

CONDENSATION OF METHYLAL WITH BUTADIENE

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By

JOHN J. HAWKINS

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Marquette University

Milwaukee, Wisconsin

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APPROVED BY:



Chairman of Thesis Committee



Member of the Thesis Committee



Head of the Department



Dean of the Graduate School

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INTRODUCTION

The Prins reaction, heretofore designating the acid-catalyzed reaction of aldehydes with mono-olefins, has been expanded in these laboratories to include the reaction of formaldehyde with a diolefin 1,3-butadiene. This work, done by Kohn (11) gave two main cyclic formal-type products which represented different ratios of addition of formaldehyde to the diolefin. It has been claimed by Arundale and Mikeska in a patent (2) that methylal is an alternate source of formaldehyde in the process of condensing formaldehyde with olefins in the production of 1,3-glycols. Kohn ran a test reaction using methylal with butadiene to attempt to duplicate the formaldehyde-butadiene results, but obtained no formals, thereby contradicting Arundale and Mikeska directly. Kohn pursued the reaction no further. The purpose of this investigation was to separate and identify the main products of the acid-catalyzed reaction of methylal with butadiene.

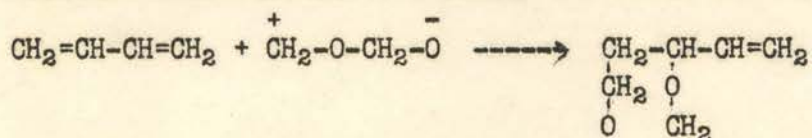
HISTORICAL

From the time Prins initially investigated the acid-catalyzed reaction between aldehydes and olefinic compounds down to the present-day investigations on the same Prins-type reaction, there have been many variations and applications of the reaction worked out and several theories concerning its mechanism put forth. Besides the typical use of aldehydes as the addendum into the double bond, additions of chloromethyl ether and our own use of methylal demonstrate the newer variations of the acid-catalyzed reaction. This extension of the Prins reaction to aldehyde derivatives seems to be slowly expanding at the present time with much promise for the future.

Insofar as aldehyde additions into olefins is concerned, the history of the Prins reaction has been thoroughly surveyed by Kohn in his thesis (11). Various mechanisms of reaction as well as the industrial applications concerned were included in this survey. Briefly, the reaction is the condensation of an aldehyde with an olefin under strongly acidic conditions in solvents such as acetic acid and ether. The products include 1,3-glycols, formals, esters and unsaturated primary alcohols. Experimentally the fact seems clear that the substance adding into the double bond orients in the following manner: the carbon atom of the C=C group which carries the most electronegative substituents becomes linked to the oxygen atom of the aldehyde or aldehyde-like group. Where 1,3-glycols and the like are produced from formaldehyde, various mechanisms have been proposed; but the rule above seems successfully to predict the orientation of the various groups into the double bond, though it may not represent the exact path that was taken to achieve the end products.

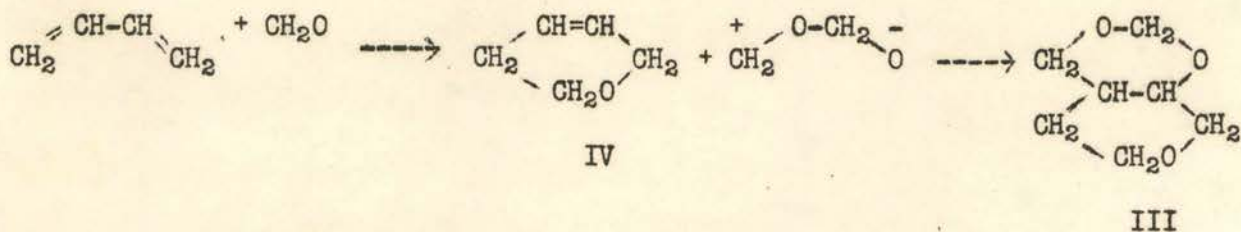
Kohn extended the Prins reaction with formaldehyde to include its addition to the diolefin 1,3-butadiene. Two main products were isolated. These were postulated to be (I) 4-vinyl-1,3-dioxane and (II) 4,4'-bi-1,3-dioxane.

Structure I was proven beyond reasonable doubt to represent the compound isolated with boiling point 144° at 742 mm. Reactivity tests indicated that the aforementioned orientation scheme was borne out in producing structure I. Thus:



The oxygen becomes linked to the carbon atom more heavily substituted with electronegative groups.

Structure II has been shown to be in error (10) and a new structure has been substantiated by the most convincing proof. Structure II was supposedly formed by the 1,2 and 3,4 addition of two moles of formaldehyde each into the double bonds of butadiene to form the bidioxane compound. However, this direct stepwise addition of formaldehyde forming successively the vinyl dioxane and then the bidioxane, does not take place under conditions used thus far. Rather, it has been found that the reaction involves an equilibrium between an initial 1,2 or 1,4 type of addition product. Thus structure III, the acceptable structure for Kohn's high-boiling compound, is apparently formed in the following manner through the 1,4 addition mechanism:

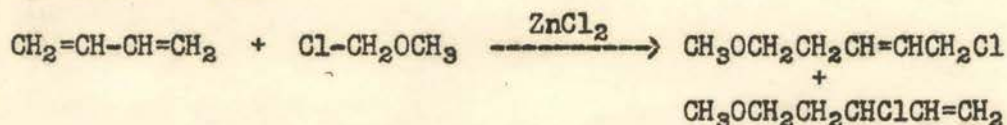


Structure III, hexahydro-2H-pyrano [3,4-d]-m-dioxin, is made even more plausible by the fact that the intermediate compound IV, 5,6-dihydro-1,2H-pyran, has recently been isolated by Paul and Tchelitcheff (16). They demonstrated that IV pyrolyzes to give butadiene and formaldehyde at 600°, and predicted a Diels-Alder reaction between formaldehyde and butadiene under pressure to get IV in much the same way that ethylene and butadiene are condensed to cyclohexene. Gresham and Steadman (9) recently tried this very Diels-Alder reaction

with no success at 185° in an autoclave. They did, however, accomplish the hoped-for reaction by using 2-methylpentadiene-1,3 with formaldehyde to form 2,4-dimethyl-5,6-dihydro-1,2H-pyran. The difference in reactivity is attributed to the activating methyl group in the methylpentadiene.

A related Prins reaction might be expected from the acid-catalyzed reaction of formaldehyde with ethyl furate or other furan derivatives since the conjugated double-bond system present is known to enter into Diels-Alder reactions. However, Dinelli and Marini (5) found that this combination does not react at the double bonds, but rather proceeds by substitution on the furan ring to form an internal ether of "5,5'-dicarbethoxydihydroxymethyldifurylmethane". Many furan derivatives form complex decomposition products with acids. Compounds containing carbethoxy or nitro groups or the like are relatively stable to acids, but react as above rather than entering into a Prins reaction.

Straus and Thiel (23) in 1936 introduced a new variation to the Prins type of reaction. They found that α -substituted chloro-ethers can be added into double bonds using various acid catalysts or no catalyst at all. With such catalysts as HgCl_2 , ZnCl_2 , SnCl_4 and SbCl_5 , they added chloro-ethers of the type $\text{PhCH}(\text{OCH}_3)\text{Cl}$ and $\text{ClCH}_2\text{OCH}_3$ to both olefins and diolefins. Styrene, cyclohexene, isobutylene, $\text{Me}_2\text{C}=\text{CHMe}$, 1,3-butadiene, 1,3-cyclohexadiene, and cyclopentadiene were the olefins used in the investigation. $\text{PhCH}(\text{OCH}_3)\text{Cl}$ and liquid butadiene were condensed in the presence of HgCl_2 to give a 65% yield of 1-phenyl-1-methoxy-5-chloro-3-pentene. With $\text{ClCH}_2\text{OCH}_3$ and butadiene, using ZnCl_2 catalyst, they obtained a 70% yield of two isomeric 1-methoxy-chloropentenes. Thus:



The two isomeric products above proved to be very similar in structure to two of the new compounds that we have synthesized, and aided in the establishment

of their structures by analogy.

Straus (21), in a patent later expanded the reaction to include other halides. In general, he claimed that compounds containing at least one olefinic linkage, treated with compounds of the formula $RCH(OR')X$, where R is H or an alkyl, aryl, or aralkyl group, R' is an alkyl group, and X is halogen, undergo an additive reaction in which higher-molecular-weight chloro-ethers are produced.

Straus (22), again through a patent claim, extended the reaction further to include combination of the starting materials that react to form the particular chloro-ether desired and thence addition to a double bond, all in one operation. That is:

$RCHO + ROH + HCl + >C=C<$ react, in that order, to give $RCH(OR)-\underset{\substack{| \\ |}}{C}-C\overset{\substack{| \\ |}}{Cl} + H_2O$

Pudovik and Arbuzov (17) recently repeated some of Straus's work, improving the procedure and generally investigating the properties of the products more thoroughly and precisely. They caused chloromethyl ether to react with butadiene to get the previously mentioned isomeric compounds along with "higher boiling products". The properties of these products are discussed later in the experimental portion of the thesis. These compounds were subject to rearrangement reactions of the allylic-ether type which they also studied considerably (18).

Martin (13) used $TiCl_4$ catalyst, an olefin such as isobutylene, and a chloroether of the type $ClCH_2OR$ to form higher halogenated ethers in further extension of Straus's work.

Allard (1) attempted an acid-catalyzed reaction of chloromethyl ether with terpenes in the hope of getting either chloromethylation or additive condensation of the chloroether at the double bonds, but obtained only terpene-HCl addition products and rearranged terpenes.

The active olefin, ketene, was condensed with α -halogenated ethers in

the presence of acid catalysts by Staudinger and Tuerck (6). The product, an alkoxypropionyl halide, is the result of addition of such ethers to the C=C with the negative chlorine linking as expected to the "carbonyl" carbon. Diketene was also utilized in the above reaction. Lewis acids of the type $ZnCl_2$ and $AlCl_3$ catalyze the reaction.

Brooks (3) similarly synthesized alkoxy-substituted esters using ketenes and acetals such as methylal. The reaction requires a strong acid catalyst; in fact H_2SO_4 was considered among the poorer catalysts as regards yield, BF_3 being the best. Thus, methylal + $CH_2=C=O$ + BF_3 gave a 73% yield of methyl β -methoxypropionate. From this it would appear that the strength of the acid catalyst is the determining factor in any difference between the addition of methylal to olefins and addition of chloromethyl ether to the same olefin--barring inductomeric and electromeric differences of the two reagents on the olefin at the time of reaction.

A thorough literature search for other additions of methylal to olefins in the presence of acid catalysts has indicated the novelty of the reaction thus far. The claim that methylal may be condensed with olefins to form cyclic formals and thence 1,3-glycols is made in a patent by Arundale and Mikeska (2). The synthesis is apparently a non-acid-catalyzed condensation of methylal with an olefin to yield a cyclic formal; this formal may then be converted to the 1,3-glycol by reaction with methanol in the presence of an acid catalyst, regenerating methylal as a side product. Hence much is open to investigation on the addition of methylal to olefins under Prins conditions.

EXPERIMENTAL

The Prins reaction involving formaldehyde in the polymerized form requires a solvent in which to conduct the reaction; however, methylal acts as its own solvent and thereby avoids introduction of any interfering or complicating solvents. Our main preparative experiment was carried out using the following amounts of materials in the reaction mixture:

700 ml. (622g)	methylal (methanol-free, supplied by the Tallant laboratory of the Cities Service Oil Co.)
200 ml.	concentrated sulfuric acid

The sulfuric acid was added slowly with mechanical stirring to the methylal previously cooled in an ice bath. The mixture was kept in the ice bath until the sulfuric acid had been completely added. This mixture was made up in a 2-liter, 3-necked flask equipped with an electric stirrer fitted with a mercury seal. While the stirred mixture was held at 0-10° with an ice-water bath, butadiene gas (Phillips pure grade) was slowly and steadily bubbled through the mixture with a gas diffuser. The time of absorption was found to be very dependent upon the efficiency of the gas diffuser used. Where a previous run required 5 to 6 hours with the small disperser used, none too evenly porous, it took only 1.5 hours for this run to go to completion when a diffuser was used that had good capillary porosity and larger surface. As the reaction progressed, the mixture darkened appreciably. The stirring was continued for an hour after stopping addition of the butadiene, to drive out any excess butadiene before weighing the mixture to determine the amount of gas absorbed. This particular run absorbed 121 g. of butadiene. The mixture was allowed to stand overnight at room temperature to achieve equilibrium.

In order to isolate the products of the reaction it was found necessary to neutralize the sulfuric acid present before separation. Previous trials had shown, as in Kohn's work, that direct extraction of the mix with

Skellysolve was complicated by the concurrent extraction of sulfuric acid and sulfur-containing intermediates. These contaminants were extremely difficult to get rid of and any attempted distillations with them present proved disastrous to the new products. The neutralization consisted of addition of the mix to a cooled solution of sodium hydroxide exactly equivalent to the original amount of sulfuric acid present. Since the usual products of the Prins reaction, being acetals, are alkali-stable and unstable (toward hydrolysis at least) in acid solution, the order of addition was made purposely as stated, mix into alkali, to keep the solution always alkaline. The neutralized batch was then refluxed for about one hour to assure complete hydrolysis of any sulfuric esters or other intermediate compounds. The refluxed batch was thence steam-distilled. The steam distillate was taken off in the following fractions: a 40-50° fraction (260 ml.) essentially methylal; a 50-70° fraction (60 ml.) consisting mostly of methanol produced in the reaction but giving tests also for carbonyl groups and unsaturation; a 70-95° fraction (50 ml.) of unidentified highly unsaturated material (with a seeming plateau of 92°); and finally the 95-100° fraction that came over as one phase only (presumably due to the solubilizing effect of the methanol present). The steam distillation was continued until a test sample of distillate yielded no separate layer when saturated with sodium sulfate.

The steam distillate after saturation with sodium sulfate and seven ether extractions yielded about 150 ml. of anhydrous new cuts when the ether was stripped off.

The non-steam-volatile material was next extracted from the neutralized mixture with ether. Eight extractions were deemed necessary to recover as much of the higher-boiling materials as possible. The solution being extracted was usually supersaturated with sodium sulfate and it was not uncommon for the ether extraction to cause abundant deposition of crystals after the second

or third extraction. This, of course, mechanically complicated the extraction process exceedingly, since removal of the salt by filtration was thought liable to entail losses of the desired products.

The steam-volatile fraction was distilled roughly and rapidly through an eight-ball Snyder column to effect further separation of the high-boiling material from the lower-boiling fractions. This preliminary fractionation indicated plateaus around 140° and 166°. The material boiling at about 140° was designated as Cut V, that at 166° as Cut X. Actually a single fraction of boiling point range 130°-175° was collected, consisting of about 110 ml. of the two cuts, V and X. Some 20 ml. of the higher products remained in the stillpot, and this was added to the rest of the high fractions after they had been isolated.

The non-steam-volatile extract was stripped of ether and vacuum-distilled rapidly to separate the desired fractions from any readily decomposable material that may have been present. A fraction (125 ml.) boiling up to 250° at 40 mm. pressure was collected. At this temperature decomposition had set in and it was deemed inadvisable to collect any further fractions. About 45 ml. of very high-boiling material was left in the distillation flask after rectification. Previously when this distillation had been attempted on the higher-boiling material that had not been refluxed and steam-distilled but merely neutralized and extracted with Skellysolve, there was a maximum of charring during an attempted rapid vacuum distillation and a minimum recovery of desired products.

The ether-extracted steam-volatile fraction was then precisely rectified to secure pure cuts for determination of physical constants and structural analysis. Two plateaus were found as before in distilling the steam-volatile fraction with the Oldershaw column and pure fractions of each cut (V and X) were taken off. When using the Oldershaw column, it had been found convenient

and beneficial to use a booster liquid, such as n-butyl phthalate in the stillpot, to minimize overheating because of low volume. Fractions taken off when this booster liquid was used were tested for esters via the hydroxamic acid test and shown to be uncontaminated by the booster liquid. Pure Cut V boiled at 136.5-137° (745 mm.) and Cut X distilled sharply at 164.3° (745 mm.). Quantitative yield data for the several cuts were compiled for the run being described. These values will be recorded as a general summary following the proofs of structure for each compound isolated.

The roughly distilled non-steam-volatile materials were next fractionated in the Oldershaw column for final separation and purification of higher cuts. n-Butyl phthalate as a booster was here considered necessary to increase recovery of desired cuts and to minimize decomposition by keeping the stillpot full enough to prevent local overheating. Cut Y, the third cut isolated, was successfully separated but not without difficulty. It was found, for example, that the column would not give Cut Y in reasonable purity when operated at very low pressures (1 and 2 mm.). An increase in pressure to 10 mm. was sufficient to permit attainment of good equilibrium for separating the pure product. Cut Y boiled at 98° (10 mm.) and 107° (30 mm.). The total yield of Cut Y from this run was 40.0 ml.

Continued distillation of higher cuts under the same conditions that produced Cut Y proved to be thoroughly inadequate. Only a rough smear of the Cut Z fraction, now known to exist, was secured; the Oldershaw column would not come to equilibrium at pressures of 10, 30 and 40 mm. in even five or six hour. The stillpot was therefore transferred to the Todd semimicro column, wherein fractionation was accomplished with no difficulties. Cut Z distilled over pure at 141.6° (40 mm.) or 137° (35 mm.). The yield of Cut Z fraction was 12.2 ml.

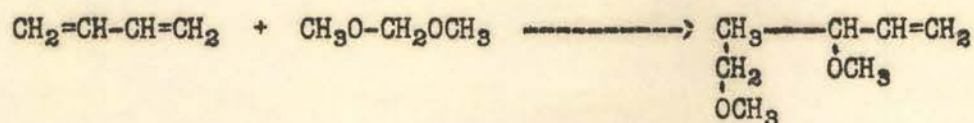
Still higher-boiling cuts in the non-steam-volatile fraction have been noted in the rough distillation of the fraction, but it was decided that our investigation should be limited to the four compounds already isolated since the yields of the higher cuts may be too insignificant to justify investigation in the time allotted for this work.

With the isolation and purification of Cuts V, X, Y, and Z accomplished, attention was directed toward structural identification of each. The knowledge we have at present concerning their various structures makes it possible to summarize the steps in the analysis of each in a comparatively smooth uneventful pattern; however, the fact is that no such uniform sequence of events was encountered. Serious delays were encountered with applying qualitative and quantitative methods to establish the structures eventually proved. A special section--an Appendix--is included in the thesis to summarize the difficulties encountered and progress made in quantitative analytical procedures.

Cuts V and X ultimately proved to be isomers but behaved so that both remained uncharacterized for some time. When a pure sample of each was tested for unsaturation via either bromine in carbon tetrachloride or neutral potassium permanganate, the reactions that did result were so slow and faint in character that they produced the erroneous decision that no unsaturation was present. This error took literally months to catch and correct. This fact and the ease of rearrangement of both of these compounds misled us despite correct carbon and hydrogen percentages that had accrued. The two cuts are isomers resulting from the condensation of one mole of methylal and one mole of butadiene. As such they both contain electronegative methoxyl groups that might be expected to hinder addition of bromine to the double bond under neutral conditions. This hindrance was demonstrated (after molar refraction data and other work made it clear that there must be unsaturation)

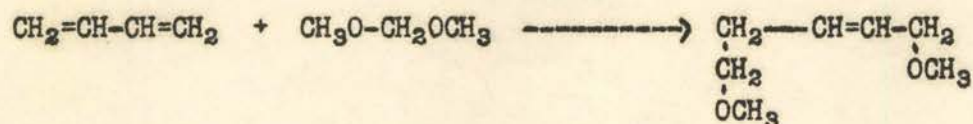
by measuring the addition of bromine under acid conditions via the potassium bromate method of Lewis and Broadstreet (12). The method is usually quantitative for double bonds; however, in the case of Cuts V and X the bromine numbers were low (see Tables II and III). The addition of bromine corresponded well enough to one double bond per molecule that it is safe to say that the unsaturation is present.

Various qualitative tests were run on Cuts V and X with the following results; methoxyl group test (19), positive for both cuts; hydroxyl test via ceric ammonium nitrate reagent (19), none; carbonyl group, trace tests via 2,4-dinitrophenylhydrazine in 2N hydrochloric acid (19) and hydroxylamine hydrochloride reagent (19); aldehyde test, positive results both with Tollens reagents and Schiff reagent; ester test via hydroxamic acid (19), negative; acidity, none; and ether test (19), both were positive. The positive aldehyde test was later shown via distillation and qualitative tests to be due to aldehyde impurity and not to an aldehyde group in the pure cuts. It has also been found that the aldehyde is apparently the result of an allylic ether type of rearrangement that the cuts undergo under certain conditions, such as standing for any length of time. Cut X notably forms this aldehyde with some ease, but Cut V has been shown to give an aldehyde (not necessarily the same one) only difficultly and in merely trace amounts. The Cut X aldehyde has been converted to the purified 2,4-dinitrophenylhydrazone derivative, m.p. 124.5-125°. This aldehyde has not been investigated any further. The foregoing chemical tests coupled with clinching quantitative physical and chemical data have shown that Cuts V and X are isomers resulting from 1,2 or 1,4 addition of one molecule of methylal to one of butadiene, as the following equations indicate:



Cut V

1,3-dimethoxypentene-4



Cut X

1,5-dimethoxypentene-2

Another isomeric possibility, 2,1 addition to butadiene, has not been considered a likely structure for various reasons. It has been noted that in the Prins acid-catalyzed addition the negative-acting group is always observed to go to the olefinic carbon which has been more heavily substituted with electronegative groups. This would mean that the negative methoxyl group would orient to the 2 position as indicated for Cut V, since the vinyl group on that carbon is more electronegative than a hydrogen atom. Another reason for our choice is the analogy drawn from the formation of two isomeric chloro-ether compounds (17) that are directly comparable with the structures of Cuts V and X. A comparison of the mole-to-mole addition products of both chloromethyl ether and methylal to butadiene is given in Table I. The addition of methylal to butadiene appears to give the same type of products as that of chloromethyl ether.

Table I

Comparison of Adducts of Methyl Chloromethyl Ether and Methylal
with Butadiene

<u>Product</u>	<u>B.P. °C</u>	<u>n_D^{20}</u>	<u>d_4^{20} (g./ml.)</u>
1-methoxy-5-chloropentene-3	168 ⁷⁵⁸	1.4540	1.0009
1-methoxy-3-chloropentene-4	<u>148⁷⁵⁶</u>	<u>1.4364</u>	<u>0.9690</u>
Differences	20°C	.0176	.0319
1,5-dimethoxypentene-2	163.4	1.4251	0.885
1,3-dimethoxypentene-4	<u>137</u>	<u>1.4092</u>	<u>0.864</u>
Differences	26.4	.0159	.021

Experimental facts support the previously postulated structures overwhelmingly. These facts are herewith tabulated in order to show the conformity of the observed values with the theoretical. Table II presents the data for Cut V, and Table III for Cut X.

Table II

Further Properties of Cut V

	<u>Experimental</u>	<u>Theoretical for $C_7H_{14}O_2$</u>
Molecular weight, avg. of 5	131	130
C, %, avg. of 2 values	63.81%	64.65%
H, %, avg. of 2 values	10.81%	10.78%
Molar refraction	37.2	37.3
Br number	110, 109	123
Methoxyl %*	39.8, 48.9, 49.3 50.6	47.7

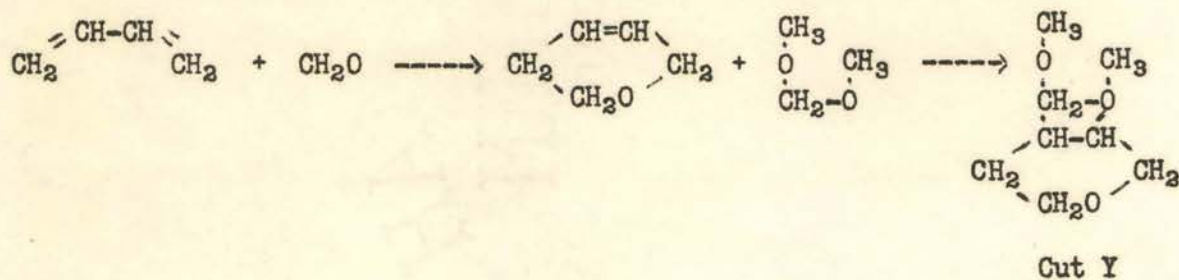
*See Appendix for explanation of high methoxyl values.

Table III
Further Properties of Cut X

	<u>Experimental</u>	<u>Theoretical for C₇H₁₄O₂</u>
Molecular weight, avg. of 3	131	130
C, %, avg. of 7 values	64.01%	64.65%
H, %, avg. of 7 values	11.38%	10.78%
Molar refraction	37.2	37.3
Br number	110, 110	123
Methoxyl, %*	54.2, 53.3, 40.8 39.1, 54.2, 49.5 44.3	47.7

*See Appendix for explanation of high methoxyl values.

Qualitative tests on Cut Y yielded the following results: unsaturation, by all methods, none; methoxyl group test, positive; carbonyl group, trace positive; ester test, none; acidity, none; and ether test, positive. Thus it is apparently a methoxyl-containing ether. A test for hydroxyl groups gave negative results. The fact that no appreciable hydrazone was formed indicated that no cyclic formal structure was present though it might have been expected according to the patent of Arundale and Mikeska (2). Attempts to isolate the the hydrazone failed owing to insignificant yields and tarring. All evidence is for the following structure and mechanism of formation:



3-methoxy-4-methoxymethyl-
perhydropyran

It should be noted that there is another structure that might represent Cut Y,

formed by the reverse orientation of the methylal molecule into the dihydro-1,2H-pyran intermediate. This compound would be 3-methoxymethyl-4-methoxyperhydropyran. The first structure would probably be favored by the orientation rule explained previously. Work on differentiation of these and other isomers is still in progress.

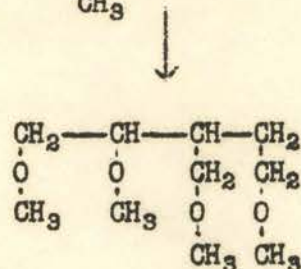
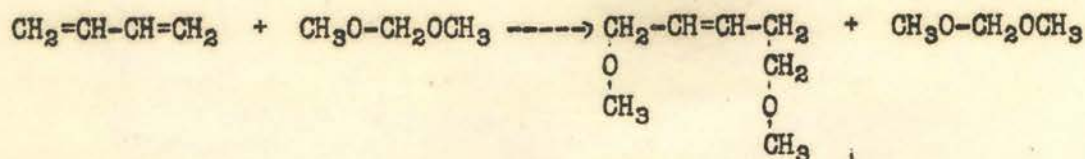
Table IV
Properties of Cut Y

	<u>Experimental</u>	<u>Theoretical for C₉H₁₆O₃</u>
Molecular weight, avg. of 3 values	156	160
C, %, avg. of 2 values	59.74%	60.00%
H, %, avg. of 2 values	10.27%	10.00%
Molar Refraction	41.55	41.87
Methoxyl, %, avg. of 2 values*	38.8%	38.7%
Boiling point at 30 mm., °C.	107	
Refractive index, n _D ^{28°}	1.4372	
Density at 28°, g./ml.	1.012	

*See Appendix on methoxyl determination

Cut Y, on the basis of the facts in Table IV, most certainly is either 3-methoxy-4-methoxymethylperhydro-pyran or the isomeric 3-methoxymethyl-4-methoxy compound.

Cut Z, our last unknown, gave the following results of qualitative tests: methoxyl, positive; hydroxyl, negative; unsaturation, negative; carboxyl, trace test; ester, negative; acidity, negative; and ether, positive. With this data and results of the usual quantitative measurements we were able to postulate and prove the structure of Cut Z except for possible position isomers. Cut Z is evidently the result of addition of two moles of methylal to one mole of butadiene in somewhat the following fashion:



Cut Z

1,2,5-trimethoxy-3-methoxymethylpentane

The above mechanism postulates an initial 1,4 addition of methylal to butadiene and then 2,3 addition of the second molecule of methylal to the remaining double bond. The orientation scheme again is based on the electronegativity rule of Prins-type addition. So far as can be determined there is as good a chance that initially a 1,2-type of addition took place, with subsequent 3,4-type of addition. In such an event Cut Z would be one of two possible isomers. The other isomer, 1,3,4,6-tetramethoxyhexane, would in any event be the higher-boiling compound (by virtue of its longer chain structure) and would consequently be the less likely of the two possible structures for Cut Z if, as seems probable, both isomers are produced in the reaction. It is known that there are still higher-boiling uninvestigated products of the reaction of methylal with butadiene.

In view of the evidence amassed (Table V following) in favor of the postulated structures for Cut Z, we feel that its structure is now established (save for the question of isomeric form) beyond any doubt.

Table V
Properties of Cut Z

	<u>Experimental</u>	<u>Theoretical for C₁₀H₂₂O₄</u>
Molecular weight (f.p. depr.)*	190, 185, 204	206
C, %, avg. of 2 values	57.97%	58.27%
H, %, avg. of 2 values	10.49%	10.68%
Molar refraction	54.2	54.9
Methoxyl, %, avg. of 3 values*	58.2%	60.3%
Boiling point at 35 mm., °C.	137	
Refractive index, n _D ^{28°}	1.4288	
Density at 28°, g./ml.	0.985	

*See Appendix for details concerning these values.

Since all four cuts are now known, it is possible to calculate the overall percentage yield of each cut in terms of butadiene for the run described previously in the thesis. This was the only yield run accomplished in the course of the work, most of the time having gone to solving difficulties of structural analysis. Table VI presents the yield data.

Table VI
Yields of Products from Methylal and Butadiene
12lg. butadiene + excess methylal

<u>Cut</u>	<u>Volume, ml.</u>	<u>Weight, gm.</u>	<u>% yield in terms of butadiene</u>
V	40.4	35	12
Intermediate	5.7	5	
X	65.0	57	20
Intermediate	5.5	5.2	
Y	40.0	40.5	13
Intermediate	3.5	3.5	
Z	12.2	12.0	3

DISCUSSION

From the foregoing results it is evident that the patent of Arundale and Mikeska (2) is misleading as to the course of addition of methylal into olefins under Prins-reaction conditions. Though we have tested the condensation of methylal with only butadiene, it seems proper to predict that methylal will also add to mono-olefins in the same way as has been demonstrated for butadiene, in view of the fact that chloromethyl ether has been shown to add to both types of olefins. Apparently methylal and chloromethyl ether add in similar fashion to olefins under Prins reaction conditions. Indeed it would be highly interesting to attempt verification of this prediction.

No concrete information on the variability of yields of the several cuts is available; however, in purely qualitative terms, it has been observed that Cuts V and X are produced almost exclusively by increasing the amount of butadiene to approach equimolarity with the methylal. A very large excess of methylal causes a shift to the production of the higher-boiling cuts, though some of the lower ones are still produced.

The four compounds have been fully characterized as to general structures and there remains only the doubt concerned with the differentiation of the various isomeric forms. It is possible to decide upon the most likely form on the basis of the general Prins type of addition, but this form of extrapolation is not fully satisfying. Unfortunately neither chemical nor physical evidence can readily distinguish the possibilities.

The compounds are of a comparatively new type, and their possible future uses can only be broadly speculated on. If a clean cleavage of the methoxyl groups could be accomplished, new polyhydroxy alcohols would be the result. Such alcohols are very like ones being used currently as potent insect repellants and insecticides. Some such compounds have been used also as solvents and plasticizers for polymers and resins. It has been observed that our

new compounds are apparently good solvents for the silicone-type greases, as evidenced by troubles encountered with maintaining sufficient stopcock lubrication, especially during vacuum distillations.

SUMMARY

The application of the Prins reaction, i.e., the acid-catalyzed addition of formaldehyde at a carbon-carbon double bond, to 1,3-butadiene has now been extended to the similar addition of methylal. Four new compounds have been isolated via this latter reaction and their structures have been established. The reaction and products are novel and the way is open for further work in this type of reaction with other mono- or diolefins.

APPENDIX

Notes on Quantitative Analytical Procedures

Determination of Methoxyl Groups.

One of the obviously desirable constants for compounds isolated in this research is methoxyl content. The Zeisel method is reputed to be the most accurate and dependable of such determinations. A survey of the literature, however, indicates numerous modifications of the method necessitated by the demands of various individual compounds. Elek (7) has reviewed a number of these alterations designed to overcome the low results obtained for compounds containing more than one methoxyl group. Essentially such modifications involve at least one of the following changes: (a) improvement of the purity and concentration of the hydriodic acid; (b) improvement of technique of introducing the sample and dissolving it in the hydriodic acid; (c) design of equipment and improvement of technique to minimize the direct volatilization of unreacted sample or incompletely cleaved molecular fragments of it; (d) improvement of absorption of the alkyl iodide via technique and equipment design.

In regard to point (a), Steyermark (20) has suggested a simple procedure for preparing suitable acid; the concentration must be kept above 1.7 specific gravity for accurate results. To avoid error due to incomplete reaction of highly volatile liquids or their decomposition products Steyermark (20) designed apparatus having an extra reaction vessel through which the gases pass, insuring complete conversion to the alkyl iodide. We have incorporated this idea into our apparatus design with success. Colson (4) devised a similar apparatus for liquids having boiling points lower than that of the hydriodic acid, consisting of a vertical tube filled with small glass beads, which are wetted with hydriodic acid, connected above the reaction flask. He also connected in the train two washing tubes to entrap any acid that may distil

over owing to the extremely high concentration of acid (1.96) necessary to cause complete reaction of the volatile material. To introduce the sample most authors use a small glass-stoppered vessel which can pass through the side arm of the reaction flask. A few crystals of phenol and propionic anhydride are previously introduced into the reaction flask to dissolve the sample. Introduction of sample in a capillary tube has also been suggested but has its drawback in the difficulty of expelling liquids from the capillary when they boil 25° or more above the hydriodic acid. In our work this would be a serious hindrance since we have found it essential to hold the temperature of the reaction vessel somewhat below the boiling point of hydriodic acid. We did not have access to a ground-glass-stoppered vessel of the type that has been suggested for use, so we were committed to trial of various other means. Our apparatus was like that of Steyermark but designed for semi-micro determinations, and so called for somewhat larger samples. In many early runs, transfer of the samples directly from the weighing bottle to the reaction flask was accomplished with a capillary-drawn eyedropper. This method of addition was rather clumsy and when applied to our highest-boiling fraction proved to give low results probably due to incomplete solution of the sample. A new method of sample introduction was then developed which will serve quite adequately for both low and high-boiling samples. A piece of 4 mm. glass tubing was sealed off at one end, drawn out to a 2 mm. capillary opening at the other end, and cut to give an overall length of about 30 mm., so that it may be introduced into the reaction flask directly. The usual precautions in weighing and handling the capillary tube are observed here. An eyedropper drawn to less than 1 mm. in diameter was used to introduce the sample into this tube and another one to add the solvent mixture mentioned before. Mixing was accomplished by gentle shaking. A third material was desired for introduction which would not interfere in the determination and

yet have sufficiently high volatility to cause expulsion of the sample mixture into the reaction flask and the hydriodic acid when the temperature was raised near the boiling point of the acid. Carbon tetrachloride was found to be an excellent substance for this purpose, and the method has yielded excellent results.

A further deviation from the apparatus for Steyermark was the use of a sintered-glass gas diffuser instead of a spiral-column scrubber to effect absorption of the alkyl iodide in the bromine-acetic acid prior to titration (15). The diffuser gives efficient absorption but creates a back-pressure which requires tightly fitting joints to avoid gas leakages. It was found that ball-and-socket joints were precisely fitted for this purpose and allowed more delicate adjustments when assembling and disassembling the apparatus. A joint separating the diffuser from the acid-washer part was useful when it was desired to halt a reaction or determine its progress periodically by replacement of the bromine-acetic acid scrubber. A joint was also placed between the acid washer and the reactor. The reactor comprised the two reaction flasks and a three-ball Snyder column which acted as an air condenser for the acid.

In the determination itself essentially the procedure of Steyermark was used until we encountered an interference that heretofore has been disregarded by investigators of the Zeisel method. It has been reported that the oxy-methylene bridge is without influence in the methoxyl determination. Our work, however, has proved that there is such an interference. Investigation of the sources that claimed absence of interference showed that every example of compounds tested was of phenolic origin--a dioxymethylene ether. It is conceivable that formaldehyde is split out of such an ether as expected but that it combines immediately with the active aromatic nucleus and is thus prevented from interfering. We have applied the Zeisel method to aliphatic

dioxymethylene compounds and found that the resultant methylene iodide does definitely give high results unless certain precautions are taken. Results of a purely qualitative run with paraformaldehyde indicated that such a reaction does occur and gave a very appreciable apparent methoxyl value (no theoretical methoxyl present). This suggested that formals would give similar interference according to the following scheme:



Three quantitative runs on 4-vinyl-1,3-dioxane (no theoretical methoxyl) upheld this theory quite well, although the results were too low to suggest stoichiometric reaction of the above type. The results of these three runs were as follows:

<u>Run</u>	<u>Time of run</u>	<u>Apparent Methoxyl</u>
1	1.5 hrs	7.4%
2	2.0 hrs	9.0%
3	3.0 hrs	9.9%

Note that the apparent methoxyl increases with time of reaction but at no time becomes very large.

Our own compounds also give interference. Three of the cuts finally gave high methoxyl results consistently, which caused us much concern. Was the fault that of the method or of the structures? The following results for methoxyl in the three cuts were accumulated:

<u>Cut</u>	<u>Experimental % Methoxyl</u>	<u>Theoretical % Methoxyl</u>
V	39.8, 48.9, 49.3 50.6	47.7
X	54.2, 53.3, 40.8 39.1, 54.2, 49.5 44.3	47.7
Y	20.7, 31.5, 46.7 47.5	38.8

Low values, obtained early, can be attributed to imperfections in apparatus and technique; but high ones must be blamed on some volatile organic iodide, which we now believe to be methylene iodide. The explanation of the formation of methylene iodide from Cuts V, X, Y, and Z is not so obvious as from paraformaldehyde and formals, but since a complex equilibrium prevails in the Prins reaction and its attainment could well be catalyzed by hydriodic acid, the regeneration of formaldehyde from these cuts is not impossible.

If methylene iodide were actually interfering, more careful controls might keep it from being swept through the system and being registered as apparent methoxyl. For one thing, the stream of carbon dioxide being swept through the system should be maintained at a minimum, and the temperature of the reaction must be regulated, probably with an oil bath. Trials showed that the time required for reaction and sweeping out of the methyl iodide was increased somewhat but the effect we had hoped to achieve was realized. Cut Y tested in an oil bath at 110° gave values approaching the theoretical:

<u>Run</u>	<u>Running Time</u>	<u>Oil Bath Temp. °C.</u>	<u>Methoxyl %</u>	<u>Theory</u>
1	7 hr 40 min	110	38.3	38.8
	10 hr 10 min	120-127	39.4	
2	5 hr 25 min	114-116	39.2	38.8
	6 hr 55 min	114-116	40.0	

It is regretted that time did not permit a similar controlled check of Cuts V and X.

Cut Z gave considerable but different trouble in attempts to determine its methoxyl content, the results being persistently low. It was finally found that by introducing the sample in the special capillary tube and running the reaction for eight to ten hours, nearly quantitative yields were obtained. In the following tabulation, Runs 1 and 2 were made with the old method of introducing the sample and the results indicated insufficient solution. Run 3 and succeeding ones used the new method of sample introduction and varying

times as noted:

<u>Run</u>	<u>Reaction Time</u>	<u>Methoxyl</u>	<u>Theoretical</u>
1	3 hrs	19.5%	60.3%
2	2.5 hrs	28.7%	"
3	2.5 hrs	43.6%	"
4	3.5 hrs	49.2%	"
5	5.5 hrs 6.5 hrs	54.3% 56.8%	" "
6	5.0 hrs 6.5 hrs	54.7% 58.2%	" "
7	6.0 hrs 8.5 hrs	58.3% 59.7%	" "

It has occurred to the author a method for purification of the hydriodic acid would be desirable so that it may be used again without carrying contaminants along. Alternatively it may be possible to circumvent interference by impurities by improvement of technique or procedure.

Molecular Weight Determinations:

Two different methods of determination were resorted to as checks on each other to assure reliable results. The freezing-point depression method, often reputed to be the better and more versatile of the various methods, had given us much trouble in reproducing results. A literature search revealed an excellent discussion by Glasstone (8) concerning the determination with an explicit procedure that has given us true values. Additional points that the author has found essential for reproducibility will be given, as well as a brief description of the whole procedure. Benzene was the solvent used. Since it has such a low molal freezing-point depression constant (5.12), the sharper the reading on the Beckmann thermometer the more accurate will be the result. Time must be sacrificed to get a reliable result. A critical point in the Beckmann determination is the regulation of the degree of supercooling that

the solution undergoes. This regulated supercooling cannot be realized unless the bath is only cold enough to lower the temperature slowly and evenly, so that premature crystallization does not occur on the sides of the tube containing the solvent. One-third or less of the cooling-jacket vessel should be filled with ice after the ice-water mixture has been made up. The apparent freezing point will vary with the degree of supercooling allowed; and the less supercooling allowed the more nearly will the concentration of the solution after crystallization approach that of the original. This is of course essential for best results. It has been found essential to the method then to allow the same minimum amount of supercooling in determining the freezing point of both the solvent and the solution. About $0.3-0.4^{\circ}$ supercooling gives best results. To get the approximate freezing point the liquid is allowed to cool fairly rapidly with stirring until the first crystals are formed and the temperature is noted at that moment. This is the rough reference point to be used in regulating the degree of supercooling for the final run. If the liquid cools too quickly at this stage a false point will result at considerably higher temperatures than the true freezing point. This will be discovered when in the final run there is no rapid rise to the freezing point when stirring starts the crystallization if it does it at all. The rough point usually can be determined at this stage however. As an example, it was found by trial that benzene freezes at roughly 4.88° . The liquid was allowed to warm up until no more crystals were present, and then the air tube was placed into the ice bath and the inner tube containing the liquid, thermometer, and stirrer was placed into the air tube. With no stirring the liquid was allowed to supercool slowly to 4.58° or .3 of a degree below the freezing point, at which it was evenly but vigorously stirred to initiate crystallization. The mercury then rose rapidly about 0.3° to the point that should be recorded as the freezing point. Both the solvent and the solution

were treated this way. This procedure has given the author amazingly consistent results, such as 204 for a theoretical 206, 156 for 160, and 141 and 143 for a theoretical 144.

The vaporimetric method of Niederl and Niederl (15) was next applied to the compounds with fair success. Since the high-boiling vaporimetric apparatus was unavailable commercially it was necessary to design our own equipment for the purpose. Various modifications of the apparatus described by Niederl and Niederl were tried and found to give good results but usually proved difficult to fill with mercury owing to a deviation in design from the apparatus that Niederl and Niederl used. A piece of apparatus was assembled, however, that proved to be quite easy to fill and gave very good results. It consisted simply of a small inverted test tube drawn down and sealed to a stem recurved at an angle very nearly parallel to the tube. The latter served as the vaporizer tube itself. The bend between the stem and the tube was made large enough so that a small capillary tube containing the sample could be easily introduced into the vaporizer chamber where it was encompassed with the mercury therein. The vaporizer and stem were enclosed in another larger test tube, the heating jacket, fitted with a reflux condenser. The stem of the vaporizer projected through and above the cork stopper of the heating jacket, which also carried a thermometer. Ball-and-socket standard-taper joints used to attach the vaporizer stem to a mercury-delivery capillary tube proved very convenient in permitting filling the vaporizer tube and stem through the capillary with mercury without getting air trapped and without delays. The filling of the vaporizer and fittings is a problem in individual technique and will not be described. The procedure of Niederl and Niederl was followed explicitly, and it was found that particular stress should be placed upon the preparation of clean dry mercury. With this precaution, the necessity of running more than one blank on the apparatus

for any one bath temperature is avoided. Except for the unexplainably poor results secured for the Cut Z fraction, the method proved reliable for all compounds tried. The following results were secured:

<u>Cut</u>	<u>Experimental M. W.</u>	<u>Theoretical</u>
V	136	130
X	129	130
Y	153	160
Z	181, 174, 214, 244	206

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BIOGRAPHY

John Hawkins was born in Los Angeles, California, August 8, 1922. He attended parochial and public schools and was graduated from Washington High School, Milwaukee, Wisconsin in June 1941.

He entered Marquette University at Milwaukee in June of 1941, and attended that school up until February 1943 at which time he was called to active duty by the U.S. Air Forces. He was separated again from the Air Corps in September 1945.

In 1945 he resumed undergraduate work at Marquette and received the degree of Bachelor of Science in Chemistry June 1947.

In June 1947 he enrolled in the Graduate School of Oklahoma A. and M. College and began working as a research assistant for Cities Service Oil Co. He served in this position until September 1948, at which time he was appointed research fellow for the same company. He is presently serving in that capacity.

Typist: Betty Billingsley