TABLE I

WILLGERODT REACTION WITH FURAN COMPOUNDS

Furan compound	Yield,[d] % Temp. A[a]	Yield,[d] % 100° B	Yield,[d] % 110° B	Amide m.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Acid m.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2,5-Dimethyl-3-furyl methyl ketone[b,c]	23	18	27	82–83	9.15	9.17	94–95	62.34	62.45	6.49	6.39
2-Methyl-5-furyl methyl ketone	10	10	10	112–114	11.2	11.07	57–58	60.00	60.34	5.71	5.44
Furfural	15	26	20	141–142	12.61	12.77	131–133				

[a] See experimental for details of Methods A and B. [b] Hurd and Wilkinson, THIS JOURNAL, **70**, 739 (1948). [c] At 130° a 29% yield was obtained by Method B. [d] At 150° neither Method A nor Method B gave any product with these three substances.

soon solidified on cooling. Recrystallization of this material from petroleum ether (60–80°) gave 2.5 g. (23%) of 2,5-dimethyl-3-furylacetamide, m.p. 82–83°.

Method B substitutes 50 g. of yellow ammonium polysulfide, 7 g. of sulfur and 60 ml. of dioxane for the above reagents.

2-Methyl-5-furylacetamide.—This compound was obtained from 2-methyl-5-furyl methyl ketone in the same manner by Methods A and B. The product was isolated from the reaction mixture by the procedure described for 2,5-dimethyl-3-furylacetamide.

2-Furoamide.—This compound was obtained from furfural in the same manner by Methods A and B. The crude amide was recrystallized from benzene or water and a mixed melting point with an authentic sample[3] of furoamide showed no depression.

Hydrolysis of the Amides.—These amides were hydrolyzed to the corresponding acids in the usual manner by refluxing with either 12% aqueous potassium hydroxide or 10% aqueous barium hydroxide. The solutions were acidified and extracted with ether. Removal of the ether gave the crude acids which were recrystallized from petroleum ether (60–80°).

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(3) R. Paul, *Bull. soc. chim.*, [5] **4**, 1115 (1937).

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Mechanism of the Hofmann Elimination[1]

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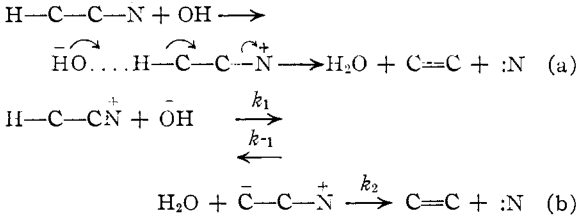
There are two variations in the current hypothesis of the mechanism of the second order elimination reaction of quaternary ammonium hydroxides. These variations, discussed for example by Dhar, *et al.*,[2] relate to the one- or two-step nature of the reaction; that is, to whether a single operationally significant transition state (a) or an intermediate bounded by two transition states (b) is involved. In the related second order elimination of bromides, Skell and Hauser[3] have shown that 2-phenylethyl bromide, recovered from an incomplete reaction in deuteroethanol, contains no deuterium. It is concluded that path (b) is invalid, this conclusion being justified, at least in terms of the operation of deuterium exchange only when k_{-1} be roughly equal to or greater than k_2, a requirement for which no experimental support was presented. In the face of the actual isolation by Wittig and Wetterling[4] of trimethylammoniummethylide ($(CH_3)_3\overset{+}{N}-\overset{-}{C}H_2$), extension of the Skell–Hauser conclusion to the Hofmann elimination is *a priori* questionable.



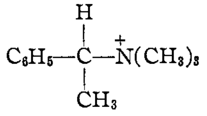
$$H-C-C-\overset{+}{N} + \overset{-}{O}H \longrightarrow$$

$$\overset{-}{H}O\ldots H-C-C-\overset{+}{N} \longrightarrow H_2O + C=C + :N \quad (a)$$

$$H-C-C\overset{+}{N} + \overset{-}{O}H \quad \underset{\xleftarrow{k_{-1}}}{\xrightarrow{k_1}}$$

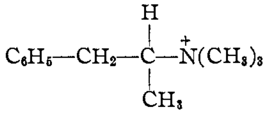
$$H_2O + \overset{-}{C}-C-\overset{+}{N} \xrightarrow{k_2} C=C + :N \quad (b)$$

The behavior of optically active trimethyl-α-phenylethyl-(I) and trimethyl-β-phenylisopropyl-(II) ammonium ions is pertinent to the one- or two-step nature of the Hofmann elimination. When (+)I and (−)II iodides are heated at 81° for 6720 min. in 0.15 N sodium hydroxide, I is recovered quantitatively and unracemized,[5] whereas II has, in part, undergone elimination to 1-phenylpropene, the remainder being recovered unracemized also.



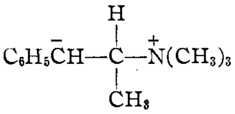
$$C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-\overset{+}{N}(CH_3)_3$$

I



$$C_6H_5-CH_2-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-\overset{+}{N}(CH_3)_3$$

II



$$C_6H_5\overset{-}{C}H-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-\overset{+}{N}(CH_3)_3$$

II″

On the reasonable conditions, first, that the tertiary hydrogen in I, activated by phenyl and adjacent ammonium ions, be more acidic than the tertiary hydrogen in II, activated only by an adjacent ammonium ion, and that the latter, in turn, be more acidic than the methylene hydrogen in II, activated by phenyl and an ammonium ion one carbon removed, and second, that the carbanion or xylides derived from I and II by removal of tertiary hydrogen (I′ and II′, respectively) racemize more rapidly than they react with protons, it is concluded that neither I′ nor II′ are formed, and consequentially, that II″ is not formed either. In terms, therefore, of the conditions for the operation of racemization, the Hofmann elimination of II proceeds by the one-step path (a).

Experimental

Attempted Racemization of Trimethyl-α-phenylethylammonium Iodide (I).—(+)I, prepared according to the procedure of Norcross and Openshaw[6] in 50% of the theoretical yield, was recrystallized from ethanol–ether as colorless prisms, m.p. 156–157.5° (reported[5] m. p. 157–157.5°). A solution of 0.291 g. (10^{-3} mole) of I in 5 cc. of 0.15 N sodium hydroxide with $[\alpha]_D + 11.8$ was heated in a sealed am-

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(1) From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

(3) P. S. Skell and C. R. Hauser, THIS JOURNAL, **67**, 1661 (1945).

(4) G. Wittig and M. H. Wetterling, *Ann.*, **557**, 193 (1947).

(5) It has already been observed that I is not racemized by sodium ethoxide: E. Biilmann, K. A. Jensen and H. B. Jensen, *Bull. soc. chim.*, [5] **3**, 2925 (1936).

(6) G. Norcross and H. T. Openshaw, *J. Chem. Soc.*, 1174 (1949).

poule at 7° for 6720 min. without change in the specific rotation or production of trimethylamine.

Attempted Racemization of Trimethyl-β-phenylisopropylammonium Iodide (II).—(−)II, prepared by methylation of β-phenylisopropylamine with methyl iodide and aqueous sodium carbonate, was recrystallized from alcohol as colorless needles, m.p. 202–203° (reported[7] m.p. 204–205°). A solution of 0.305 g. (10^{-3} mole) of II in 7 cc. of 0.15 *N* sodium hydroxide with $[\alpha]_D$ −3.9 was heated at 81° for 6720 min. The reaction mixture, smelling strongly ammoniacal, contained an oil which was extracted with ether. The residue from the dried, concentrated ether solution was dissolved in 0.5 cc. of carbon tetrachloride and treated with bromine until permanently colored. Evaporation of the solvent left a solid which was crystallized from ethanol to give 1-phenyl-1,2-dibromopropane, m.p. 65–66.5° (reported[8] m.p. 65–66°), showing no depression of m.p. on admixture with authentic material.

Concentration of the aqueous portion of the reaction mixture gave solid material which was extracted with chloroform. Evaporation of the chloroform left crystalline starting material, $[\alpha]_D$ −3.9 (*c* 4.4, 0.15 *N* sodium hydroxide).

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(7) K. Freudenberg and F. Nikolai, *Ann.*, **510**, 223 (1934).

(8) W. H. Perkin, *J. Chem. Soc.*, **32**, 660 (1877).

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Thermal Decomposition of Glyceryl Carbonates

BY HERMAN A. BRUSON AND THOMAS W. RIENER

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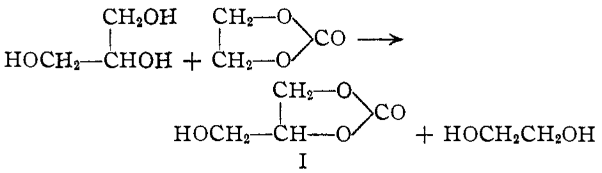
While attempting to prepare glyceryl monocarbonate (I) by heating equimolar proportions of glycerol and ethylene carbonate to effect an ester exchange it was noticed that after the ethylene



glycol had been removed by vacuum distillation there remained in the still-pot a thick, balsam-like, resinous material which, upon further distillation *in vacuo*, decomposed almost entirely to yield glycidol  $CH_2\text{-}CH\text{-}CH_2OH$ (O bridging the first two carbons).

This unexpected reaction affords a convenient method for preparing glycidol in 60–85% yields directly from glycerol.

When an open chain dialkyl carbonate such as for example diethyl carbonate was used in place of the cyclic ethylene carbonate as above (1:1 mole ratio), the alcoholysis did not readily take place without the use of a catalyst because of the immiscibility of diethyl carbonate with glycerol at the boiling point of the mixture. The use of an alkaline catalyst, however, such as sodium or sodium methoxide together with rapid stirring caused a more rapid alcoholysis of the mixture, with formation of a glyceryl carbonate. This product, however, upon further distillation *in vacuo*, gave considerable non-distillable resin and only a very mediocre yield (7%) of glycidol.

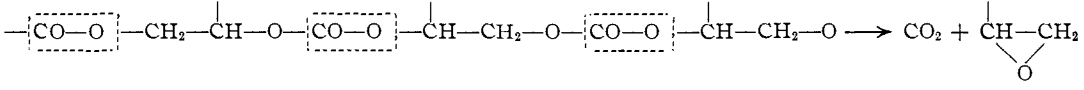
Since it was possible that the alkaline catalyst might exert a deleterious influence upon the yield of glycidol in this decomposition, an attempt was made to prepare glyceryl carbonate by heating glycerol with diphenyl carbonate in the absence of a catalyst, and distilling off under reduced pressure the phenol formed. This reaction is reported[1] to give a crystalline glyceryl tricarbonate $C_9H_{10}O_9$ melting at 148°, when the mole ratio of glycerol to the diphenyl carbonate used is 2:3; and to give liquid or resinous glyceryl carbonates containing free hydroxyl groups when an excess of glycerol is employed. We have confirmed this work and isolated the crystalline glyceryl tricarbonate in pure form. This compound when subjected to vacuum distillation yielded no glycidol but decomposed instead to form a resinous material together with traces of acrolein, and gases which did not condense in a Dry Ice trap at −80°.

Upon heating glycerol with diphenyl carbonate (1:1 mole ratio) and distilling off under reduced pressure the phenol formed, a still-pot residue was obtained which upon further distillation *in vacuo* gave a 60% yield of glycidol.

It is apparent that no glycidol is formed (or can be expected) if all three hydroxyl groups of the glycerol are esterified with carbonate radicals. Obviously, one primary hydroxyl group must be free if glycidol is to be obtained. Ethylene carbonate is superior to diphenyl carbonate because a smaller weight of it is required per mole of glycerol and the reaction is more rapid, giving less opportunity for side reactions and in general a higher yield.

Application of the reaction with ethylene carbonate to glycerol derivatives such as glycerol-mono-α-chlorohydrin and glyceryl-α-ethyl ether did not yield the respective epichlorhydrin or glycidyl ethyl ether. Likewise, an attempt to convert 1,2,6-hexanetriol into the epoxide  $CH_2\text{-}CH\text{-}(CH_2)_3\text{-}CH_2OH$ by heating with ethylene carbonate was unsuccessful.

Since one would expect monomeric glyceryl monocarbonate (I) to be a vacuum-distillable liquid that on prolonged heating might yield a polyester resin, and since the viscous character of the still-pot residue which is obtained in the transesterification of glycerol with ethylene carbonate (1:1 mole ratio) is that of a polymeric resinous material; it is believed that the reaction involves the formation of a poly-(glyceryl-1,2-dicarbonate) which subsequently loses carbon dioxide on further heating with formation of glycidol as



Experimental

Raw Materials.—The glycerol used was anhydrous, vacuum-distilled C.P. grade. The ethylene carbonate was

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(1) German Patent 252,758 (1912), Chem. Fabrik Dr. Rudolf Scheuble and Dr. A. Hochstetter; *Chem. Zentr.*, **83**, II, 1756 (1912).