

both demethylation (*cf.* compound I) and isomerization (*cf.* compound II) had taken place. Both these compounds are carbinolamines in equilibrium with their open chain aldehydic tautomers and are undoubtedly difficult to isolate. It is likely that the resinous material in the reaction mixture contained some of these compounds. Compound III should have arisen if the reaction had followed the course which led to oxostychnine (*vide supra*) and, finally, compound V if this mode of reaction were coupled with demethylation. The latter reaction actually took place. It constitutes a greater structural change than was observed previously. This may well be due to the fact that substituted anilines are more sensitive to oxidizing agents than is strychnine or codeine. It is nevertheless remarkable that the action of aqueous dichromate on an amine oxide has once again led to a lactam as in the case of oxostychnine.<sup>5</sup>

#### Experimental Part<sup>16,17</sup>

**Kairolinone from 1,2,3,4-Tetrahydroquinoline.**—Following the procedure of Gilman and Banner<sup>8</sup> kairolinone was prepared from freshly distilled 1,2,3,4-tetrahydroquinoline (Eastman Kodak Co., White Label) and freshly distilled dimethyl sulfate. The product immediately upon distillation was a colorless oil, b.p. 128–129° (25 mm.) (52% yield).

The picrate melted at 121° (recorded 123–124°<sup>18</sup> and 136–137°<sup>19</sup>).

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>7</sub>: C, 51.06; H, 4.29; N, 14.9. Found: C, 51.09; H, 4.20; N, 14.7.

**Kairolinone-N-oxide.**—The successful procedure which was finally adopted was fashioned after that of Meisenheimer and Dodonow.<sup>13</sup> In occasional runs the oxide crystallized spontaneously in colorless chunky needles after the solvent had been removed *in vacuo*. In general, no attempt was made to obtain the substance crystalline.

A picrate was prepared: fragile yellow needles from EtOH, m.p. 122–123°, turning green on melting (recorded m.p. 122°<sup>18</sup>).

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>8</sub>: C, 48.98; H, 4.11; N, 14.3. Found: C, 48.72; H, 4.00; N, 14.3.

**Dichromate Reaction with Kairolinone-N-oxide.**—The crude N-oxide was subjected to this reaction in 7-g. batches. The oxide was dissolved in 60 ml. of water and warmed to 65°. One mole per cent. of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> dissolved in 20 ml. of water also at 65° was added slowly with stirring. The dichromate color was discharged immediately and although there was considerable frothing, no odor of formaldehyde could be detected. Stirring was continued for 10 minutes. The brown solution was separated from considerable amounts of tarry material and extracted thoroughly with ether at *pH*'s of 3, 7 and 12. All three extracts upon drying over Na<sub>2</sub>SO<sub>4</sub> and concentration on the steam-bath furnished small amounts of light brown needles, totaling 1 g., m.p. 145–150°. After 6 recrystallizations from MeOH–H<sub>2</sub>O the colorless needles melted at 163–164°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>NO: C, 73.45; H, 6.16; N, 9.5. Found: C, 73.15, 73.61; H, 6.21, 6.00; N, 8.9, 9.4.

**Infrared spectrum.**<sup>20</sup> six-membered lactam band at 5.98  $\mu$ . The tarry residue was dissolved in 1 *M* HCl and on cooling was made basic with 6 *M* NH<sub>4</sub>OH. Several ether extractions furnished only films of brown oil which could not be identified.

**Anilide of  $\beta$ -Chloropropionic Acid.**—Prepared from freshly distilled aniline (J. T. Baker Analyzed) and  $\beta$ -chloro-

propionyl chloride (Eastman Kodak Co., White Label); m.p. of product recrystallized from MeOH 117–119° (reported<sup>16</sup> 119°).

**Hydrocarbostyryl.**—The anilide was cyclized with AlCl<sub>3</sub> without solvent as described by Mayer, *et al.*,<sup>15</sup> and obtained as gray needles, m.p. 140–155°. After 5 recrystallizations from dilute MeOH, m.p. 167.0–167.5° (reported<sup>15</sup> 163°). Mixed m.p. with the product from the dichromate reaction was 164–167°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>NO: C, 73.45; H, 6.16; N, 9.5. Found: C, 73.15; H, 6.38; N, 9.7.

**Infrared spectrum,** identical with degradation product; six-membered lactam band at 5.98  $\mu$ .

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### Cleavage of 3-Bromo-2,2-dimethyl-1-propanol by Base<sup>1</sup>

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In the course of a study of substituted trimethylene oxides, the compound 2,2-dimethyltrimethylene oxide (I) was desired. This compound has been reported by Bennett and Philip<sup>3</sup> and by Fonteyne and Ticket<sup>4</sup> who prepared it by heating 3-bromo-2,2-dimethyl-1-propanol (II) with solid and aqueous potassium hydroxide. Although no information was given regarding the yield, several factors would appear to be favorable: (1) impossibility of 1,2-elimination, (2) steric hindrance of intermolecular substitution, and (3) gem-dialkyl structure, which generally favors ring closure. Related intramolecular Williamson reactions generally give good yields—for example, 1,1-diethyltrimethylene oxide (90% from 1-chloro-3-ethyl-3-pentanol),<sup>5</sup> 1,1-dimethyltrimethylene oxide (43% from 4-chloro-2-methyl-2-butanol)<sup>3</sup> and 2,2-bis-(bromomethyl)-trimethylene oxide (79% from pentaerythryl tribromide).<sup>6</sup>

The reaction of II with powdered and aqueous potassium hydroxide gave only 10–25% yields of I in this Laboratory, however, and it was of interest that a substantial amount of isobutylene was found to be a gaseous product. This compound, which apparently was overlooked previously, was identified by its boiling point, its 2,4-dinitrobenzenesulfonyl chloride adduct, and its bromination products. The yield of isobutylene was about 20% in the Bennett and Philip procedure, but became 60% when 15% aqueous potassium hydroxide is the base and 75% when the bromoalcohol is added to a melted NaOH–KOH mixture at 200°.

The other primary cleavage product appears to be formaldehyde, which was isolated in small yield as its dimedone derivative from the reaction mixture obtained with 15% potassium hydroxide. The Cannizzaro products of formaldehyde, methanol and formic acid, were identified in all the reaction mixtures.

(1) Abstracted from the B.S. Thesis of Melvin J. Gortatowski, University of Illinois, February, 1950.

(2) Department of Chemistry, Kansas State College, Manhattan, Kansas.

(3) G. M. Bennett and W. G. Philip, *J. Chem. Soc.*, 1938 (1928).

(4) R. Fonteyne and M. Ticket, *Natuurw. Tijdschr.*, **25**, 49 (1943).

(5) C. Moureu and C. Barrett, *Bull. soc. chim.*, [4] **29**, 994 (1921).

(6) F. Govaert and M. Beyaert, *Natuurw. Tijdschr.*, **22**, 73 (1940).

(16) Microanalyses by Drs. G. Weiler and F. B. Strauss, Oxford, England.

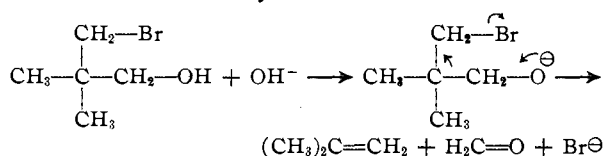
(17) Melting points were taken on a Koffler micro hot stage. Melting points and boiling points are uncorrected.

(18) F. H. Beilstein, "Handbuch der Organischen Chemie," Erstes Ergänzungswerk, Vol. 20, Vierte Auflage, Julius Springer, Berlin, 1935, pp. 94–95.

(19) J. F. Thorpe and A. S. Wood, *J. Chem. Soc.*, 1611 (1913).

(20) Taken in chloroform solution with a Baird double-beam recording instrument.

Pyrolysis of I would be expected to give isobutylene and formaldehyde,<sup>7</sup> but this possible source seems untenable in view of the observation that even at 250° I is stable in the presence of potassium hydroxide. Furthermore, the cleavage in 15% potassium hydroxide occurs at a temperature of 100° or less, which is much too low for a pyrolysis. It would appear reasonable, however, that isobutylene and formaldehyde result from a rearrangement of the same alkoxide ion which is the intermediate for the cyclization reaction



Thus, this cleavage reaction is an extended chain analog of the usual elimination reaction which generally accompanies substitution, but which is impossible here because of the lack of  $\beta$ -hydrogen atoms. A few other examples of this type of elimination have been reported, as in the cases of  $\beta$ -dimethylpivalophenone methiodide<sup>8</sup> and  $\alpha$ -tosyloxy- $\beta$ , $\beta$ -dimethyl- $\gamma$ -butyrolactone,<sup>9</sup> and the reverse aldol reaction is, of course, closely related. The alkali-instability of the bromoalcohol considered here was observed in 1913 by Franke,<sup>10</sup> who reported its decomposition by boiling sodium carbonate solution to an unknown steam volatile oil which reduced Tollens reagent. The nature of the decomposition was not recognized but the latter observation indicated that some cleavage had occurred, since I does not reduce Tollens reagent. On repeating the experiment it was observed that the cleavage reaction proceeds so slowly under these conditions that the steam distillate is principally unreacted bromoalcohol, contaminated with small amounts of I and formaldehyde.

#### Experimental

**Reaction of 3-Bromo-2,2-dimethyl-1-propanol (II) with Alkali.** (A).—An intimate mixture of 110 g. of powdered sodium hydroxide and 21.5 g. of II (prepared by the method of Fonteyne and Ticket<sup>4</sup> in 55% yield) was immersed in an oil-bath maintained at 200°. The distillate was collected in two traps kept at 0 and -70°, respectively, and after drying over potassium carbonate was fractionally distilled.

Isobutylene, b.p. -6.5 to -6° (lit. -6°<sup>11</sup>), was obtained in the amount of 1.5 g. (23% yield); m.p. of 2,4-dinitrobenzenesulfonyl chloride adduct,<sup>12</sup> 85-86° (lit. 86-87°<sup>12</sup>). Addition of bromine dissolved in methylene dichloride to a solution of the olefin in methylene dichloride, cooled by an ice-salt bath, gave a 41% yield of 1,2-dibromo-2-methylpropane, b.p. 143-145° (750 mm.),  $n_D^{21}$  1.5072 and a 12% yield of 1,2,3-tribromo-2-methylpropane, b.p. 111-114° (22 mm.),  $n_D^{21}$  1.5644, in agreement with the results of Hurd and Spence.<sup>14</sup>

2,2-Dimethyltrimethylene oxide, b.p. 77-79° (752 mm.) was obtained in the amount of 1.3 g. (13% yield) and from a low boiling (66-70°) fraction was obtained 0.5 g. of methyl

3,5-dinitrobenzoate, m.p. 106-107° (lit. 108°<sup>15</sup>). Evidence for the formation of potassium formate was obtained by dissolving the reaction residue in water, acidifying with phosphoric acid and distilling. The distillate was acidic, decolorized potassium permanganate and reduced mercuric oxide to a dark gray precipitate of elemental mercury.

(B).—Dropwise addition of 40 g. of II to a stirred molten mixture of 60 g. of potassium hydroxide and 40 g. of sodium hydroxide at 200°, which is a good reagent for preparing trimethylene oxide from 3-chloropropyl acetate, gave 10 g. of isobutylene (77% yield) and 2.5 g. of 2,2-dimethyltrimethylene oxide (12% yield).

(C).<sup>12</sup>—To 100 g. of 15% potassium hydroxide at 90°, 25 g. of I was added dropwise with stirring over a period of 50 minutes; the bath temperature was then slowly raised to 150° over a period of two hours. The products which distilled off were collected as described in (A), but a water layer in the 0° trap was separated before the remainder was dried over potassium carbonate. Acidification of this water layer with acetic acid and addition of dimedone gave a few milligrams of formaldehyde dimedone, fine needles melting at 187° (lit. 189°<sup>16</sup>). Distillation of the non-aqueous products gave 5 g. (60% yield) of isobutylene and 1.3 g. (10% yield) of 2,2-dimethyltrimethylene oxide.

(15) W. M. D. Bryant, *ibid.*, **54**, 3760 (1932).

(16) D. Vorlander, *Z. anal. Chem.*, **77**, 247 (1929).

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### Condensations of $\alpha$ -Carbethoxy- $\alpha$ -methyl- $\gamma$ -butyrolactone

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In continuation of the study of the reaction of  $\alpha$ -alkyl- $\alpha$ -carbethoxy- $\gamma$ -butyrolactones<sup>1</sup> with urea and related compounds the methyl homolog has been prepared and condensed with urea, thiourea, guanidine and benzamidine.

The reactions proceeded in the expected manner in all cases. However, the following comparisons should be noted. The condensation of this lactone ester with thiourea required milder temperature conditions to obtain good yields. It was necessary to modify the procedures also on account of the marked differences in the solubilities of the barbituric acid derivatives. The intermediate sodium salt obtained from the condensation with urea is much more insoluble in alcohol and the free acid is so much more soluble in water as to require very specific conditions for its isolation.

This lactone ester was condensed with benzamidine to test the validity of the proposal<sup>2</sup> that the active hydrogen of the unalkylated lactone ester participates in the reaction leading to the tetrahydropyrimidine derivative.

Another possible explanation is that the non-formation of the tetrahydropyrimidine derivative from the alkylated lactone esters is due to steric hindrance. Actually, the substitution of the smaller methyl radical for the active hydrogen led only to the lactone amidine. Within the limits of the possibilities of decreasing the size of the alkyl group it would therefore appear that the hindrance to the cleavage of the lactone ring is not steric in nature.

(1) Last previous report of this series: G. S. Skinner and W. H. Waitz, Jr., *THIS JOURNAL*, **74**, 498 (1952).

(2) G. S. Skinner, Ethel Anderson and R. F. Bogart, *ibid.*, **71**, 1482 (1949).

(7) A. Barbot, *Ann. chim.*, **11**, 519 (1939).

(8) H. R. Snyder and J. H. Brewster, *THIS JOURNAL*, **71**, 1061 (1949).

(9) H. Bretschneider and H. Hass, *Monatsh.*, **81**, 945 (1950).

(10) A. Franke, *ibid.*, **84**, 1893 (1913).

(11) C. C. Coffin and O. Maass, *THIS JOURNAL*, **50**, 1483 (1928).

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