$$CH_2(OCH_3)_2 + CH_2(OC_2H_5)_2 \rightleftarrows 2CH_2(OCH_3)(OC_2H_5) \quad (1)$$

cording to eq. 1 are presented in Table I. These data were employed to calculate[4] the equilibrium constant

$$K = \frac{[CH_2(OCH_3)_2][CH_2(OC_2H_5)_2]}{[CH_2(OCH_3)(OC_2H_5)]^2} = 0.30 \quad (2)$$

which has a standard error,[4] $s$, of 0.04. This equilibrium constant was used to calculate the values given in parentheses in Table I for the mole percentage of the various compounds at equilibrium. It is interesting to note that the equilibration according to eq. 1 does not proceed in the absence of a catalyst. Trace amounts of acids act as catalysts. A comparison of the equilibrium constant with that for the statistically random case ($K_{\text{rand}} = 0.250$) shows that the equilibrium of eq. 1 is quite close to this case as found earlier for ester–ester interchanges of some inorganic alkoxy compounds.[5]

TABLE I

EQUILIBRIUM DATA FOR SCRAMBLING OF $OCH_3$ WITH $OC_2H_5$ GROUPS IN THE SYSTEM $CH_2(OCH_3)_2$ *vs.* $CH_2(OC_2H_5)_2$ AT 65°

| | Mole % | | |
|---|---|---|---|
| $R = OCH_3/CH_2$ | $CH_2(OCH_3)_2$ | $CH_2(OCH_3)(OC_2H_5)$ | $CH_2(OC_2H_5)_2$ |
| 0.250[a] | 1.6 | 23.4 | 75.0 |
| (0.266)[b] | (1.8)[c] | (21.4) | (76.8) |
| 0.667 | 9.2 | 41.5 | 49.3 |
| (0.599) | (12.0) | (42.7) | (45.3) |
| 1.000 | 24.0 | 47.6 | 28.4 |
| (0.956) | (26.1) | (47.8) | (26.1) |
| 1.333 | 38.8 | 44.5 | 16.7 |
| (1.221) | (45.3) | (42.7) | (12.0) |
| 1.750 | 74.0 | 24.7 | 1.3 |
| (1.727) | (76.8) | (21.4) | (1.8) |

[a] From the ingredients. [b] Values in parentheses are calculated from the gas chromatographic data. [c] Values in parentheses are calculated using $K = 0.30$.

In a related study by others,[6] equilibrium constants were determined for the alcoholysis of diethyl- and dimethylacetal, $K_{\text{I}} = [CH_3CH(OCH_3)(OC_2H_5)][C_2H_5OH]/[CH_3CH(OC_2H_5)_2][CH_3OH] = 4.61$ with $s = 0.09$ and $K_{\text{II}} = [CH_3CH(OCH_3)_2][C_2H_5OH]/[CH_3CH(OCH_3)(OC_2H_5)][CH_3OH] = 1.01$ with $s = 0.04$. It is seen that $K_{\text{II}}/K_{\text{I}} = K = 0.22$. This indirectly measured value of the constant of eq. 2 has a standard error of 0.003 and is in fair agreement with our value, and the concept[1,2] that exchange reactions of this type follow the statistics of random sorting.

**The Orthoformate System.**—Data for the scrambling of alkoxy groups in orthoformates are given in Table II. The resulting equilibria obtained after 7 days at 120° without a catalyst are expressed by eq. 3 and 4

$$HC(OCH_3)_3 + HC(OCH_3)(OC_2H_5)_2 \rightleftarrows 2HC(OCH_3)_2(OC_2H_5) \quad (3)$$

$$HC(OC_2H_5)_3 + HC(OCH_3)_2(OC_2H_5) \rightleftarrows 2HC(OCH_3)(OC_2H_5)_2 \quad (4)$$

and the experimental data in Table II were used to calculate[4] the equilibrium constants $K_1$ and $K_2$ which

$$K_1 = \frac{[HC(OCH_3)_3][HC(OCH_3)(OC_2H_5)_2]}{[HC(OCH_3)_2(OC_2H_5)]^2} = 0.46 \quad (5)$$

$$K_2 = \frac{[HC(OC_2H_5)_3][HC(OCH_3)_2(OC_2H_5)]}{[HC(OCH_3)(OC_2H_5)_2]^2} = 0.33 \quad (6)$$

have standard errors $s_1 = 0.03$ and $s_2 = 0.02$, respectively. This system is also quite close to the statistically random case ($K_{1(\text{rand})} = K_{2(\text{rand})} = 0.333$). The constants $K_1$ and $K_2$ quantitatively describe all possible exchange equilibria in the orthoformate system, a system which has been studied earlier in a qualitative manner by Post and Erickson.[7]

TABLE II

EQUILIBRIUM DATA FOR THE SCRAMBLING OF $OCH_3$ WITH $OC_2H_5$ GROUPS IN THE SYSTEM $HC(OCH_3)_3$ *vs.* $HC(OC_2H_5)_3$ AT 120°

| | Mole % | | | |
|---|---|---|---|---|
| $R = OCH_3/C$ | $HC(OCH_3)_3$ | $HC(OCH_3)_2$-$(OC_2H_5)$ | $HC(OCH_3)$-$(OC_2H_5)_2$ | $HC(OC_2H_5)_3$ |
| 0.375[a] | 0.1 | 3.0 | 35.9 | 61.0 |
| (0.420)[b] | (0.3)[c] | (4.1) | (28.5) | (67.1) |
| 1.000 | 3.5 | 23.5 | 41.5 | 31.5 |
| (0.990) | (4.5) | (21.3) | (43.8) | (30.4) |
| 1.500 | 15.1 | 35.2 | 37.9 | 14.0 |
| (1.503) | (14.3) | (34.9) | (37.3) | (13.5) |
| 2.000 | 33.9 | 40.2 | 20.5 | 5.4 |
| (2.025) | (31.6) | (40.9) | (23.0) | (4.4) |
| 2.625 | 68.4 | 27.5 | 3.9 | 0.2 |
| (2.641) | (67.4) | (27.4) | (4.9) | (0.3) |

[a] From the ingredients. [b] Values in parentheses are calculated from the gas chromatographic data. [c] Values in parentheses are calculated using $K_1 = 0.46$ and $K_2 = 0.33$.

Attempts to extend these studies to the systems $CH_3C(OCH_3)_3$ *vs.* $CH_3C(OC_2H_5)_3$ and $C(OCH_3)_4$ *vs.* $C(OC_2H_5)_4$ failed owing to difficulties in finding a suitable support–substrate combination for the gas chromatographic analysis and formation of low-boiling side products, respectively.

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[4] L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

[5] K. Moedritzer, G. M. Burch, J. R. Van Wazer, and H. K. Hofmeister, *Inorg. Chem.*, **2**, 1152 (1963); K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 268 (1964); J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964).

[6] R. S. Juvet, Jr. and J. Chiu, *J. Am. Chem. Soc.*, **83**, 1560 (1961).

[7] H. W. Post and E. R. Erickson, *ibid.*, **55**, 3851 (1933).

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# Ketene Acetals. II. The Synthesis of Ketene Acetals from Dichloro Olefins and Sodium β- and γ-Alkoxy Alcoholates[1]

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Simons and Vebanc[2] observed the formation of an acetate ester as the terminal product in the reaction of vinylidene chloride with a polyoxypropylene glycol in the presence of a base. Evidence for the intermediates or a choice of proposed mechanisms was not offered, however, by these authors. Earlier work by Coleman, Wiley, and Hadler[3] suggested the formation

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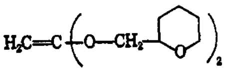
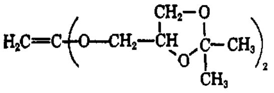
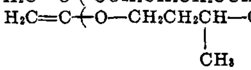
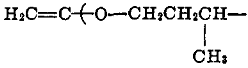
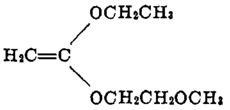
[1] Paper I: W. C. Kuryla and D. G. Leis, *J. Org. Chem.*, **29**, 2773 (1964).

[2] D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

[3] G. H. Coleman, R. M. Wiley, and B. C. Hadler (to the Dow Chemical Co.), U. S. Patent 2,245,962 (June 17, 1941).

TABLE I

NEW KETENE ACETALS[a]

| Compd. no. | Structure | Halo-olefin | Solvent | Yield, % | B.p., °C. (mm.) | Formula | Calcd. % C | Calcd. % H | Found, % C | Found, % H | Mol. wt. Calcd. | Mol. wt. Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1a** | $H_2C=C(OCH_2CH_2OCH_3)_2$ | A | DG | 75.6 | 81–83 (1.9) | $C_8H_{16}O_4$ | 54.5 | 9.16 | 54.5 | 9.05 | 176 | 178 |
| **1b** | $H_2C=C(OCH_2CH_2OCH_3)_2$ | B | DG | 63.1 | 80–83 (1.7) | ... | ... | ... | ... | ... | ... | ... |
| **1c** | $H_2C=C(OCH_2CH_2OCH_3)_2$ | C | DG | 58.5 | 80–82 (1.8) | ... | ... | ... | ... | ... | ... | ... |
| **1d** | $H_2C=C(OCH_2CH_2OCH_3)_2$ | A | XY | 75.0 | 83–86 (2.2) | ... | ... | ... | ... | ... | ... | ... |
| **2** | $H_2C=C[O-CH(CH_2OCH_3)_2]_2$ | B | XY | 36.4 | 121–122 (1.8) | $C_{12}H_{24}O_6$ | 54.5 | 9.09 | 54.5 | 9.15 | 264 | 277 |
| **3** | $ClHC=C(OCH_2CH_2OCH_3)_2$ | D | XY | 53.2 | 103–106 (1.6) | $C_8H_{15}ClO_4$ | 45.6[b] | 7.12 | 46.0 | 7.51 | 211 | 211 |
| **4** |  | C | XY | 60.5 | 142–145 (1.5) | $C_{14}H_{24}O_4$ | 65.6 | 9.38 | 65.8 | 9.26 | 256 | 274 |
| **5** |  | C | DG | 30.6 | 130–132 (1.1)<br>m.p. 27–30 | $C_{14}H_{24}O_6$ | 58.3 | 8.39 | 57.9 | 8.60 | 288 | 288 |
| **6** | $H_2C=C(O-CH_2CH_2OCH_2CH_2CH_2CH_3)_2$ | A | XY | 72.8 | 132–133 (2.3) | $C_{14}H_{28}O_4$ | 64.6 | 10.85 | 64.5 | 10.79 | 260 | 268 |
| **7** | $H_2C=C[O-CH_2CH_2-N(CH_3)_2]_2$ | A | XY | 30.9 | 90–91 (2.0) | $C_{10}H_{20}N_2O_2$ | 59.4[c] | 10.95 | 59.5 | 10.96 | 202 | 201 |
| **8** | $H_2C=C(OCH_2CH_2CH_2OCH_3)_2$ | A | DG | 15.7 | 101–102 (2.8) | $C_{10}H_{20}O_4$ | 58.8 | 9.81 | 59.0 | 9.97 | 204 | 203 |
| **9a** |  $H_2C=C(O-CH_2CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-OCH_3)_2$ | A | XY | 35.8 | 100–104 (1.5) | $C_{12}H_{24}O_4$ | 62.1 | 10.35 | 62.3 | 10.67 | 232 | 237 |
| **9b** |  $H_2C=C(O-CH_2CH_2\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-OCH_3)_2$ | B | XY | 37.5 | 104–105 (1.6) | ... | ... | ... | ... | ... | ... | ... |
| **10** |  $H_2C=C\begin{matrix}\diagup OCH_2CH_3\\ \diagdown OCH_2CH_2OCH_3\end{matrix}$ | E | XY | 48.0 | 40–40.5 (0.5) | $C_7H_{14}O_3$ | 57.5 | 9.65 | 57.3 | 9.89 | 146 | 148 |

[a] A = 1,1-dichloroethene (vinylidene chloride), B = *cis*-1,2-dichloroethene, C = *trans*-1,2-dichloroethene, D = 1,1,2-trichloroethene, E = 1-bromo-2-ethoxyethene, DG = diethylene glycol dimethyl ether, and XY = xylene (mixed isomers). [b] *Anal.* Calcd.: Cl, 16.9. Found: Cl, 17.3. [c] *Anal.* Calcd.: N, 13.84. Found: N, 13.74.

of either an acetate ester or a 1-chloro-1,1-dialkoxyethane from the reaction of vinylidene chloride with a metal alcoholate. Again, very little evidence was offered, and the analyses were completely lacking.

Ketene acetal derivatives of β- and γ-alkoxy alcohols have been synthesized by a simple one-step process which provides good yields from inexpensive and readily available starting materials. The slow addition of a 1,1- or 1,2-dichloroethene to a sodium β- or γ-alkoxy alcoholate, dissolved or suspended in a solvent, results in an exothermic reaction which yields the ketene acetal as the principal product (if an inert solvent is used), with the concomitant precipitation of sodium chloride. If the solvent used is an alcohol, the resultant product may be an ortho ester.[1]

Table I summarizes the compositions, yields, analyses, and properties of the new ketene acetals synthesized since the last publication.[1] The dichloro olefin and solvent in the synthesis of a particular ketene acetal are also shown in Table I. Likewise described in Table I is the ketene acetal derivative of N,N-dimethylethanolamine, which was made from the corresponding sodium alcoholate and 1,1-dichloroethene using identical synthesis conditions as described for the synthesis of other ketene acetals.

Ketene di(2-methoxyethyl)acetal has been shown to be quite stable in the presence of the hot sodium alcoholate, in experiments in which only half of the 1,1- or 1,2-dichloroethene normally utilized in these reactions was added to the sodium alcoholate (0.62 mole used, instead of the normal 1.24 moles/2.00 moles of NaOR).

Table I summarizes the synthesis of the previously described[1] ketene di(2-methoxyethyl)acetal (**1**), using three different dichloroethenes and two different solvents under identical processing conditions. It is interesting to note that the nature of the solvent has very little effect on the yield of product, while the yield appears to be inversely proportional to the relative ease with which the dichloroethene may be dehydrochlorinated with a strong base.[4,5] The infrared spectra of these ketene acetal products were identical in all respects.

Evidence to support the previously proposed mechanism includes the synthesis of ketene acetals from sodium β- and γ-alkoxy alcoholates and 1,1-dichloroethene, *cis*-1,2-dichloroethene, and *trans*-1,2-dichloroethene. Similarly, the chloroketene acetal was obtained from 1,1,2-trichloroethene and, as previously reported,[1] the methyl ketene acetal from 1,1-dichloro-1-propene.

In each of these examples, the dihalo olefin is added dropwise to the hot sodium alcoholate–solvent mixture, thus generating, in relatively high dilution and in close proximity to one another, the corresponding chloroacetylene and alcohol. Combination of these species followed by the reaction sequence in the proposed mechanism[1] gives the ketene acetal product.

Additional evidence in support of this mechanism was furnished by the synthesis of a mixed ketene acetal from sodium 2-methoxyethylate and 1-bromo-2-ethoxyethene. In this experiment, *which is itself a new ketene acetal synthesis*, 1-bromo-2-ethoxyethene was added dropwise to a hot sodium 2-methoxyethylate–xylene mixture, to give the mixed ketene acetal and sodium bromide in a manner exactly analogous to the ketene acetal synthesis as previously described. Thus, the presence of an alkoxyacetylene intermediate as proposed in the mechanism appears to be confirmed.

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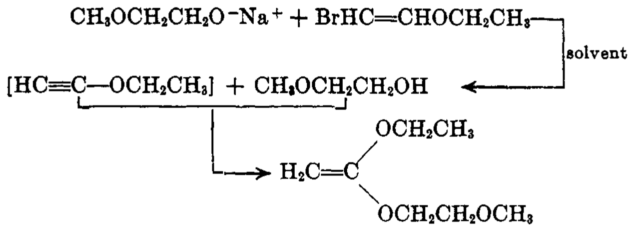
[4] J. Flynn, Jr., V. V. Badiger, and W. E. Truce, *J. Org. Chem.*, **28**, 2298 (1963).

[5] S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 629 (1952).

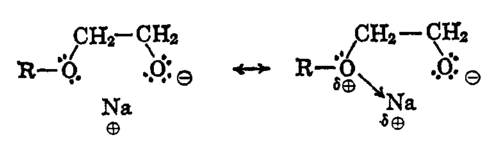


10

The properties of this mixed ketene acetal (10) are found in Table I.

As previously reported,[1] attempts to prepare ketene acetal derivatives of simple alcohols using 1,1-dichloroethene and a sodium alcoholate–alcohol mixture under the relatively mild conditions of this synthesis resulted in failure as neither the exothermic reaction nor salt precipitation was observed. Also, the infrared spectra of the crude liquid products showed no trace of C=C absorption near 1640 cm.$^{-1}$, which is characteristic of the ketene acetal structure.[6] Similarly, a ketene acetal could not be made from potassium *t*-butoxide and 1,1-dichloroethene using an inert solvent such as xylene or dimethyl sulfoxide at 140°. Likewise, attempts to prepare the corresponding ketene acetals from 1,1-dichloroethene and sodium 4-methoxy-1-butylate (a $\delta$-alkoxy alcoholate), or from an equimolar mixture of paraformaldehyde and sodium methylate (which might form, *in situ*, an $\alpha$-alkoxy alcoholate) resulted in failure. Xylene was used as the solvent in each of these cases, and the infrared spectra of the crude liquid products showed a complete absence of an absorption at or near 1640 cm.$^{-1}$. Thus, sodium $\beta$- and $\gamma$-alkoxy alcoholates appear to be quite unusual in regard to their reaction with 1,1- or 1,2-dichloro olefins to give ketene acetals.

An intramolecular solvation phenomenon is postulated as the reason for the unusual reactivity of the sodium $\beta$- and $\gamma$-alkoxy alcoholates in this ketene acetal synthesis. Both the sodium $\beta$- and $\gamma$-alkoxy alcoholates may form a cyclic intermediate wherein the metal cation is solvated by coordination with the electrons on the ether oxygen, thus markedly increasing the effective basicity or electron density of the alkoxide oxygen. Similarly, in the case of sodium N,N-dimethylaminoethylate, the sodium cation could be internally solvated by coordination with the electrons on the nitrogen atom of the dimethylamino group. This may be illustrated by the following scheme.



It is presently believed that this cyclic alkoxy alcoholate is the active species in the synthesis of ketene acetals. This may explain why simple alcohols such as methanol, ethanol, 1-butanol, and 2-butanol, which cannot form such an internally solvated cyclic intermediate, do not give any appreciable reaction with 1,1-dichloroethenes under the relatively mild conditions of the ketene acetal synthesis. Similarly, with sodium $\alpha$- and $\delta$-alkoxy alcoholates, which might form four- and seven-membered rings, respectively, the nonreactivity is probably due to the unstable nature of the four- and seven-membered coordination rings, which would thus result in a poor over-all solvation of the sodium cation. Support for this postulation can be found in the work of Ugelstad, Mörk, and Jenssen[7] who observed marked increases in the base-catalyzed double-bond isomerization rates of methyl linolenate with potassium $\beta$-alkoxy alcoholates over a potassium *t*-butylate control. Some support for this postulated coordination may also be found in a related cation solvation study by Ugelstad and Rokstad,[8] and by analogy to the work of Zook and Russo.[9]

In comparing the behavior of lithium, sodium, and potassium cations in this ketene acetal synthesis, one is struck with the marked difference among these three species. No reaction was observed when 1,1-dichloroethene was added to lithium 2-methoxyethylate in xylene at 140°. Sodium cation, as the sodium $\beta$- or $\gamma$-alkoxy alcoholates, gives good yields of the corresponding ketene acetals in the same reaction. Potassium cation, on the other hand, renders the same reaction explosively uncontrollable. The addition of 1,1-dichloroethene to potassium 2-ethoxyethylate in the corresponding alcohol at 100° resulted in a minor explosion within the flask, lifting the addition funnel and condenser from the flask, and leaving them with a blackened coating, but not actually rupturing the glass. The use of a potassium salt in this reaction has not since been repeated. The most likely explanation for this explosion is that a buildup of chloroacetylene had occurred, which violently decomposed.

## Experimental Section

The ketene acetals of Table I were all synthesized by essentially the same procedure, which is described below for ketene di[2-(1-butoxy)ethyl] acetal (6). The synthesis of a "mixed" ketene acetal, prepared by this procedure using an alkoxybromoethene, is fully described below. The reagents utilized were obtained from standard chemical supply houses, except where noted.

**Ketene Di[2-(1-butoxy)ethyl] Acetal** (6).—To a solution of 2-(1-butoxy)ethanol (Butyl Cellosolve solvent, 236 g., 2.00 moles) in xylene (50 g.), was added metallic sodium (46 g., 2.00 g.-atoms) at a temperature of 100–130°, and under a nitrogen atmosphere. When solution of the sodium was complete, 1,1-dichloroethene (vinylidene chloride, 120 g., 1.24 moles) was added dropwise to the above mixture over a 20-min. period, at 110° with rapid stirring and under a nitrogen atmosphere. The temperature of the reaction mixture increased from 110 to 176° during the addition of the vinylidene chloride, with the concomitant precipitation of solid sodium chloride. The reaction mixture was then vacuum filtered to give a brown filtrate and tan solid sodium chloride. The solid was washed several times with anhydrous ether and oven-dried overnight to give 123 g. of sodium chloride.

The ether washings and brown filtrate were combined and vacuum distilled to yield, as the principal product fraction, 189 g. (0.73 mole, 72.8%, b.p. 132–133° at 2.3 mm.) of ketene di[2-(1-butoxy)ethyl] acetal: infrared spectrum, $\nu_{C=C}$ 1640 cm.$^{-1}$ (very strong).

*Anal.* Calcd. for $C_{14}H_{28}O_4$: C, 64.6; H, 10.85; mol. wt., 260. Found: C, 64.5; H, 10.79; mol. wt., 268 (Menzies–Wright determination in benzene).

**Ketene Ethyl 2-Methoxyethyl Acetal** (10).—To a solution of 2-methoxyethanol (Methyl Cellosolve solvent, 38.0 g., 0.50 mole) in xylene (25 g.), was added metallic sodium (11.5 g., 0.50

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[6] S. M. McElvain and R. E. Starn, Jr., *J. Am. Chem. Soc.*, **77**, 4571 (1955).

[7] J. Ugelstad, P. C. Mörk, and B. Jenssen, *Acta Chem. Scand.*, **17**, 1455 (1963).

[8] J. Ugelstad and O. A. Rokstad, *ibid.*, **18**, 474 (1964).

[9] H. D. Zook and T. J. Russo, *J. Am. Chem. Soc.*, **82**, 1258 (1960).

g.-atom) at a temperature of 100–130°, and under a nitrogen atmosphere. When solution of the sodium was complete, 1-bromo-2-ethoxyethene [prepared according to the method of Nazarov and co-workers[10] as modified by Wasserman[11] by the use of a light petroleum ether (b.p. 60–71°) solvent and a −40° reaction temperature in the vinyl ether bromination step, 76.5 g., 0.50 mole] was added dropwise to the above mixture over a 50-min. period, at 130–140° with rapid stirring and under a nitrogen atmosphere. Stirring was continued for an additional 2 hr. at 140°, with the precipitation of solid sodium bromide. The reaction mixture was then vacuum filtered to give a yellow filtrate and tan solid sodium bromide. The solid was washed several times with anhydrous ether and oven dried overnight to give 39 g. (76% based on the sodium) of sodium bromide.

The ether washings and yellow filtrate were combined and vacuum distilled to yield 35.0 g. (0.240 mole, 48.0%, b.p. 40.0–40.5° at 0.5 mm.) of ketene ethyl 2-methoxyethyl acetal as the principal product fraction: infrared spectrum, $\nu_{C=C}$ 1640 cm.$^{-1}$ (very strong).

*Anal.* Calcd. for $C_7H_{14}O_3$: C, 57.5; H, 9.65; mol. wt., 146. Found: C, 57.3; H, 9.89; mol. wt., 148 (Menzies–Wright determination in benzene).

**Acknowledgment.**—It is a pleasure to acknowledge the laboratory assistance of L. J. Ford, and the analytical services of Johanna Holm and T. R. Lawrence.

[10] I. N. Nazarov, Zh. A. Krasnaya, and V. P. Vinogradov, *Zh. Obsch. Khim.*, **28**, 460 (1958).

[11] H. H. Wasserman, private communication, July 2, 1964.

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# The Reaction of Diborane with Some Steroidal Thioketals

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*Received May 4, 1965*

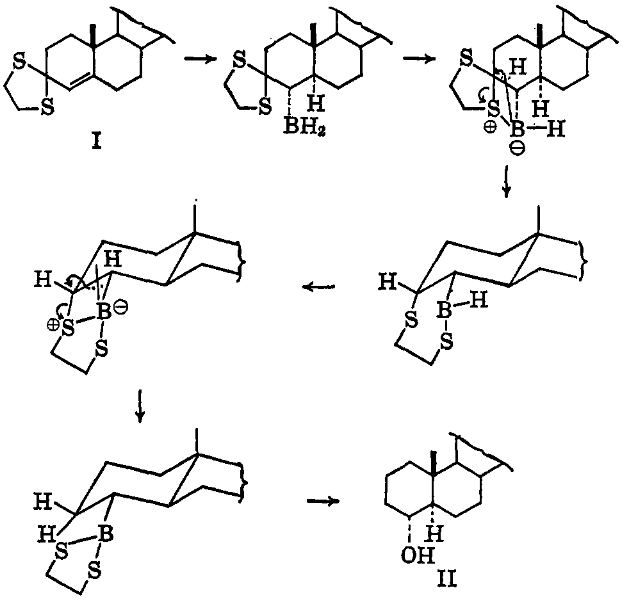
Some time ago the hydrogenolytic reduction of thioketals with hydrazine to the corresponding hydrocarbons was reported.[1] Apparently attempts have not so far been made to effect the same reduction with diborane, and this Note refers to the interesting reduction of some steroidal thioketals with this reagent. The results described here show that this reaction is unexpectedly complicated.

The product of the reaction of excess diborane in ether at 20° with 3-cycloethylenedithiocholest-4-ene (I) was oxidized in the usual way with alkaline hydrogen peroxide to give a mixture of starting material and hydroxy compounds, none of which contained sulfur. Separation by chromatography on alumina gave starting material (44%), 5α-cholestan-4α-ol (II, 13%), and, very surprisingly, 5β-cholestan-3α-ol (III, 32%). 3-Cycloethylenedithio-5α-cholestane did not react with diborane under the same conditions and was recovered unchanged from the reaction sequence. This is in agreement with the reported stability of thio ethers to diborane.[2]

7-Cycloethylenedithio-5α-cholestane was likewise inert to diborane, while 7-cycloethylenedithiocholest-5-ene gave 5α-cholestan-6α-ol (16%) and 5α-cholestan-7β-ol (38%).

These results clearly show that diborane cannot be used for the simple hydrogenolytic desulfurization of thioketals, since only those formed from α,β-unsaturated ketones react, and moreover react to give unexpected products. The following mechanisms are suggested for these interesting reactions though at the moment these are admittedly tentative. First, the formation of 5α-cholestan-4α-ol (II) in the reaction of diborane with 3-cycloethylenedithiocholest-4-ene (I) will be considered (Scheme I).

SCHEME I



The initial addition of diborane to the double bond is believed to be followed by boron–sulfur coordination, and then hydride shift from boron to C-3, thereby breaking the $>\!C-\overset{\oplus}{S}<$ bond. A repetition of this sequence results in complete removal of sulfur from C-3 The boron–sulfur fragment produced in the reaction, in accordance with the known chemistry of boron–sulfur compounds,[3] would not be expected to withstand these alkaline oxidizing conditions. The addition of diborane to the double bond is believed a necessary initial step, since the fact that 3-cycloethylenedithio-5α-cholestane was not desulfurized by diborane seems to exclude the possibility that the 5α-cholestan-4α-ol (II) could have arisen by the addition of diborane to cholest-4-ene produced by a preliminary desulfurization. The stereochemistry of the product (II) is what would be expected from the addition of diborane to the less-hindered α face of the molecule in the anti-Markovnikov sense.[4]

An explanation for the quite surprising formation of 5β-cholestan-3α-ol (III) in this reaction is inevitably more complicated, and is thought to involve as the important preliminary step the formation of a B–S bond instead of a B–C bond (Scheme II).

Several points require comment here. First, though this mechanism satisfactorily accounts for the formation of 5β-cholestan-3α-ol (III), it is not immediately obvious why the formation of a 5α-cholestane deriva-

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[2] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp. 29, 238.

[3] H. Steinberg, "Organoboron Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 20.

[4] M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **29**, 1120 (1964).