[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

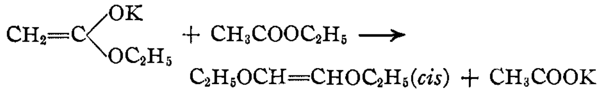
The Preparation and Properties of 1,2-Diethoxyethylene

BY S. M. MCELVAIN AND CHARLES H. STAMMER

1,2-Diethoxyethylene (II) has been prepared by the dealcoholation of ethoxyacetaldehyde diethylacetal over alumina at 190°. The physical and chemical properties now described for this symmetrical isomer of ketene diethylacetal demonstrate that the recently reported *cis* and *trans* forms of this compound (Scheibler and Baganz, *loc. cit.*) are spurious.

The relatively high boiling points of the various ketene acetals, as compared to those of the corresponding normal esters and orthoesters, have been attributed to the polarization associated with the ketene acetal structure.[1] Only in the case of tetraethoxyethylene (diethoxyketene diethylacetal) has an authentic ketene acetal been found to boil lower than the corresponding normal ester, and this anomaly was considered to be due to a repression of the polarization of this particular ketene acetal by its symmetrical structure. It seemed of interest in this connection to prepare the symmetrical diethoxyethylene (II) and compare its properties with those of its unsymmetrical isomer, ketene diethylacetal ($CH_2{=}C(OC_2H_5)_2$), as well as with those of its saturated analog, ethylene glycol diethyl ether ($C_2H_5OCH_2CH_2OC_2H_5$).

While this work was in progress, the preparation and properties of both the *cis* and *trans* forms of 1,2-diethoxyethylene were reported by Scheibler and Baganz.[2] The *cis* structure is assigned to a product obtained from the reaction of ethyl acetate with its potassium enolate. Earlier claims[3] that



$$CH_2{=}C\begin{matrix}OK\\OC_2H_5\end{matrix} + CH_3COOC_2H_5 \longrightarrow C_2H_5OCH{=}CHOC_2H_5(cis) + CH_3COOK$$

these reactants yield ketene diethylacetal are now withdrawn and a new reaction mechanism to rationalize the formation of the symmetrical rather than the unsymmetrical diethoxyethylene is proposed.[4] The *trans* structure is claimed to be formed by the dealcoholation of ethoxyacetal (I) with (a) phosphorus pentoxide and quinoline (39% yield), (b) phthalic anhydride (87% yield), (c) ethylmagnesium bromide (44.5% yield) and (d) by the action of sodium on ethoxybromoacetal, $C_2H_5OCHBrCH(OC_2H_5)_2$, (25% yield). The boiling points of the *cis* and *trans* compounds are reported as 76–77° and 78–79°, respectively.[5]

In this Laboratory, after some unsuccessful attempts to prepare and dehydrochlorinate ethyl 1-chloro-2-ethoxyethyl ether ($C_2H_5OCH_2CHClOC_2H_5$), the preparation of 1,2-diethoxyethylene (II) was accomplished by the dealcoholation of ethoxyacetal (I) over alumina[6] at 190°. This dealcoholation occurs to some extent (*ca.* 30%) when the acetal (I, b. p. 166°) is refluxed with alumina, but when passed through a column of alumina at 190°, I is converted to II in 70% yield.

$$\underset{\text{I}}{C_2H_5OCH_2CH(OC_2H_5)_2} \xrightarrow[190^\circ]{Al_2O_3} \underset{\text{II}}{C_2H_5OCH{=}CHOC_2H_5} + C_2H_5OH$$

1,2-Diethoxyethylene, as produced in this reaction, is a colorless liquid that boils at 133–134°, $n^{25}D$ 1.4215[7]; it has a dipole moment of 2.76 debye units, which suggests the *cis* structure. Catalytic hydrogenation converts II to ethylene glycol diethyl ether, b. p. 120–121°, $n^{25}D$ 1.3890. In the presence of a trace of ferric chloride or hydrogen chloride, II adds alcohol to yield the ethoxyacetal (I). When II is treated with a crystal of ferric chloride, it rapidly polymerizes, with the evolution of considerable heat, to a viscous, red liquid.

The diethoxyethylene (II) rapidly absorbs bromine in carbon tetrachloride at 0–10° in amounts varying from 75 to 120 mole per cent., depending on the order of mixing the reactants, but attempts to obtain a product from these brominations invariably yielded hydrogen bromide and an intractable tar. However, when II was directly treated with bromine and water added immediately to the product, the initially insoluble material completely dissolved in the cold on stirring, and from the resulting aqueous solution an 85% yield of the bis-*p*-nitrophenylhydrazone of glyoxal was precipitated by the addition of *p*-nitrophenylhydrazine.[8] This behavior indicates that the initially formed dibromide III is quite unstable, but that it may be

$$\text{II} \xrightarrow{Br} \underset{\text{III}}{C_2H_5OCHBrCHBrOC_2H_5} \xrightarrow{H_2O} \underset{\text{IV}}{OCHCHO} + 2HBr + 2C_2H_5OH$$

---

[1] S. M. McElvain, *Chem. Revs.*, **45**, 465 (1949).

[2] H. Scheibler and H. Baganz, *Ann.*, **565**, 157 (1949).

[3] H. Scheibler, *et al.*, *Ber.*, **55**, 789, 791, 798, 2921 (1922).

[4] H. Scheibler, *Ann.*, **565**, 176 (1949).

[5] In the first paper describing the preparation and properties of ketene diethylacetal (F. Beyerstedt and S. M. McElvain, THIS JOURNAL, **58**, 529 (1936)) it was pointed out that one of the most cogent reasons for doubting the existence of Scheibler's ketene acetal was its reported boiling point (77–78°), which is 24° below that of the saturated analog, acetaldehyde diethylacetal (b.p. 101–103°). An even greater difference now appears between the boiling points of these reported 1,2-diethoxyethylenes and that of the corresponding saturated compound, ethylene glycol diethyl ether (b.p. 119–121°). The German authors[2] recognize that this difference in boiling points is quite considerable and make an attempt to rationalize it.

[6] The use of alumina was resorted to when it was found that aluminum ethoxide caused no dealcoholation of the acetal (I). While the aluminum alkoxides dealcoholate orthoesters to the corresponding ketene acetals, alumina has been found to convert methyl orthophenylacetate mainly to the normal ester and dimethyl ether (S. M. McElvain and (a) W. R. Davie, *ibid.*, in press, (b) J. T. Venerable, *ibid.*, **72**, 1661 (1950)).

[7] Scheibler and Baganz[2] report $n^{20}D$ 1.3646 and 1.3682 for their *cis* and *trans* forms of 1,2-diethoxyethylene.

[8] Scheibler and Baganz (ref. 2, p. 174) report that their *trans* compound, in a quantitative determination of the double bond, absorbed only 15.2% of the theoretical quantity of bromine after 24 hours. They also state that the bis-phenylhydrazone of glyoxal was obtained in 14% yield from either of their isomers after bromination in sunlight for 24 hours, followed by refluxing the reaction product with aqueous alcoholic hydrochloric acid and treatment with phenylhydrazine; when the bromination was conducted at 100° in a sealed tube, a 30% yield of the glyoxal derivative was reported.

hydrolyzed readily to glyxoal (IV) if it is not permitted to undergo spontaneous decomposition.

Both the ethoxyacetal (I) and the diethoxyethylene (II) yield the hydrazone of ethoxyacetaldehyde together with a small amount of the bis-hydrazone of glyxoal when treated with an aqueous ethanol solution of 2,4-dinitrophenylhydrazine hydrochloride. The formation of the glyoxal derivative is doubtless the result of an acid cleavage of ethoxyacetaldehyde to glycolic aldehyde ($HOCH_2CHO$) followed by a conversion of this compound to its osazone.

Inasmuch as the properties of the diethoxyethylene (II) obtained in the present work are so markedly different from those reported by Scheibler and Baganz, it seemed advisable to repeat their preferred procedure for the preparation of the *trans* compound, which involves the dealcoholation of ethoxyacetal (I) with phthalic anhydride. When this experiment was repeated as described,[2] a liquid boiling at 77–78° was indeed obtained. However, this product was found to be mainly ethyl alcohol, as it gave an 86% yield of ethyl N-phenylcarbamate when treated with phenyl isocyanate. In view of these results, a sample of II was heated with one equivalent of phthalic anhydride. This mixture darkened rapidly and gave a distillate consisting of ethyl alcohol and II; continued heating up to 200° yielded no phthalic anhydride and left a residue of tar. It is, therefore, apparent that 1,2-diethoxyethylene is extensively decomposed by heating with phthalic anhydride.

From these observations, from earlier reports of the nature of the product obtained in attempts to prepare ketene acetal from ethyl acetate and sodium ethoxide,[9] and more particularly from the properties of 1,2-diethoxyethylene found in the present work, it is evident that neither form of this compound has been prepared by the German workers.[2]

Experimental

Ethoxyacetaldehyde Diethyl Acetal (I).—A cooled solution of sodium ethoxide, prepared by the reaction of 115 g. (5.0 g.-atoms) of sodium with 3200 ml. of absolute ethanol, was placed under nitrogen in a 3-necked 5-liter round-bottomed flask fitted with condenser and stirrer, and 822 g. (4.17 moles) of bromoacetaldehyde diethyl acetal[10] added over a period of 40 minutes. A slow stream of nitrogen was passed over the mixture while it was heated under reflux for 24 hours. The precipitated sodium bromide was filtered off and approximately 2 l. of ethanol was removed from the filtrate by distillation through a 30-cm. Vigreux column. The remaining solution was refluxed overnight and the precipitated sodium bromide (total yield 95%) filtered off. After removal of the ethanol from this filtrate, fractionation of the residue through a 50 cm. × 1.2 cm. column packed with wire saddles yielded two fractions: (a) 200 g., b.p. 145–164°, and (b) 351 g. of the ethoxyacetal (I), b.p. 164–166.5°, $n^{25}\text{D}$ 1.3989.[11] Fraction (a) was combined with an ether extract of the solid residue from the above distillation and this mixture refractionated. An additional 57.0 g. of I was obtained, bringing the total yield to 408 g. (60.5%). The lower boiling material was mainly ethyl orthoacetate.

Reaction of Ethoxyacetal (I) **with 2,4-Dinitrophenylhydrazine.**—To a boiling solution of 1.88 g. of 2,4-dinitrophenylhydrazine and 3 ml. of concentrated hydrochloric acid in 150 ml. of 95% ethanol and 30 ml. of water was added 1.4 g. of ethoxyacetal (I). After boiling the solution 5 minutes, 0.25 g. of dark brown needles, m.p. 311–314°, precipitated and was filtered from the hot solution. On placing the filtrate in the refrigerator, 2.00 g. (87%) of the ethoxyacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 110–112°, crystallized. After recrystallization from ethanol, it melted 114–115° (lit. 116–117°[12]). Concentration of the mother liquor to about 100 ml. yielded another 0.11 g., m.p. 307–309°, of brown needles, bringing the total yield of glyoxal bis-(2,4-dinitrophenylhydrazone) to 0.36 g. (10%). After recrystallization from pyridine, it melted 315–316° (lit. 311–312°[13]). A mixed melting point with an authentic sample showed no depression.

Reaction of Ethoxyacetal (I) **with Phthalic Anhydride.**—A mixture of 25 g. (0.169 mole) of finely pulverized phthalic anhydride and 20 g. (0.123 mole) of I was heated in an oil-bath at 145° under a reflux condenser for 1 hour. During this time no reflux was observed, but darkening of the solution occurred as soon as the phthalic anhydride had dissolved. Distillation of the solution yielded 12.3 g. of distillate and a black residue (31.0 g.). This residue, when heated under diminished pressure, yielded a small quantity (3.5 g.) of phthalic anhydride sublimate and turned to a black tar. The distillate was added to 5 g. of pulverized phthalic anhydride and refluxed for 1 hour. The resulting solution was distilled and 9.75 g. of distillate collected. After refluxing this distillate with 5 ml. of aniline for 1 hour, the product was fractionated directly from the aniline through a 25-cm. Podbielniak column. The main fraction, 7 g., b.p. 77–78°, $n^{25}\text{D}$ 1.3615, was water-soluble, did not decolorize bromine in carbon tetrachloride or 2% aqueous potassium permanganate solution, reacted vigorously with acetyl chloride and gave an iodoform test. When 0.5 g. of this product and 1.45 g. (0.012 mole) of phenyl isocyanate were mixed together, heat was evolved and 1.55 g. (86%), ethyl N-phenylcarbamate, m.p. 49–51°, was extracted with boiling petroleum ether (90–100°) from the mixture. This was recrystallized from 50% ethanol and dried under vacuum, m.p. 50–51°. A mixed melting point with an authentic sample showed no depression.

1,2-Diethoxyethylene (II).—In a vertical glass column, 45 cm. × 2.5 cm., drawn at the lower end to a diameter of 8 mm. and to such a length as to extend through a rubber stopper into a receiving flask, was placed 25 g. of alumina pellets prepared from alumina obtained by the hydrolysis of aluminum isopropoxide. The alumina was heated to 190° and 85 g. of ethoxyacetal (I) (0.524 mole) dropped onto it at a rate of about 50 ml./hr. from a dropping funnel. A slight pressure of nitrogen was kept on the acetal to overcome the pressure developed in the tube during the reaction. The products were collected in a flask surrounded by an ice-bath and attached to a Dry Ice–acetone cold trap. When all the acetal had been added, nitrogen was passed through the tube for about 10 minutes. Fractionation of the reaction products yielded a small quantity of acetaldehyde, 11.4 g. (0.248 mole) of ethanol, 23.8 g. (0.205 mole) of the 1,2-diethoxyethylene, b.p. 130.5–137°, $n^{25}\text{D}$ 1.4205, and 37.6 g. (0.232 mole) of unchanged acetal. The yield of II, based on unrecovered I amounted to 70%. After fractionation through a 50 cm. × 1.2 cm. column packed with wire saddles, the 1,2-diethoxyethylene had the following physical properties: b.p. 133–134° (737 mm.), $n^{25}\text{D}$ 1.4215, d^{25}_4 0.8838; MR_D calcd. 32.73, found 33.39. It showed a dipole moment of 2.76 debye units as determined in benzene solution by the heterodyne beat method.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.03; H, 10.42. Found: C, 61.78; H, 10.68.

Reactions of 1,2-Diethoxyethylene (II) (a) **Hydrogenation.**—A solution of 5.9 g. (0.051 mole) of II in 150 ml. of absolute ether was shaken with 1.004 g. of palladium–charcoal catalyst in a 250-ml. pressure bottle under approximately three atmospheres of hydrogen. Absorption of 0.05 mole of hydrogen was complete in 5 minutes. After removal of the catalyst and ether, fractionation through a 23 cm. × 0.6 cm. Fenske column yielded 4.2 g. (70%) of ethylene glycol diethyl ether, b.p. 118–119.5°, $n^{25}\text{D}$ 1.3890, d^{25}_4 0.8346. This was compared with an authentic sample, b.p. 119–121°, $n^{25}\text{D}$ 1.3903, d^{25}_4 0.8281.

---

[9] J. M. Snell and S. M. McElvain, This Journal, **55**, 416, 427 (1933). This work showed that the product now claimed by Scheibler and Baganz[2] to be *cis*-1,2-diethoxyethylene was ethyl alcohol containing small amounts of ethyl acetate and water.

[10] "Organic Syntheses," Vol. 23, p. 8 (1943).

[11] E. Späth, *Monatsh*., **36**, 4 (1915).

[12] N. L. Drake, *et al.*, This Journal, **60**, 73 (1938).

[13] T. L. Jacobs and W. J. Whitcher, *ibid.*, **64**, 2635 (1942).

(b) **With Ethanol.**—A solution of 5.00 g. (0.0431 mole) of II in 19.80 g. (0.431 mole) of ethanol containing three drops of 10% solution of ferric chloride[14] in ethanol was refluxed 8 hours and allowed to stand overnight. A pellet of sodium hydroxide was added to the solution followed by refluxing for 15 minutes. After removal of the excess ethanol, distillation yielded 3.88 g. (55.5%) of the ethoxyacetal (I), b.p. 161–166°, $n^{25}D$ 1.3993. A somewhat lower yield of I was obtained when hydrogen chloride was substituted for the ferric chloride in this experiment.

(c) **With Bromine.**—(i) A solution of 0.094 g. (0.81 millimole) of II in 10 ml. of carbon tetrachloride at 0° was found to decolorize 18.22 ml. (0.638 millimole, 78.8%) of an 0.035 *M* bromine in carbon tetrachloride solution added dropwise from a buret. If the order of addition were reversed, and a 0.025 *M* solution of II in carbon tetrachloride added to 10 ml. of the standard bromine solution at 0°, 122% of the theoretical amount of II was required to completely decolorize the bromine.

(ii) In an attempt to isolate the bromo derivative of II, a solution of 4.728 g. (40.7 millimoles) of II in 5 ml. of carbon tetrachloride at 25° was treated dropwise with an 0.8 *M* bromine in carbon tetrachloride solution; only 22.7 millimoles (55%) of bromine was absorbed. When an attempt was made to distill the solvent from the solution, a black liquid separated and large quantities of hydrogen bromide were evolved. Attempts to distil this separated liquid gave more hydrogen bromide and left a black tar.

(iii) To 1.0 g. of II, in a small glass sample tube surrounded by an ice-bath, bromine was added dropwise from a micro buret. Considerable heat was evolved and the solution darkened gradually as the addition proceeded. The bromine absorption stopped after 1.0 g. (73%) of bromine was added. The reaction product was treated with 2 ml. of water and the mixture stirred vigorously for 2 to 3 minutes until the lower organic layer had dissolved. A red precipitate was formed immediately when this dark solution was added to a boiling solution of 2.64 g. of *p*-nitrophenylhydrazine and 3 ml. of concentrated hydrochloric acid in 25 ml. of 95% ethanol. When filtered off and dried, the glyoxal bis-*p*-nitrophenylhydrazone weighed 2.37 g. (84%), m.p. 290–293°. After two recrystallizations from pyridine it melted 309–310° (lit.[15] 309–310°). A mixed melting point with an authentic sample showed no depression.

(d) **With 2,4-Dinitrophenylhydrazine.**—Using the procedure described for the reaction of ethoxyacetal (I) with 2,4-dinitrophenylhydrazine, 1.00 g. of II was allowed to react with 1.88 g. of 2,4-dinitrophenylhydrazine. Yields of 1.72 g. (75%) of the ethoxyacetaldehyde 2,4-dinitrophenylhydrazone and of 0.44 g. (12%) of the glyoxal bis-2,4-dinitrophenylhydrazone were obtained.

(e) **With Phthalic Anhydride.**—In a 25-ml. distilling flask were placed 8.0 g. (0.068 mole) of II and 10.0 g. (0.068 mole) of pulverized phthalic anhydride. After heating in an oil-bath at 110–120° for 1 hour, distillation of the mixture yielded 3.86 g. of distillate, b.p. 80–129°, and 14.12 g. of a black tarry residue, from which no phthalic anhydride was obtained when heated under diminished pressure. Redistillation of the distillate gave the following fractions: (a) 1.66 g., b.p. 69–79°, $n^{25}D$ 1.3641; (b) 1.17 g., b.p. 79–150°, $n^{25}D$ 1.4062. When 0.25 g. of fraction (a) was treated with 0.65 g. of phenyl isocyanate, heat was evolved and 0.5 g. (55.5%) of ethyl N-phenylcarbamate, m.p. 45–48°, was extracted from the mixture with boiling petroleum ether (b.p. 90–100°). After recrystallization from 50% ethanol it melted 50–51°; a mixed melting point with an authentic sample showed no depression. Three drops of fraction (b) absorbed about one-third as much bromine as did a similar amount of II, indicating that this fraction was a mixture of ethanol and II.

---

[14] Solid ferric chloride when added to II causes it to polymerize exothermically to a viscous, red oil.

[15] W. L. Ruigh and R. T. Major, This Journal, **53**, 3131 (1931).

MADISON, WISCONSIN RECEIVED OCTOBER 16, 1950

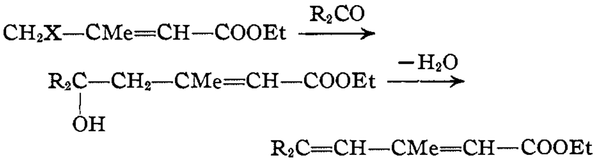
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

New Approaches to the Synthesis of Compounds Containing Conjugate Unsaturation

BY CHARLES D. HURD AND H. E. WINBERG

The synthesis of β-methyl-γ-halocrotonic esters from the epoxide of methallyl chloride is described, followed by use of the halo ester in the Reformatsky reaction with aldehydes or ketones. Some reactions of γ-ethynyl-γ-valerolactone are presented.

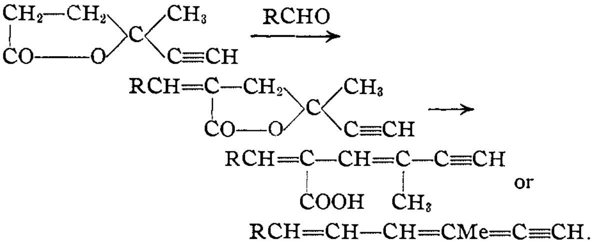
The objective of the present study was to develop new methods of preparation of unsaturated esters which might be adapted to the introduction of isoprene units in organic molecules. Two approaches were considered. First was condensation of γ-halo-β-methylcrotonic ester with aldehydes or ketones, followed by dehydration if necessary



$$CH_2X\text{—}CMe\text{=}CH\text{—}COOEt \xrightarrow{R_2CO} \underset{\displaystyle OH}{R_2C}\text{—}CH_2\text{—}CMe\text{=}CH\text{—}COOEt \xrightarrow{-H_2O} R_2C\text{=}CH\text{—}CMe\text{=}CH\text{—}COOEt$$

Obviously, unsaturation could exist also in the carbonyl compound (R_2CO), for crotonaldehyde, citral or β-ionylideneacetaldehyde would be representative. If the last of these condensed as shown, the compound formed[1] would be closely related to vitamin A.

The second approach was the condensation of aldehydes with γ-ethynyl-γ-valerolactone, made from levulinic acid



As before, unsaturation may exist also in the R group.

Regarding the first of these processes, it is known[2] that the halogen of γ-halocrotonic ester is sufficiently activated through the vinylogous system to undergo this type of reaction. As a matter of fact, the Reformatzsky reaction with ethyl γ-bromo-β-methylcrotonate and β-ionylideneacetaldehyde has been announced recently.[3] In the present work the halo esters selected were

---

[1] This compound has been made previously by another method: Heilbron, Jones, Lowe and Wright, *J. Chem. Soc.*, 561 (1936).

[2] Fuson, Arnold and Cooke, This Journal, **60**, 2272 (1938).

[3] Huisman, *Rec. trav. chim.*, **69**, 851 (1950).