

CONDENSATION OF FORMALDEHYDE WITH BUTADIENE

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By

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INTRODUCTION

The acid-catalyzed Prins type of condensation of olefins with aldehydes has been recently extended in these laboratories to the addition of formaldehyde into 1,3-butadiene. Kohn (1), who accomplished this reaction, obtained two products of cyclic formal type which were consequences of addition of formaldehyde to butadiene in two different ratios. The first product obtained, a monoformal, was satisfactorily characterized, but the structure of the second, a solid, still needed further clarification. Kohn also attempted to improve the yields of these two products by variations of the reaction conditions.

The purpose of this investigation was (a) to repeat and, if possible, improve Kohn's preparations from paraformaldehyde and 1,3-butadiene, (b) to isolate and characterize new products of this synthesis, and (c) to make derivatives of the primary products.

HISTORICAL

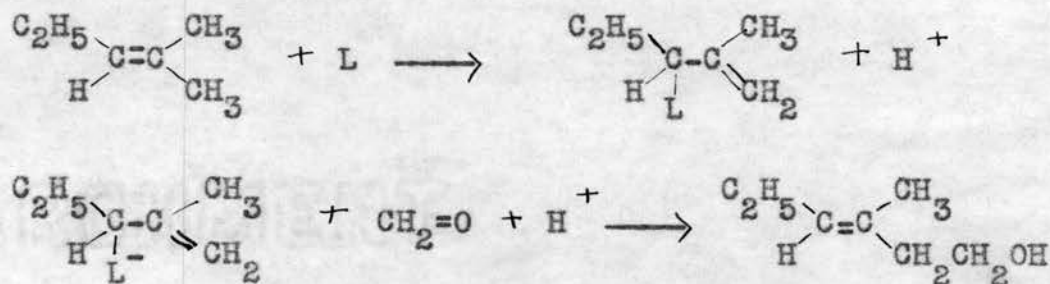
There have been a number of different applications and variations made of the Prins reaction since the first condensation of aldehydes into olefinic linkages was effected by Prins in 1919. Utilization of derivatives of aldehydes rather than aldehydes themselves has been achieved for addition into the double bond; notable among these derivatives are methylal and chloromethyl ether. Many catalysts for the reaction have also been tried. The Prins reaction appears to be growing in importance both industrially and theoretically.

The history of the Prins reaction as concerned with condensations of aldehydes and olefins has been thoroughly surveyed by Kohn in his thesis, and nearly all the literature since the time of his work has been covered by Hawkins (2) in his thesis. The latter survey includes newer variations of the Prins reaction using aldehyde-related substituents. In these literature reviews are mentioned variations of such factors in reaction as catalyst, solvent, temperature, pressure, etc. Mechanisms for the addition of the aldehyde into the C=C group have been postulated, but none are completely satisfactory. These literature surveys also discuss some of the industrial applications involved.

The original Prins type of reaction consisted of the addition of an aldehyde into the double bond of an olefin under strongly acidic conditions in the presence of a solvent such as acetic acid or ether. Products obtained from this addition are

esters, formals, 1,3-glycols, and unsaturated primary alcohols. The relative orientation of the aldehyde and the olefinic linkage as postulated by Prins and experimentally borne out may be described as follows: the carbon atom of the C=C group which has attached to it the more electronegative substituents becomes linked to the oxygen atom of the aldehyde or aldehyde-like reagent. This rule seems to predict quite successfully the orientation of various groups into the double bond even though it probably does not picture the nature of the mechanism involved.

A recent publication not mentioned in either of the previous surveys is a defense by Baker (3) of his proposed mechanism of reaction of formaldehyde with olefins of the type $R_2C=CRCH_3$ to form unsaturated alcohols, $R_2C=CRCH_2CH_2OH$. A British patent (4) cited by him describes the synthesis of 3-methyl-3-hexen-1-ol from 2-methyl-2-pentene; Baker's mechanism formulates this synthesis thus: (L represents a Lewis acid)



Price (5) in a recent monograph challenges this mechanism of attack at the 'active' β -position of the double bond. He states that it is very difficult to account for the catalytic effect of acids by Baker's mechanism. It seems more likely to Price that all reactions go through a common intermediate, supposedly formed by the addition of a formaldehyde-derived cation,

CH_2OH^+ , to $\text{C}=\text{C}$. However, Baker says that the Price mechanism gives the correct structure for the reaction product only when the olefin is of the type $\text{CH}_3\text{CR}=\text{CH}_2$. In such cases it is impossible to differentiate structurally between a $=\text{CH}_2$ group formed from an initial $-\text{CH}_3$ group and a $=\text{CH}_2$ group of the parent olefin. The essential feature of Baker's mechanism challenged by Price is that addition of a Lewis acid to an olefin can cause direct separation of a proton (which is already activated by hyperconjugation) in the presence of a proton acceptor.

The British patent mentioned above claims the reaction for all olefins of type $\text{R}_2\text{C}=\text{CRCH}_3$. This same patent also claims the use of non-acidic catalysts, meaning those in which no hydrogen is present. The reaction is run in aprotic solvents with catalysts such as stannic chloride which are strong acids in the Lewis sense.

Arundale and Mikeska (6) have reported the synthesis of unsaturated esters from the condensation of a tertiary olefin with formaldehyde and anhydrous organic acids or their anhydrides. Effective catalysts for the reactions are metallic halides or metallic salts of halogenated organic acids; the metals specified are those of the 2nd and 4th groups in the periodic table.

The above co-workers have also produced monoethers of unsaturated dihydric alcohols (7) by treating tertiary alkenyl ethers, such as dimethallyl ethyl ether, with formaldehyde. The same types of catalysts as mentioned in the paragraph above

were used. These monoethers may be used for motor-fuel additives and as solvents.

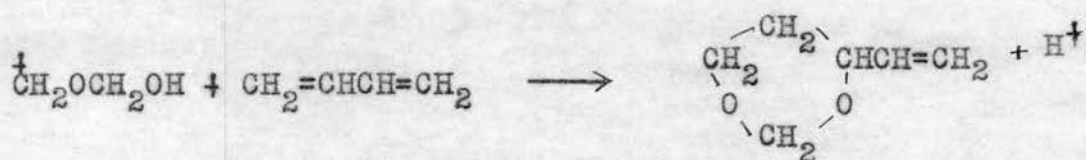
Another patent to Arundale and Mikeska (8) describes the formation of cyano-m-dioxanes. These are synthesized by the addition of formaldehyde to unsaturated nitriles in the presence of 50 per cent sulfuric acid. The same workers (9) have also patented a synthesis of 1,3-diols by the addition of an aldehyde to an olefin under pressure with a sulfuric acid catalyst. Alkoxy-m-dioxanes are also claimed by them (10); these result from the reaction of one mole of dimethylallyl ethyl ether with two moles of a saturated aldehyde in the presence of a dilute acid-reacting catalyst.

A more recent patent by Whitner (11) claims the use of a product from a Prins-type reaction as a liquid plasticizer for cellulose esters and ethers. The product is derived from formaldehyde and butadiene in glacial acetic acid solvent with a concentrated sulfuric or an aromatic sulfonic acid catalyst. Other olefins such as isoprene, a pentadiene, or a hexadiene may be used.

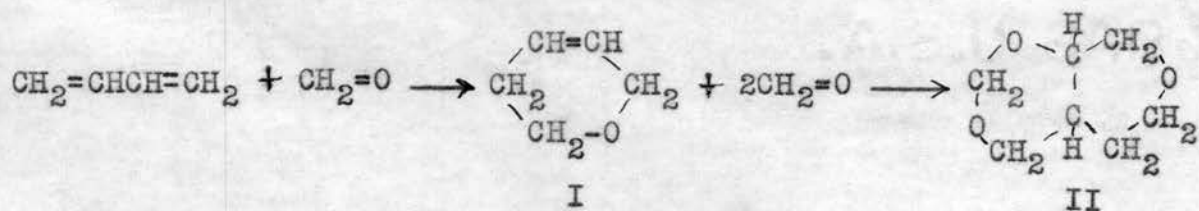
Hawkins has extended the Prins reaction to include the addition of methylal to 1,3-butadiene with concentrated sulfuric acid as the catalyst. Four products were isolated and characterized: 3,5-dimethoxy-1-pentene (I), 1,5-dimethoxy-2-pentene (II), 3-methoxy-4-methoxymethylperhydropyran (III), and 1,2,5-trimethoxy-3-methoxymethylpentane (IV). For structure III another isomer might be produced, 3-methoxymethyl-4-methoxyperhydropyran, but the orientation rule given previously favors formation of

the first compound. Similarly structure IV could be the isomer 1,3,4,6-tetramethoxyhexane.

The addition of formaldehyde into 1,3-butadiene via the Prins reaction was achieved by Kohn, and from this condensation were obtained two main products, a liquid boiling at 144° and a solid melting at 51.0-51.5°. These he believed to be respectively the monoformal, 4-vinyl-1,3-dioxane, and a diformal, 4,4'-bi-1,3-dioxane. The structure of the monoformal was proven conclusively. Here again the orientation rule mentioned heretofore was experimentally supported; that is, the oxygen atom of the aldehyde is linked to the carbon atom which has the more electronegative groups.



However, Kohn's diformal structure has been demonstrated to be incorrect by new and more satisfactory evidence (2). Originally it was thought that the bidioxane was formed by the 1,2 addition of two moles of formaldehyde into butadiene giving 4-vinyl-1,3-dioxane first; this was supposed then to react with two more moles of formaldehyde at the 3,4 positions yielding the 4,4'-bi-1,3-dioxane. Kohn obtained consistently high C and H values which were unaccountable to him. It is now thought that the structure for this solid formal is a result of consecutive 1,4 and 2,3 additions as follows:



The intermediate compound I, 5,6-dihydro-1,2H-pyran, is known to exist, having been obtained by Paul and Tchelitcheff (12) from 1,5-epoxy-3-bromopentane by slow distillation with a solution of potassium hydroxide in ethylene glycol. This intermediate is thought to condense with two moles of formaldehyde to give structure II, hexahydro-2H-pyrano [3,4-d]-m-dioxin. It has been suggested by Paul and Tchelitcheff that the dihydropyran could be synthesized by addition of formaldehyde to butadiene in an uncatalyzed, Diels-Alder reaction.

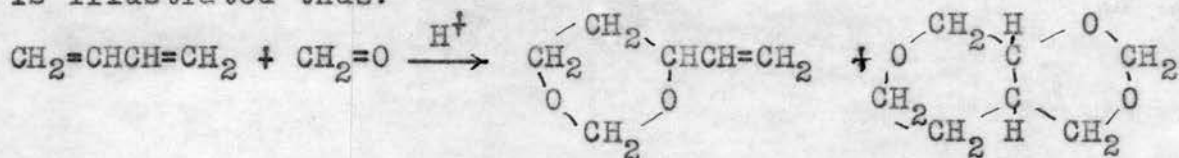
Kohn also tried several other catalysts for the condensation of formaldehyde and butadiene, but none were satisfactory. Aluminum chloride exhibited some activity, but phosphoric acid was ineffective. He also utilized ether as a solvent for the reagents, for it was found that separation of the two formals was simplified greatly when ethyl ether rather than acetic acid was used.

The reaction is believed to yield a series of products which are in equilibrium with each other. This idea was confirmed by the increase in yield when a mixture of byproducts was added during a synthesis run.

EXPERIMENTAL

The condensation of formaldehyde with 1,3-butadiene was previously done with relatively large quantities of concentrated sulfuric acid as the catalyst. However, if this reaction were to become commercially important, much smaller quantities of acid would be desirable since in the purification process the acid and an equivalent amount of alkali are consumed.

With this technological possibility in mind, three more runs repeating Kohn's synthesis in ether were made. In each was used a decreased amount of sulfuric acid compared with the quantity previously included. The reaction with known products expected is illustrated thus:



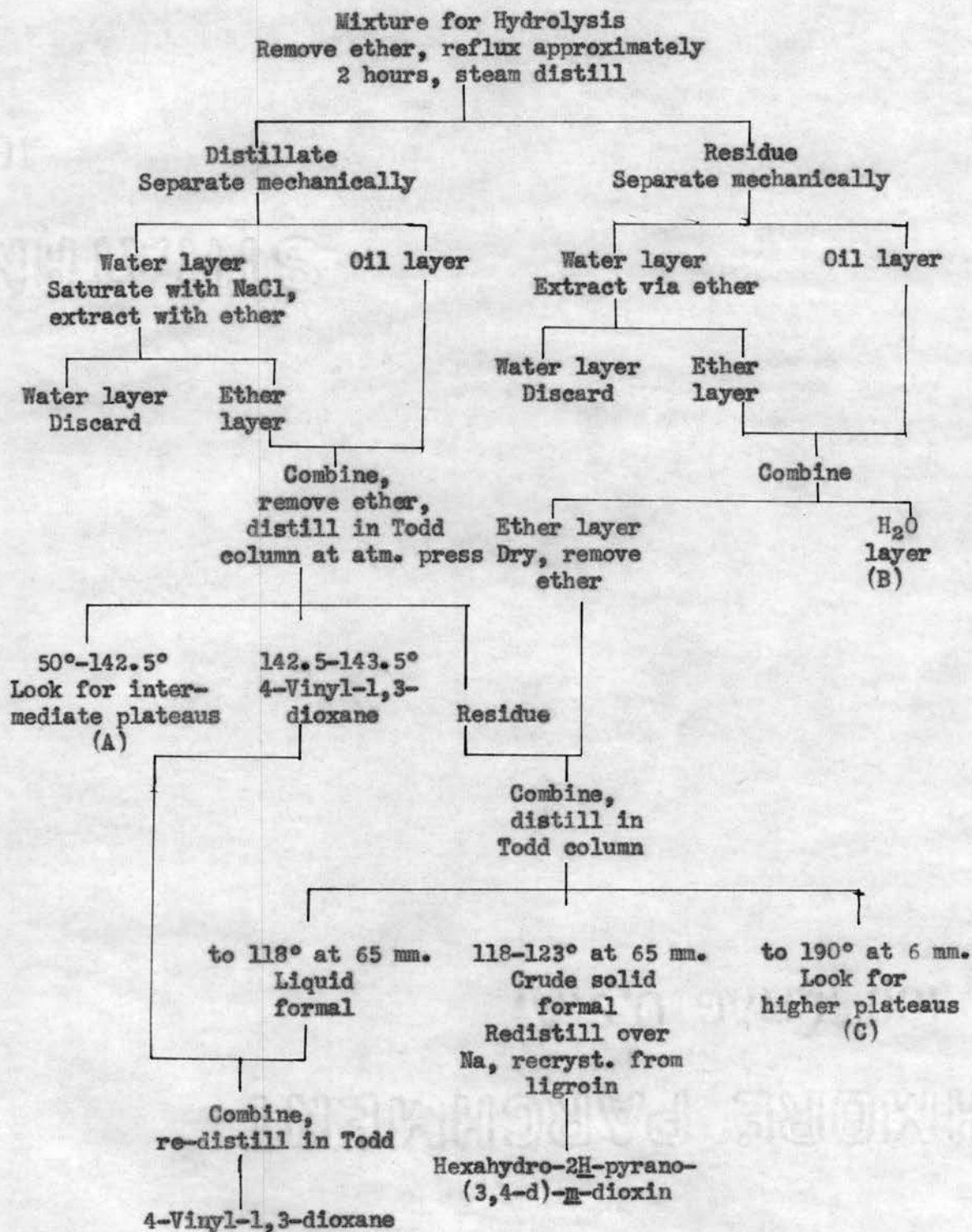
In the first preparation the following amounts of reactants were mixed:

- 200 ml. commercial anhydrous ethyl ether
- 50 ml. concentrated sulfuric acid
- 100 g. paraformaldehyde (Cities Service pilot-plant product, about 94% purity)

The acid was added slowly to the ether with cooling to prevent loss of solvent, and this mixture was then placed into a three-neck flask equipped with a mercury-sealed stirring apparatus and a gas-diffusing inlet tube. The paraformaldehyde was then put in and stirring commenced. Following this, butadiene (Phillips pure grade) was bubbled in as fast as the mixture would absorb it. The reaction was slightly exothermic, and the mixture darkened appreciably with absorption of the diolefin. After several

periods of addition totalling five hours, 53.5 grams of butadiene gas had been absorbed. It was found that unreacted paraformaldehyde still remained in the reaction mass. Nevertheless, the mixture was poured into ice water containing excess sodium hydroxide to neutralize the acids present. The ether was then removed by distillation after which the mixture was refluxed for several hours in order to hydrolyze esters among the products. (A flow sheet beginning at this point of procedure is given on the following page). This mixture was then steam-distilled, and both the distillate and residue were extracted with ether and the extracts dried over anhydrous calcium sulfate. A considerable amount of ether-insoluble products remained in the non-steam-volatile residue. The steam-volatile portion was stripped of solvent and distilled through a Todd semi-micro column; this gave 27.3 grams of 4-vinyl-1,3-dioxane in a boiling range of 143-143.5° at atmospheric pressure. There was no intermediate plateau such as we were hoping to find in the range between 50° and 143°. A two-phase system came over during part of this range, one of which was found to be water; evidently the calcium sulfate used in drying was not satisfactory for this purpose. In this first fraction we assumed the dihydropyran postulated by Paul and Tchelitcheff would be present if any had been formed.

The ether extracts of the steam-distillation residue were stripped of solvent, added to the residue which remained in the stillpot after removal of 4-vinyl-1,3-dioxane, and fractionated through the Todd column at 65 mm. pressure until all of the solid formal had been removed at 118-123°. The yield of the crude hexahydro-2H-pyrano [3,4-d]-m-dioxin was 24.1 grams. The pressure

FLOW SHEET

was then reduced still farther to 6 mm. and fractionation continued, but no further plateaus were encountered and decomposition resulted when the temperature of the column had reached 190°. Stillpot temperature was, of course, much higher. A very dark, viscous mass remained which turned out to be quite insoluble in water and thus evidently altered. However, it was still soluble in ether.

A second run was made using similar quantities of materials except for the acid catalyst:

200 ml. anhydrous ether
40 ml. conc. sulfuric acid
100 g. paraformaldehyde

This mixture was prepared as before and the butadiene gas was bubbled in as quickly as the mixture would absorb it; a total of 59 grams was added. Decreasing the amount of catalyst was found to increase the time required for absorption of butadiene. Here again, excess paraformaldehyde remained visible before treatment with sodium hydroxide. The run was worked up like the first, and fractionation of the volatile materials gave 18.7 grams of 4-vinyl-1,3-dioxane. As before, two phases appeared in the lower-boiling portions, and there seemed to be a plateau at 78°. This, however, did not remain long enough for a workable fraction. The steam-distillation residue yielded 16.9 grams of the solid formal.

Aqueous residues (those which remained after ether extraction of steam-distillate residues), thought to contain some organic material, were exhaustively extracted with ethyl acetate. This operation did not produce enough material to be worth saving, however. Only a small amount of viscous oil remained after removal of the solvent.

A third small preparation of the primary products followed. The same quantities of ethyl ether and paraformaldehyde were

employed, but only 30 ml. of concentrated sulfuric acid was used. Butadiene was bubbled into the stirred mixture over intermittent periods totalling nine hours. During this time, 60 grams of the diolefin was absorbed. The absorption of butadiene gas into this mixture was effected with much more difficulty than in either of the previous ones. Decreasing the amount of acid catalyst thus appears to increase the time required for absorption of the gas. The steam-volatile portion, worked up as before, was distilled through the Todd column at atmospheric pressure. A small cut came off at 78°; this was due to the alcohol impurity in the ether or to cleavage of ether to alcohol during the reaction. Another two-phase system appeared next, and an appreciable cut of this was taken between 78-84°. The two phases were separated mechanically, and the top one was dried over anhydrous potassium carbonate and redistilled. From this distillation was obtained a small amount of material boiling between 85-140°; most of it came over at 95-6°. This we thought might be the 5,6-dihydro-1,2H-pyran sought - the compound isolated by Paul and Tchelitcheff.

This preparation gave 36.6 grams of the 4-vinyl-1,3-dioxane and 20.8 grams of the solid formal distilled at 2 mm. Yield data of the three runs just described are compared in the following table. Per cent yields are based on quantities of 1,3-butadiene absorbed since, as noted, some formaldehyde remained unreacted.

| | Run I | Run II | Run III |
|----------------------------------|-------|--------|---------|
| Butadiene used, g. | 53.5 | 59 | 60 |
| 4-Vinyl-1,3-dioxane produced, g. | 27.3 | 18.7 | 36.6 |
| Yield, % | 24 | 16 | 29 |
| Solid formal produced, g., crude | 24.1 | 19.9 | 20.8 |
| Yield, % | 17 | 13 | 13 |
| Overall yield of both formals, % | 41 | 29 | 42 |

The yields of these two identified products, although not very high, are somewhat better than Kohn attained. The unduly low yield in Run II may have been caused by the numerous intermittent additions of butadiene into the reaction mixture. The greater time involved here may have allowed greater amounts of other products to be formed irreversibly. A decrease in the amount of acid catalyst apparently does not impair the yields.

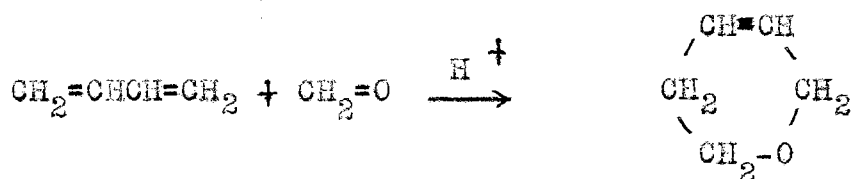
From the higher-boiling residues ((C) on flow sheet) it was impossible to distill over any product which could be recognized as a pure substance. These residues were found to contain hydroxyl groups, which evidently cause the boiling point to be so high that decomposition results even at 2 mm. Layer B (indicated on flow sheet), the water layer obtained by mechanical separation of combined oil and ether layers of the steam-distillation residue, also contained products giving a test for alcohols, but no workable quantity was obtainable.

The 95-96° cut of the steam-volatile portion mentioned as a product of the third run proved to be quite interesting, for it was approximately at the boiling range where we hoped to find a dihydropyran. It has been stated that the 5,6-dihydro-1,2H-pyran was assumed to be a possible product of butadiene and formaldehyde condensation. By combining materials boiling up to 140° from all three runs and distilling through the Todd column, about 10 ml. of this material was obtained. This 94-96° fraction proved to be highly unsaturated; bromine numbers of 183 and 184 were determined via the method of Lewis and Bradstreet (13). From these figures, the molecular weight of the compound would be approximately 87. Other physical properties were measured and

the results compared with published values for the 5,6-dihydro-1,2H-pyran. The following table gives physical constants for Paul and Tchelitcheff's product and our own:

| | Our Product | 5,6-Dihydro-1,2H-pyran |
|-------------------------------------|--------------------------|------------------------|
| Boiling point, °C. | 94-6 | 93-4 |
| Density, g./ml. | 0.943 at 28.5° | 0.940 at 19° |
| Refractive Index, n_D | 1.4451 at 20° | 1.4477 at 19° |
| Bromine number | 183,184 | 190 (theoret.) |
| Mol. wt. via f.p. method in benzene | 96, 99 (very approx.) | 84 (theoret.) |

These constants together with the mode of formation are considered complete proof that the fraction is 5,6-dihydro-1,2H-pyran. The reaction below illustrates the 1,4-addition of formaldehyde into butadiene to give this product:



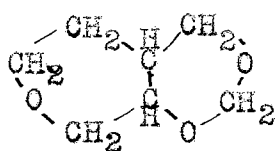
The postulation of this compound as an intermediate in formation of the hexahydro-2H-[3,4-d]-m-dioxin now stands on a more satisfactory basis with isolation and characterization of the intermediate.

To establish the true boiling point of the solid formal and also to finish purification of the yields obtained in the three runs, it was refluxed over sodium metal and distilled. Since the substance does not react with sodium, this is a convenient method of purification. An uncorrected boiling point of 207-208° was determined with a Bureau of Standards thermometer, and since stem correction of the thermometer amounted to 5° at such temperatures,

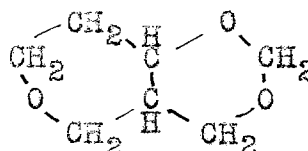
the true boiling point is 212-213°. Kohn reported a boiling point of 205-207°, a value which was apparently not corrected. The substance is very soluble in water and ether; it may be recrystallized from benzene or ligroin since its solubility is not so pronounced in these solvents. The compound is very hygroscopic, and displays marked supercooling below its melting point. We also repeated Kohn's attempts at measurement of the formaldehyde produced upon hydrolysis of this compound via 2,4-dinitrophenylhydrazine reagent in 2N HCl. Values similar to Kohn's were obtained. He obtained 85% of the amount expected from a 1 mole
 → 1 mole process, whereas we obtained results of 70-85%. In connection with this work, however, we did find that the reaction of 2,4-dinitrophenylhydrazine with paraformaldehyde is quantitative; therefore, this method of analysis should have indicated all of the formaldehyde produced from hydrolysis. However, the acid solution of the 2,4-dinitrophenylhydrazine reagent may have caused some other kind of decomposition of the formal during hydrolysis. Repetition of measurements of other physical constants reported by Kohn also supported his data; our results are listed as follows:

| | |
|---|------------------------------|
| Refractive index, n_D at 26° | 1.4668, 1.4672 (dif. preps.) |
| Density at 26°, g./ml. | 1.159 (supercooled) |
| Molecular refraction, observed | 35.1 |
| Molecular refraction, calculated for $C_7H_{12}O_3$ with all oxygen atoms as ethers | 35.05 |

These values substantiate the dioxin structure. However, there is the possibility of an isomeric structure, as illustrated:



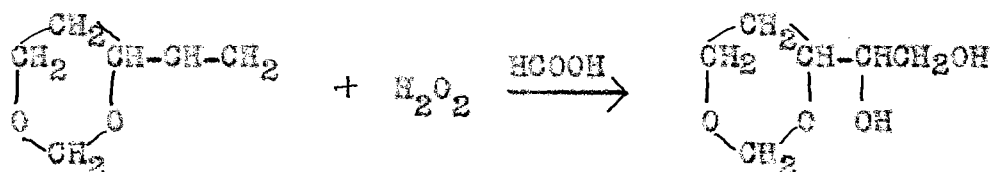
I



II

The periodic acid test applied by Kohn and also by us to material from hydrolysis of the solid formal (see p. 21) is positive; thus, the presence of structure I is proved, but not the absence of II.

The conversion of 4-vinyl-1,3-dioxane to 4-(1,2-dihydroxyethyl)-1,3-dioxane was completed via the procedure of Roebuck and Adkins (14) for making trans-1,2-cyclohexandiol. This hydroxylation of the vinyl dioxane is represented by the following equation:



In a 200-ml. three-neck flask equipped with a thermometer, dropping funnel, and motor-driven stirrer were placed 109 ml. of 90% formic acid and 26 ml. of 50% hydrogen peroxide. With continuous stirring and maintenance of temperature at 40-45° by cooling, this mixture was treated with 20 grams of 4-vinyl-1,3-dioxane added over a period of 20 minutes. The resulting mixture was then held at 40° for one hour; stirring was continued during this time. It then stood overnight, and subsequent distillation through a 3-ball Snyder column under reduced pressure diminished the volume of solution to about 50 ml. This residual volume was then carefully treated with 14.4 grams of sodium hydroxide in 27 ml. of water. Care was taken to keep the temperature of the mixture below 45°. The alkali was used to saponify the formates present. The product was then extracted with 7 portions of ethyl acetate totalling 500 ml., and after removal of the extraction solvent a gummy white paste appeared. Several recrystallizations using ethyl acetate gave 0.7 g. of a white crystalline solid. The yield here is quite

insignificant, being only 2.7% based on the weight of vinylidioxane used. This recrystallized derivative did not give a sharp melting point, however, the value ranging from 89° to 98° in several determinations. It was again recrystallized, this time from isopropyl ether, and melting points of 96-98° and 96-97.5° were observed which indicated higher purity. Carbon and hydrogen values determined by Mr. John Hawkins were C=48.1, 48.1%, H=8.2, 8.3%. Theoretical values for C and H are 48.64% and 8.16% respectively.

Kohn had originally used acetic acid as the solvent in effecting this Prins reaction, but as mentioned, he found ether to be more satisfactory in the preparation of the two formals. We decided to return to the utilization of acetic acid hoping to isolate and characterize other products of the reaction, particularly esters. A mixture of the following components was prepared:

300 ml. glacial acetic acid
50 ml. conc. sulfuric acid
100 g. paraformaldehyde

These reactants were put together as in the ether runs previously discussed. Concentrated sulfuric acid was added to cooled acetic acid; then this acid mixture was placed in a 1000-ml. three-neck flask fitted with stirrer and gas diffuser, and the paraformaldehyde was added to it. Butadiene gas was bubbled in quite rapidly, and it was necessary to cool the reaction mixture with an ice bath since addition of the gas proved to be exothermic. At the end of seven hours, 139 grams of butadiene had been absorbed, and the resulting mixture had darkened greatly. Very little paraformaldehyde remained visible. The acidic reaction mass was then neutralized with soda ash and extracted with ethyl ether. After ether had been distilled out, the mixture was subjected to

alkaline hydrolysis, the hydrolyzate extracted with ether, and the extract dried over anhydrous calcium sulfate. After sufficient time for drying, the ether was distilled off and the residue was distilled through the Todd column. Decomposition became apparent when the temperature of the column reached 85° at 40 mm. pressure, the stillpot as usual being much higher. We considered reesterifying the black, viscous mass left in the stillpot and then attempting fractionation of the acetates which should result. However, the products remaining appeared to be so much altered that it appeared more feasible to make a new run, this time without saponifying the neutralized mixture.

The same quantities of reactants as in the above preparation were mixed. Over intermittent periods, 95 grams of butadiene was added. The mixture was then neutralized and extracted with ether. The hydrolysis step was eliminated in order to leave the products as esters if present as such. Distillation of these should involve less difficulty since they are not so viscous as the hydroxy compounds. The ether was removed by means of an 8-ball Snyder column, and it was decided to continue distillation of residue through this column as a means for a rapid crude separation. Distillation at 30 mm. gave yellow-colored materials obviously contaminated with sulfur compounds. Thus, in order to remove the sulfur-containing intermediates and byproducts, refluxing the neutralized mixture with the soda ash cannot be avoided.

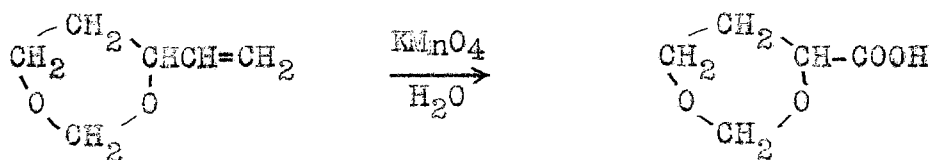
We decided to saponify the reaction products as usual and then reesterify after the crude alcohols had been separated.

300 ml. glacial acetic acid
50 ml. conc. sulfuric acid
100 g. paraformaldehyde

were used, and a total of 72 grams of butadiene was added. The reaction mixture was then worked up through hydrolysis and isolation of ether-soluble products as in the first acetic acid run. Following this, reesterification was attempted using excess acetic anhydride, with pyridine as catalyst. Refluxing these reactants for several hours produced a very dark solution. Subsequent distillation at 5 mm. first removed the excess anhydride, pyridine, and acetic acid formed in the reaction. Upon an attempt to fractionate the residue through the Todd column decomposition was apparent at the beginning since highly colored material came over. The residue was therefore distilled as rapidly as possible at 5 mm. Cooling of the almost colorless distillate yielded crystals which proved to be the solid formal. The liquid portion left was decanted and run through the Todd column. More of the formal came over at first, but continued distillation yielded only decomposed material again. The residue in the stillpot gave a positive result in the hydroxamic acid test for esters, indicating that at least some of the alcohols had been esterified. Hydroxyl groups also were shown to be present via the ceric nitrate reagent; therefore, complete esterification had not been effected. An attempt to benzoylate about a milliliter of this residue was also made, but no crystals were obtained. A small portion of the alcoholic material produced by hydrolysis which had not been subjected to either esterification or distillation was also tried with benzoyl chloride and alkali, but it also failed to give a satisfactory product.

The oxidation of the side chain (15) on 4-vinyl-1,3-dioxane to the carboxyl group was attempted by means of the following

reaction:



Ten grams of 4-vinyl-1,3-dioxane and 150 ml. of water were placed into a three-neck flask equipped with a stirrer, reflux condenser, and dropping funnel. With stirring, 10 grams of potassium permanganate in 250 ml. of water was added over a period of one hour. This mixture was then refluxed for an hour, and after cooling overnight was filtered to remove manganese dioxide. By slow evaporation, the filtrate was reduced to about 75 ml. in volume. Upon acidification with hydrochloric acid, it gave only an insignificant and unworkable quantity of white precipitate. Additional evaporation to about 25 ml. did not produce any more material. Sturzenegger (16) was similarly unable to isolate either m-dioxane-5,5-dicarboxylic acid or the -5-carboxylic acid from products of oxidizing pentaerythritol monoformal with potassium permanganate, and showed that even the formal is readily attacked by this reagent. Thus, it appears that the dioxane ring is not stable under such conditions.

Acid hydrolysis of hexahydro-2H-pyrano [3,4-d]-m-dioxin was tried using sulfuric acid. To 10 grams of the compound was added 100 ml. of 10% sulfuric acid, and hydrolysis was gradually accomplished by refluxing this solution. The formaldehyde produced in the reaction was removed by addition of methyl alcohol to the solution and subsequent distillation of the methylal formed (17). When no more methylal so formed could be detected by the 2,4-

dinitrophenylhydrazine reagent, the hydrolysis was assumed to be complete. The solution was then neutralized with barium hydroxide and decolorized using Norit A, but removal of the precipitated barium sulfate and carbon by filtration proved to be a difficult operation. A cloudy filtrate which probably contained colloidal barium sulfate resulted. By slow evaporation the volume of solution was reduced to approximately 5 ml. This comprised a viscous liquid, apparently glycolic, from which a white solid began to separate. Burning a small amount of the material on a spatula left considerable residue, indicating that barium sulfate probably had not been removed. Separation of the salt from the liquid proved to be difficult since the quantity of material was hardly workable, and therefore, another hydrolysis with larger amounts of the formal was effected.

Twenty grams of the solid was refluxed with 190 ml. of 10% sulfuric acid solution. This operation was continued for about 21 hours during which removal of formaldehyde produced was accomplished as before via methylal formation. This batch was also neutralized with barium hydroxide and decolorized with Norit A. Filtration yielded about 100 ml. of almost clear liquid which was slowly evaporated to a volume of about 50 ml. Trials at separating water from the presumably glycolic material by distillation at 5 mm. did not prove satisfactory, for bumping caused by heating under reduced pressure forced the viscous liquid over without any fractionation. It was then slowly heated at atmospheric pressure to drive off most of the remaining water; this operation apparently caused no ill effects. The hydroxylated

material expected should have a much higher boiling point than water, and thus should remain as the residue. When the volume had been reduced to about 20 ml., the liquid was placed over anhydrous sodium sulfate to dry. A viscous light yellow liquid remained which gave a positive result with the ceric nitrate reagent and in the periodic acid test. This confirms Kohn's results. Preparation of the α -naphthylurethan and the 3,5-dinitrobenzoate of this undistilled alcoholic material failed. The residue probably still contained enough water to prevent formation of the α -naphthylurethan.

DISCUSSION

The condensation of formaldehyde with 1,3-butadiene using reduced quantities of sulfuric acid as the catalyst gives slightly better yields of the two formals than Kohn obtained. Since the use of more than the minimum amount of sulfuric acid is inconvenient in purification, wasteful, and probably detrimental to the yield, trials with even smaller amounts of acid might prove beneficial. However, with less amounts of acid, the time required for addition of butadiene would probably be lengthened considerably unless the gas were forced in under pressure. By addition of side-products to a reaction mixture, such as Kohn did in one preparation, it is highly probable that his best yield of 51% could be improved.

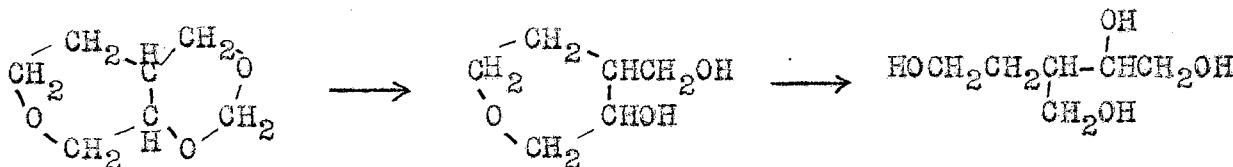
Other catalysts for the reaction should also be tried. Aluminum chloride and 85% phosphoric acid have been mentioned as being ineffective. Perhaps a somewhat diluted solution of sulfuric acid would make for an easier separation process; some patent literature relates the use of 50-85% acid for this Prins type of reaction. The reaction products and the acid solution form two layers and are mechanically separated. Boron trifluoride would probably be an effective catalyst as reported, but not a feasible one since large amounts are required. Other possible activating agents are halogenated organic acids, other mineral acids, and acid-acting substances and halides of elements from the 2nd and 4th groups of the periodic table.

The condensation of formaldehyde with other dienes should

also be of interest. 2-Methyl-1,3-pentadiene and formaldehyde have already been condensed without the use of any catalyst (13); the Prins reaction would likely succeed at least as well.

Increasing the yield of 5,6-dihydro-1,2H-pyran might be possible if excess butadiene were used since the pyran contains a smaller ratio (1:1) of formaldehyde to butadiene than any other of the known products of the reaction. Also, addition of the solid formal to a reaction mixture might suppress its formation and leave more of the dihydropyran.

Repeated attempts to isolate new products from the reaction done in glacial acetic acid solvent have failed, for decomposition resulted consistently. Since conversion of the glycols to the acetates was done to cut down viscosity (for easier distillation) other derivatives might be more effective. Methylation would probably reduce the boiling point and increase the stability, but it is definitely a more difficult process than acetylation. Since distillation of higher boiling glycols results in decomposition, it may be that the reaction in acetic acid gives a highly hydroxylated product such as $\text{HOCH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$, which could not be distilled in such a column as the Todd; distillation in a molecular still would be the only possibility. Also, by similar reasoning, the hydrolysis of hexahydro-2H-pyrano [3,4-d]-m-dioxin must have proceeded farther than the first step below:



The first product here should be distillable at the reduced pressure that was used. The positive periodic acid test is also evidence for extended hydrolysis. The tetrahydroxy compound illustrated is an isomeric form suggested (1) as a product of saponifying the esters obtained in an acetic acid run.

The yield of the new product, 4-(1,2-dihydroxyethyl)-1,3-dioxane, needs to be improved. Perhaps more familiarity with the method of preparation would produce some increase. However, other methods of oxidation, such as making and hydrolyzing the epoxide, might prove more desirable.

SUMMARY

A variation in conditions for the Prins reaction of formaldehyde with 1,5-butadiene has produced slightly higher yields of the identified products.

The intermediate, 5,6-dihydro-1,2H-pyran, which has been postulated as a possible product of this reaction, has been isolated and characterized.

Hydrolysis of the hexahydro-2H-pyran [3,4-d]-m-dioxin has been proved possible, but no pure compound could be obtained.

A new compound, 4-(1,2-dihydroxyethyl)-1,3-dioxane, has been synthesized from 4-vinyl-1,3-dioxane and characterized.

No other products of the reaction could be identified when glacial acetic acid was used as the solvent.

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BIOGRAPHY

William Nelson was born near Alpha, Illinois, July 14, 1925. He attended the public schools and graduated from Oxford Township High School, Alpha, Illinois, in 1943.

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