of 1,2,3,4-tetrahydronaphthalene-1,2-diacetic acid, carried out as described for VI, yielded 1.24 g. of α-1′-(or 3′)-**carbomethoxy-2′-keto-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene**, which after three recrystallizations from methanol formed colorless prisms; m. p. 108–109°.

Similarly from the ester of 1.29 g. of the β-acid 0.98 g. of the **β-form** of the keto ester was obtained, which after three recrystallizations from methanol formed fine colorless needles; m. p. 113–115°. A mixture of the two pure forms melted at 90–95°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: (α-form) C, 73.94; H, 6.74; (β-form) C, 73.70; H, 6.82.

The cyclic keto esters can be separated from each other more readily and in better yield than can the original acids. Cyclization of the dimethyl esters prepared from 1.66 g. of the mixture of acids yielded 1.48 g. of a mixture of the two forms of the keto esters; m. p. 70–91°. The mixture was dissolved in the minimum of hot methanol and a one-third excess of the solvent was added. On chilling, the β-form of the keto ester precipitated in nearly pure state. When the filtrate was concentrated to one-half its volume and chilled, a small amount of the mixed isomers separated; from the concentrated filtrate the nearly pure α-form of the keto ester separated. Two recrystallizations from methanol yielded the pure compounds. About equal amounts of the two forms were obtained.

Hydrolysis and decarboxylation of 0.7 g. of the α-form of the cyclic keto ester by a mixture of acetic acid and hydrochloric acid gave a quantitative yield of the α-form of **2′-keto-1,2,3,4-tetrahydro-1,2-cyclopentenonaphthalene (X)**; m. p. 83–85°. It crystallized from methanol in colorless rectangular plates; m. p. 85–86°.

Similarly, the **β-form of X** was obtained in 94% yield (m. p. 48–49°) from the isomeric keto ester; it crystallized from methanol in colorless needles; m. p. 51–52°.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: (α-form) C, 83.74; H, 6.64; (β-form) C, 83.94; H, 7.71.

The **2,4-dinitrophenylhydrazones** were recrystallized from methanol–chloroform; α-form, yellow needles with m. p. 260–261°; β-form, orange-yellow needles with m. p. 240–241° dec.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: N, 15.29. Found: (α-form) N, 15.11; (β-form) N, 15.12.

The **semicarbazones** of both forms crystallized in very fine colorless plates; α-form, m. p. 254–256° dec.; β-form, m. p. 220–222° dec.

Anal. Calcd. for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: (α-form) C, 69.43; H, 6.94; N, 17.34; (β-form) C, 69.09; H, 7.34; N, 16.81.

A suspension of 0.25 g. of the semicarbazone (α- or β-form) in ethanolic sodium ethoxide from 0.46 g. of sodium and 13 ml. of absolute alcohol was heated at 170° for twenty hours in a bomb tube. The isolated yellow liquid was heated with 0.2 g. of 10% palladium-charcoal catalyst at 300–320° for forty-five minutes. The product formed a picrate, which after two recrystallizations from ethanol melted at 106–107°, alone and when mixed with an authentic specimen of the picrate of 1,2-cyclopentenonaphthalene.

Summary

Three 3-ketohydrophenanthrenes and two 2′-ketohydro-1,2-cyclopentenonaphthalenes were synthesized by methods involving the Reformatsky and Dieckmann reactions.[15]

[15] A similar series of ketones has been prepared from 2-carbomethoxy-1-keto-1,2,3,4-tetrahydrophenanthrene by L. E. Miller in this Laboratory. These results will be published soon.

Ann Arbor, Michigan Received June 20, 1949

[Contribution from the Process Development Laboratory, Carbide and Carbon Chemicals Corporation]

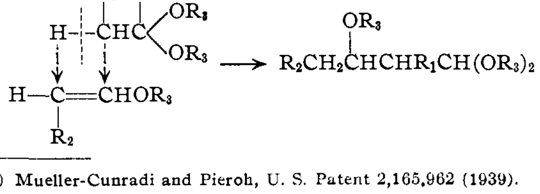
Reaction of Acetals and α,β-Unsaturated Ethers

By R. I. Hoaglin and D. H. Hirsh

During the course of an investigation of the chemistry of vinyl ethers the reaction of acetals and α,β-unsaturated ethers was studied. Examples of this reaction were reported by Mueller-Cunradi and Pieroh in a U. S. patent[1] which describes the condensation of acetaldehyde acetals and vinyl ethers in the presence of catalysts capable of effecting the polymerization of vinyl ethers.

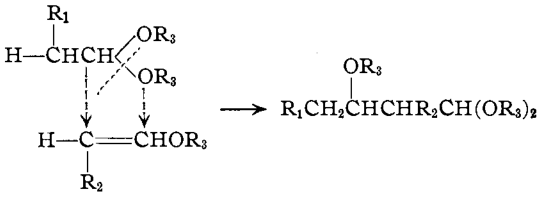
A priori the reaction of an acetal with an α,β-unsaturated ether could involve a splitting of either an alpha hydrogen, as suggested by Mueller-Cunradi and Pieroh, or an alkoxy group from the acetal with addition of the corresponding resulting fragments to the double bond of the unsaturated ether as shown in reactions (a) and (b).

(a)



$$\text{R}_2\text{CH}_2\overset{\text{OR}_3}{\overset{|}{\text{C}}}\text{HCHR}_1\text{CH(OR}_3)_2$$

(b)

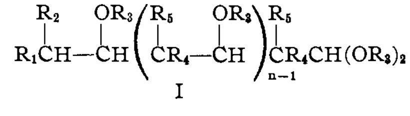


$$\text{R}_1\text{CH}_2\overset{\text{OR}_3}{\overset{|}{\text{C}}}\text{HCHR}_2\text{CH(OR}_3)_2$$

R_1 and R_2 may be hydrogen atoms or alkyl radicals; R_3 is an alkyl radical.

The present study showed that an alkoxy group is split from the acetal molecule and that the course of reaction indicated in (b) is correct. The investigation also showed that the reaction could be extended to include acetals of aldehydes other than acetaldehyde and also α,β-unsaturated ethers other than those derived from vinyl alcohol. The results may be generalized by the following equation, where R_1, R_2, R_4 and R_5 may

(c)



$$\text{R}_1\overset{\text{R}_2}{\overset{|}{\text{C}}}\text{HCH(OR}_3)_2 + n\text{R}_4\overset{\text{R}_5}{\overset{|}{\text{C}}}{=}\text{CHOR}_3 \longrightarrow \text{R}_1\overset{\text{R}_2}{\overset{|}{\text{C}}}\text{H}{-}\overset{\text{OR}_3}{\overset{|}{\text{C}}}\text{H}\left(\overset{\text{R}_5}{\overset{|}{\text{C}}}\text{R}_4{-}\overset{\text{OR}_3}{\overset{|}{\text{C}}}\text{H}\right)_{n-1}\overset{\text{R}_5}{\overset{|}{\text{C}}}\text{R}_4\text{CH(OR}_3)_2$$

I

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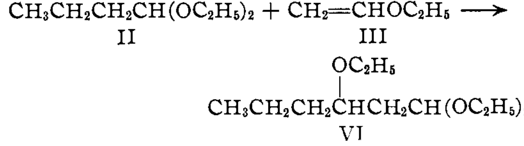
[1] Mueller-Cunradi and Pieroh, U. S. Patent 2,165,962 (1939).

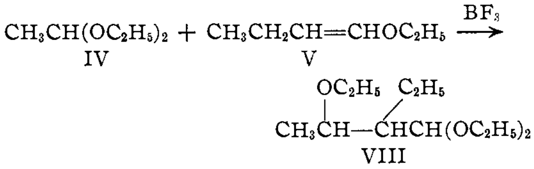
be hydrogen atoms or alkyl radicals, R_3 is an alkyl radical and n is a whole number.

The manner in which acetals and α,β-unsaturated ethers react was determined by means of two syntheses, the first involving the condensation of diethyl butyral (II) and vinyl ethyl ether (III), reaction (d), while the second entailed the addition of diethyl acetal (IV) to 1-butenyl ethyl ether (V), reaction (f). The product of the first reaction, 1,1,3-triethoxyhexane (VI), was simultaneously hydrolyzed and de-ethanolated with a mineral acid, reaction (e), to give 2-hexenal (VII), a known compound. The product of the second reaction, 1,1,3-triethoxy-2-ethylbutane (VIII), was similarly treated, reaction (g), giving 2-ethyl-2-butenal (IX), also a known compound.

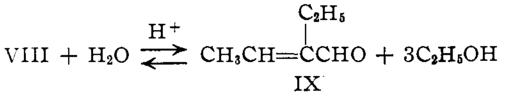
(d)


$$\underset{\text{II}}{CH_3CH_2CH_2CH(OC_2H_5)_2} + \underset{\text{III}}{CH_2{=}CHOC_2H_5} \xrightarrow{BF_3} \underset{\text{VI}}{CH_3CH_2CH_2\overset{\displaystyle OC_2H_5}{\overset{|}{C}}HCH_2CH(OC_2H_5)_2}$$

$$\text{(e)}\quad \text{VI} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{VII}}{CH_3CH_2CH_2CH{=}CHCHO} + 3C_2H_5OH$$

(f)


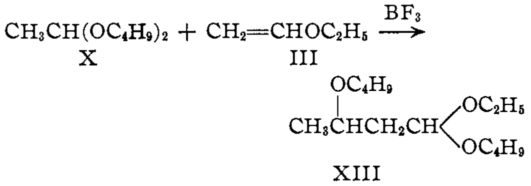
$$\underset{\text{IV}}{CH_3CH(OC_2H_5)_2} + \underset{\text{V}}{CH_3CH_2CH{=}CHOC_2H_5} \xrightarrow{BF_3} \underset{\text{VIII}}{CH_3\overset{\displaystyle OC_2H_5}{\overset{|}{C}}H{-}\overset{\displaystyle C_2H_5}{\overset{/}{C}}HCH(OC_2H_5)_2}$$

(g)


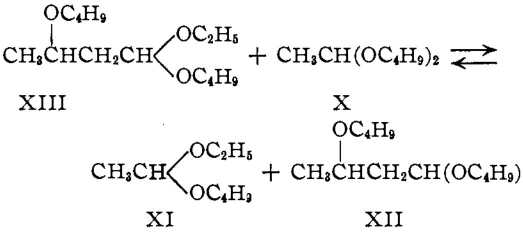
$$\text{VIII} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{IX}}{CH_3CH{=}\overset{\displaystyle C_2H_5}{\overset{|}{C}}CHO} + 3C_2H_5OH$$

Had the mechanism indicated by Mueller-Cunradi and Pieroh been correct, the structures of VI and VIII would have been reversed and the products of reactions (e) and (g) would also have been the reverse of those actually observed. Because of the fact that acetals of only acetaldehyde and ethers of only vinyl alcohol were used in the examples of the patent, the error in the mode of reaction was not observed by the inventors.

Examination of the general reaction shown in equation (c) shows that the alkoxy radicals in the acetal and unsaturated ether molecules are identical (OR_3). The reaction occurs with equal ease when reactants are used in which the alkoxy radicals are not identical, although the products are so numerous that isolation of pure compounds is difficult. For example, dibutyl acetal (X) reacted with vinyl ethyl ether (III) to give a mixture of products, two of which, 1-ethoxy-1-butoxyethane (XI) and 1,1,3-tributoxybutane (XII), were isolated. These compounds were assumed to have been formed by an alkoxy interchange between dibutyl acetal and 1,3-dibutoxy-1-ethoxybutane (XIII). These transformations are shown in equations (h) and (i).

(h)


$$\underset{\text{X}}{CH_3CH(OC_4H_9)_2} + \underset{\text{III}}{CH_2{=}CHOC_2H_5} \xrightarrow{BF_3} \underset{\text{XIII}}{CH_3\overset{\displaystyle OC_4H_9}{\overset{|}{C}}HCH_2CH\begin{matrix}OC_2H_5\\OC_4H_9\end{matrix}}$$

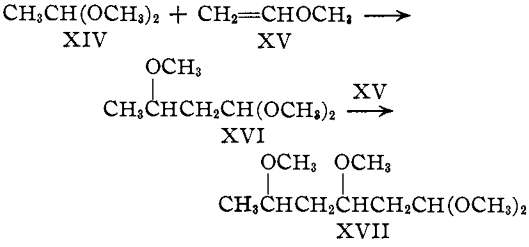
(i)


$$\underset{\text{XIII}}{CH_3\overset{\displaystyle OC_4H_9}{\overset{|}{C}}HCH_2CH\begin{matrix}OC_2H_5\\OC_4H_9\end{matrix}} + \underset{\text{X}}{CH_3CH(OC_4H_9)_2} \rightleftharpoons \underset{\text{XI}}{CH_3CH\begin{matrix}OC_2H_5\\OC_4H_9\end{matrix}} + \underset{\text{XII}}{CH_3\overset{\displaystyle OC_4H_9}{\overset{|}{C}}HCH_2CH(OC_4H_9)_2}$$

Compound XIII was not isolated but was believed to be present in intermediate fractions obtained in the distillation of the reaction product.

Several new alkoxyacetals were prepared which further illustrate the mechanism of the reaction and its versatility in the synthesis of compounds of specific structure. In Table I are presented yields and some physical properties of several of these alkoxyacetals prepared from acetals and α,β-unsaturated ethers.

The reaction of acetals and α,β-unsaturated ethers is similar to the addition of alcohols to ethylene oxide in that several products are formed, the distribution of which depends primarily on the mole ratio of the reactants. In Fig. 1 are shown graphically the data from several experiments in which the mole ratio of dimethyl acetal (XIV) to vinyl methyl ether (XV) was varied between 1:1 and 5:1. The main products of this reaction are 1,1,3-trimethoxybutane (XVI) and 1,1,3,5-tetramethoxyhexane (XVII) at the mole ratios employed.

(j)


$$\underset{\text{XIV}}{CH_3CH(OCH_3)_2} + \underset{\text{XV}}{CH_2{=}CHOCH_3} \longrightarrow \underset{\text{XVI}}{CH_3\overset{\displaystyle OCH_3}{\overset{|}{C}}HCH_2CH(OCH_3)_2} \xrightarrow{\text{XV}} \underset{\text{XVII}}{CH_3\overset{\displaystyle OCH_3}{\overset{|}{C}}HCH_2\overset{\displaystyle OCH_3}{\overset{|}{C}}HCH_2CH(OCH_3)_2}$$

Because these experiments were carried out batchwise, the mole ratios shown merely indicate a ratio of moles of acetal used to the total moles of vinyl ether added. Actually, the mole ratio varied between infinity and the finite value indicated. The data show, as expected, that the yield, based on vinyl methyl ether, of 1,1,3-trimethoxybutane increases and that of 1,1,3,5-tetramethoxyhexane decreases with an increase in the acetal : vinyl ether mole ratio.

Differences in reactivity between various acetals and vinyl ethers are also illustrated by the

TABLE I

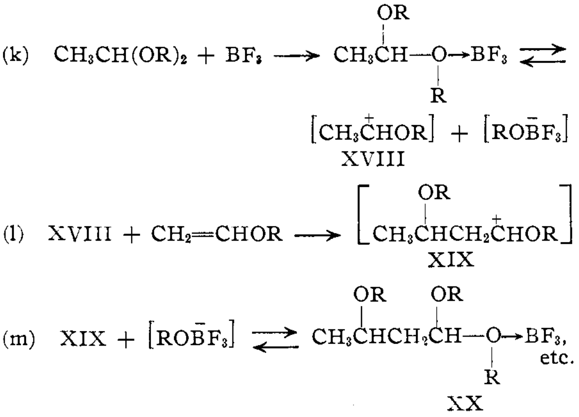
PREPARATION OF ALKOXYACETALS FROM ACETALS AND α,β-UNSATURATED ETHERS

Acetal	Unsaturated ether	Mole ratio of acetal to unsaturated ether	Product isolated	Yield of product based on ether	Physical properties: Boiling point, °C.[a]	Sp. gr., 20/15.6°C.	$n^{20}D$	Molecular refractivity Calcd.	Obs.
Dimethyl acetal	Vinyl methyl ether	3	1,1,3-Trimethoxybutane	79	157 (760) 46 (10)	0.921	1.4030	39.37	39.3
			1,1,3,5-Tetramethoxyhexane	10	83–85 (5)	.958	1.4206	54.86	54.6
Diethyl acetal	Vinyl ethyl ether	3	1,1,3-Triethoxybutane	67	190 (760) 68 (10)	.878	1.4069	53.19	53.3
			1,1,3,5-Tetraethoxyhexane	18	107 (5)	.902	1.4200	73.28	73.5
			1,1,3,5,7-Pentaethoxyoctane	..	110–116 (0.5)	.917	1.4281	93.21	93.6
Diethyl butyral	Vinyl ethyl ether	3	1,1,3-Triethoxyhexane	72	84–86 (5)	.873	1.4138	62.85	62.4
			1,1,3,5-Tetraethoxyoctane	16	100–105 (1)	.896	1.4258	82.48	82.7
1,1-Diethoxy-2-ethylhexane	Vinyl ethyl ether	5	1,1,3-Triethoxy-4-ethyloctane	67	93–95 (1)	.872	1.4277	80.80	81.0
Diethyl acetal	1-Propenyl ethyl ether	3	1,1,3-Triethoxy-2-methylbutane	71	69 (5)	.880	1.4115	57.9	57.7
Dimethyl acetal	1-Butenyl methyl ether	5	1,1,3-Trimethoxy-2-ethylbutane	74	65 (10)	.918	1.4171	48.58	48.3
Diethyl acetal	1-Butenyl ethyl ether	3	1,1,3-Triethoxy-2-ethylbutane	48	76–78 (5)	.880	1.4172	62.35	62.4
1,1-Diethoxy-2-ethylbutane	1-Butenyl ethyl ether	3	1,1,3-Triethoxy-2,4-diethylhexane	54	81–84 (1)	.881	1.4306	80.80	80.4
1,1-Diethoxy-2-ethylhexane	1-Butenyl ethyl ether	3	1,1,3-Triethoxy-2,4-diethyloctane	40	105–107 (1.5)	.878	1.4342	90.00	89.7
Diethyl acetal	2-Ethyl-1-hexenyl ethyl ether	3	1,1,3-Triethoxy-2-butyl-2-ethylbutane	24	87–90 (1)	.886	1.4343	80.80	80.7

[a] Boiling points uncorrected.

data shown in Fig. 1. These data show a distinct difference in the yields of products obtained when dimethyl acetal and diethyl acetal were treated with vinyl methyl ether and vinyl ethyl ether, respectively. Apparently the difference in reactivity between dimethyl acetal and trimethoxybutane with vinyl methyl ether is greater than the difference in reactivity between diethyl acetal and triethoxybutane with vinyl ethyl ether.

The ease with which boron trifluoride forms complexes suggested that the catalyst plays a role as shown in the equations



$$\text{(k)}\quad CH_3CH(OR)_2 + BF_3 \longrightarrow CH_3\overset{OR}{\overset{|}{C}}H-\underset{R}{\underset{|}{O}}\rightarrow BF_3 \rightleftharpoons \underset{XVIII}{[CH_3\overset{+}{C}HOR]} + [RO\overset{-}{B}F_3]$$

$$\text{(l)}\quad XVIII + CH_2{=}CHOR \longrightarrow \underset{XIX}{\left[CH_3\overset{OR}{\overset{|}{C}}HCH_2\overset{+}{C}HOR\right]}$$

$$\text{(m)}\quad XIX + [RO\overset{-}{B}F_3] \rightleftharpoons \underset{XX}{CH_3\overset{OR}{\overset{|}{C}}HCH_2\overset{OR}{\overset{|}{C}}H-\underset{R}{\underset{|}{O}}\rightarrow BF_3,}\ \text{etc.}$$

The activated forms XVIII and XIX are thus the points attacked by the unsaturated ether and a higher boiling alkoxyacetal is formed when a molecule of unsaturated ether reacts with the active form shown in XIX. In this manner the reaction proceeds indefinitely, resulting in products of the general type indicated in formula I.

A detailed catalyst study was not made for the acetal–α,β-unsaturated ether reaction. However, a single experiment was carried out in which zinc chloride was found to be just as effective as boron trifluoride in the reaction of diethyl acetal and vinyl ethyl ether.

The reaction of acetals and α,β-unsaturated ethers represents a new method of increasing the length of a carbon chain and the products obtained are similar in structure to those obtained by the aldol condensation. For example, for the synthesis of 1-hexanol by the acetal–unsaturated ether reaction, diethyl butyral and vinyl ethyl ether may be used. These intermediates are prepared from butyraldehyde and acetaldehyde, respectively, which raw materials are also involved in the synthesis of 1-hexanol *via* the aldol condensation. The aldol reaction, however, results in the formation of several unsaturated aldehydes because of the ability of each of the raw materials to condense with itself or with another aldehyde. A complex mixture of aldehydes, consisting of both straight and branched chains, is obtained requiring precise rectification for its resolution. The alkoxyacetals, formed in the acetal–unsaturated ether reaction, are straight- or branched-chained compounds, but both types are not obtained from the same reaction product. The alkoxyacetals are easily separated by distillation because of their difference in molecular weight, this difference being the molecular weight of the unsaturated ether used.

From the alkoxyacetals, obtained by the reaction of acetals and α,β-unsaturated ethers, may be prepared a multitude of chemical intermediates. Although publication of the details of the preparation of these intermediates is not in the scope of this paper the names of a few of the compounds derived from the reaction products of diethyl acetal and vinyl ethyl ether will serve to illustrate the potential utility of these alkoxyacetals. From 1,1,3-triethoxybutane may be obtained by hydrogenolysis 1,3-diethoxybutane (diethyl ether of 1,3-butanediol). Hydrolysis of triethoxybutane with mineral acid gives 3-ethoxybutanal or crotonaldehyde, the product obtained depending on the concentration of acid used.[2] From 3-ethoxybutanal may be obtained, by standard procedures, 3-ethoxybutanol and its esters and 3-ethoxybutanoic acid and its esters. Simultaneous dehydration and de-ethanolation of 3-ethoxybutanol gives butadiene.[1]

By analogous reactions 1,1,3,5-tetraethoxyhexane gives 1,3,5-triethoxyhexane, 3,5-diethoxyhexanal, 3,5-diethoxyhenanol and its esters, 3,5-diethoxyhexanoic acid and its esters, 2,4-hexadienal, hexanal, 1-hexanol, hexanoic acid, sorbic acid, hexyl ether, hexylamine and others. Analogous compounds can be prepared from alkoxyacetals derived from various acetals and α,β-unsaturated ethers.

Experimental[3]

The preparation of a few alkoxyacetals and unsaturated aldehydes is described and will serve to illustrate the experimental procedures employed.

Preparation of Reactants

Acetals used were prepared in the usual way, by the acid-catalyzed reaction of the appropriate aldehydes and alcohols. The unsaturated ethers were obtained by the catalytic vapor-phase decomposition of acetals.

Condensations

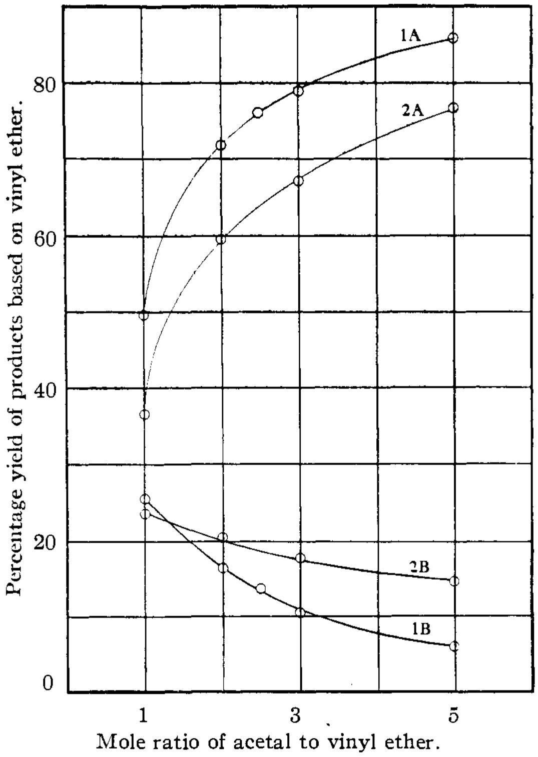


Fig. 1.—Reaction of dimethyl acetal with vinyl methyl ether and diethyl acetal with vinyl ethyl ether. Mole ratio of acetal to vinyl ether *vs.* yield of products based on vinyl ether: 1A, 1,1,3-trimethoxybutane; 2A, 1,1,3-triethoxybutane; 1B, 1,1,3,5-tetramethoxyhexane; 2B, 1,1,3,5-tetraethoxyhexane.

(a) **1,1,3-Trimethoxybutane and 1,1,3,5-Tetramethoxyhexane.**—Dimethyl acetal, 1943 g. (21.58 moles), was placed in a 5-l., 3-necked flask equipped with stirrer, brine-cooled condenser, gas diffuser and thermometer. Three and seven-tenths grams of boron trifluoride etherate (25% boron trifluoride in ethyl ether), was added to the acetal solution (0.05% of boron trifluoride based on the weight of acetal). This solution was warmed to 34° and 422 g. (7.19 moles) of vinyl methyl ether (99%) was vaporized into the agitated solution. Reaction took place at once with the evolution of heat. The temperature was maintained at 35 to 40° by regulation of the rate of addition of vinyl ether and by external cooling with water. The addition of vinyl methyl ether was completed in one hour and twenty minutes after which the reaction mixture was stirred another hour. The catalyst was then neutralized with 15 g. (400% excess) of anhydrous powdered sodium carbonate. The mixture was agitated four hours and then filtered to remove salts. Fractionation of the filtrate in the presence of a small amount of sodium carbonate gave 1,1,3-trimethoxybutane and 1,1,3,5-tetramethoxyhexane in yields of 79 and 10%, respectively, based on the vinyl methyl ether used. By-products, 1,1-dimethoxy-2-butene and 1,1,3-trimethoxy-4-hexene, were obtained in yields of 0.1 and 0.8%, respectively, although the former compound was not isolated in a pure form. The positions of the methoxy groups and double bond in trimethoxyhexene were indicated by mass spectrometric data. Trimethoxyhexene was obtained in 98% purity by redistillation of intermediate fractions composited from several similar reaction products: b. p. 72–74° (10 mm.); d^{20}_{20} 0.926; n^{20}_{D} 1.4261; *MR*, observed 48.2, calcd. 48.18.

(b) **1,1,3-Triethoxyhexane and 1,1,3,5-Tetraethoxyoctane.**—A mixture of 3070 g. (21 moles) of diethyl butyral and 6 g. of boron trifluoride etherate (25% boron trifluoride in ethyl ether) was stirred and warmed to 49°. To this mixture was added with good agitation 511 g. (7 moles) of vinyl ethyl ether (98.8%). The rate of addition was regulated, so that by cooling the reaction flask with water a reaction temperature of 49 to 50° was maintained. The addition of vinyl ether required forty-five

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[2] Halbig and Kaufler, U. S. Patent 1,902,070 (1933).

[3] Boiling points and melting points are uncorrected.

minutes, after which the catalyst was neutralized by agitation with 72 g. of 10% alcoholic sodium hydroxide solution. The reaction product was distilled under vacuum to recover the unreacted diethyl butyral and the products, 1,1,3-triethoxyhexane and 1,1,3,5-tetraethoxyoctane, which were obtained in yields of 72 and 16%, respectively, based on vinyl ethyl ether.

(c) **1,1,3-Triethoxy-2-ethylbutane.**—Three hundred grams (3 moles) of 1-butenyl ethyl ether was added dropwise to 1063 g. (9 moles) of diethyl acetal containing 1 cc. of an ethyl ether solution of boron trifluoride etherate (35% boron trifluoride). The mixture was stirred constantly during the addition of the ether and the temperature was maintained between 45 and 48° with slight cooling of the reaction flask. The addition of the ether was complete in fifteen minutes, although the reaction continued for another fifteen minutes. The catalyst was neutralized by agitation with 5 g. of anhydrous, powdered sodium carbonate for a period of three hours. Distillation of the reaction product gave 1,1,3-triethoxy-2-ethylbutane in 48% yield, based on 1-butenyl ethyl ether.

Hydrolysis and De-alkanolation

(a) **2,4-Hexadienal and 5-Methoxy-2-hexenal.**—One mole (206.2 g.) of 1,1,3,5-tetramethoxyhexane was distilled with 220 g. of 5.0% aqueous sulfuric acid solution. Methanol was removed as fast as formed until the vapor temperature could no longer be maintained at 65°. The removal of methanol (110 g.) required three and one-half hours. Distillation was stopped and the kettle residue was cooled to room temperature. This product consisted of a lower layer containing 5.75% sulfuric acid and 6.0% of aldehyde (as 5-methoxy-2-hexenal), and an upper layer containing essentially 2,4-hexadienal and 5-methoxy-2-hexenal. The upper layer was distilled under vacuum in the presence of 0.5 g. of sodium acetate. The yields of 2,4-hexadienal and 5-methoxy-2-hexenal were 47 and 38%, respectively. Physical properties of 2,4-hexadienal: b. p. 43° (5 mm.); d^{20}_{20} 0.898; $n^{20}\text{D}$ 1.5384. Physical properties of 5-methoxy-2-hexenal: b. p. (approx.) 58° (5 mm.); d^{20}_{20} 0.931; $n^{20}\text{D}$ 1.4615; *MR*, observed 36.1; calcd. 35.8.

(b) **2-Hexenal and 2-Ethyl-2-butenal.**—1,1,3-Triethoxyhexane, 327 g. (1.5 moles), was distilled with 375 cc. of 2% aqueous hydrochloric acid solution. After refluxing this mixture ten minutes the vapor temperature dropped to 77.5° and an ethanol fraction was removed. After five hours the removal of ethanol was essentially complete, water was added to the kettle and crude 2-hexenal (94% purity) was recovered as the upper layer of the 2-hexenal–water steam distillate. The yield of 2-hexenal was 94%. Physical properties of 2-hexenal: b. p. 50–51° (20 mm.); d^{20}_{20} 0.845; $n^{20}\text{D}$ 1.4464. 1-Hexanol was prepared from the aldehyde by hydrogenation; 3,5-dinitrobenzoate, m. p. 58°.

Using the same procedure, 2-ethyl-2-butenal was prepared in 95% yield from 1,1,3-triethoxy-2-ethylbutane. Physical properties of 2-ethyl-2-butenal: b. p. 58° (50 mm.); d^{20}_{20} 0.858; $n^{20}\text{D}$ 1.4478. 2-Ethyl-1-butanol was prepared from the aldehyde by hydrogenation; 3,5-dinitrobenzoate, m. p. 50°.

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Summary

1. The reaction of acetaldehyde acetals and vinyl ethers was extended to include acetals of other aldehydes and α,β-unsaturated ethers of alcohols other than vinyl alcohol.

2. The manner in which acetals and α,β-unsaturated ethers react was shown to be in disagreement with that suggested by Mueller-Cunradi and Pieroh.

3. The utility of the acetal–α,β-unsaturated ether reaction is discussed.

SOUTH CHARLESTON, W. VA. RECEIVED MAY 12, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, CORNELL UNIVERSITY MEDICAL COLLEGE]

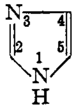
Studies of Imidazole Compounds. II. The Structure of Certain Simple Imidazole Derivatives

BY ROBERT A. TURNER

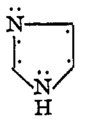
Although the structures of several aromatic nuclei have been discussed extensively in the chemical literature, the structure of the imidazole nucleus has been given scant attention. In this paper we discuss the structure of imidazoles, as revealed by the spectrophotometric data of certain simple derivatives.

Discussion

Imidazole (I) possesses an aromatic sextet (II) and thus satisfies one of the known requirements for aromatic character.



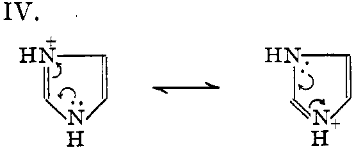
I



II

The nitrogen atom in position 3 has an electron pair, not included in the sextet, and which may be donated to a proton. Imidazole is a basic substance which readily forms salts with acids. Since the two unshared electrons of the nitrogen atom in position 1 are needed to form the sextet, they may not be donated to a proton, and consequently imidazole is a monoacid base.[1]

When the imidazole nucleus has acquired a proton, the charged molecule has the resonance forms III and IV.



III IV

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[1] The structure of pyrrole is, by contrast, enlightening in this connection. It loses its aromatic stability in the presence of hydrogen ions because the sextet is destroyed when the two unshared electrons of the nitrogen atom are donated. Not only is pyrrole a weak base, but it is unstable in the presence of acids.