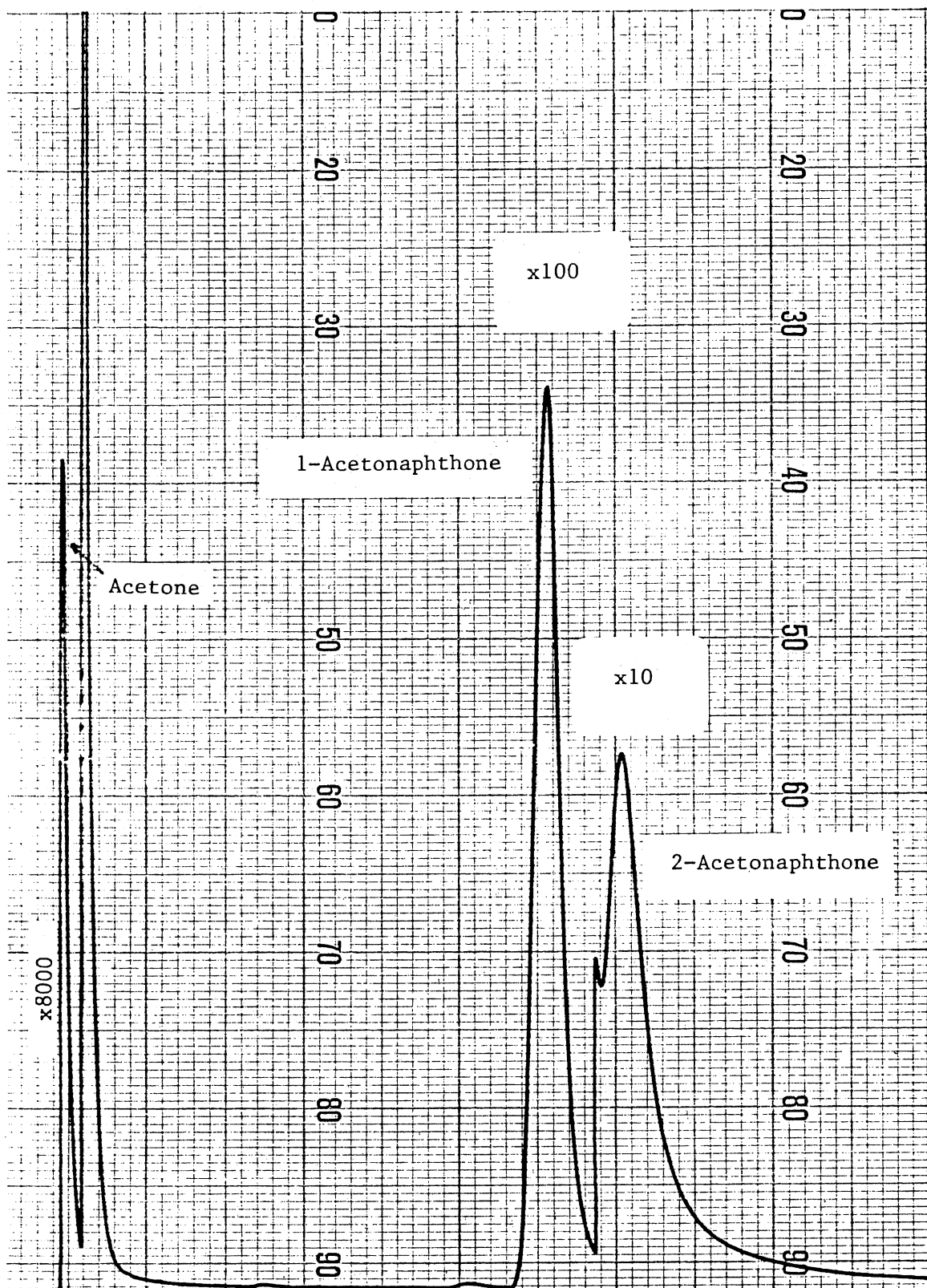


Figure 11. The GC Trace From Eastman 1-Acetonaphthone in Acetone

APPENDIX C

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