

g. (30%), m.p. 139.5–140°. A sample was recrystallized from ethyl alcohol for analysis. The compound was unsaturated (it decolorized cold, neutral permanganate solution and a solution of bromine in carbon tetrachloride) and gave a positive carbonyl test with 2,4-dinitrophenylhydrazine. The molecular weight was found by the Rast camphor method to be about 450.

Anal. Calcd. for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 86.92; H, 5.96.

A hot solution of 10 g. of potassium permanganate in 50 cc. of water was slowly added to 5 g. of the photodimer of dibenzalacetone. After this mixture had been refluxed for three hours it was treated with sufficient sodium bisulfite to dissolve the manganese dioxide, acidified and extracted with 200 cc. of ether to remove the benzoic acid produced during the oxidation. The mixture was then made basic with sodium hydroxide, filtered and reacidified. The acid which precipitated melted at 174–175°. δ -Truxinic acid is reported to melt at 175°. The melting points of the other truxinic acids are: β , 209–210°; ξ , 239°; ν , 209–210°; μ , 196°; ω , 245°; and the melting points of the isomeric truxillic acids are: α , 274°; γ , 228–230°; ϵ , 192°; η , 266°; and ϵ , 285–287°.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 73.00; H, 5.42; neut. equiv., 151.0. Found: C, 72.92; H, 5.23; neut. equiv., 148.5.

(7) R. Stoermer and F. Bacher, *Ber.*, **55**, 1882 (1922).

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The Reaction of Amine Oxides with Aqueous Potassium Dichromate

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When Freund and Speyer¹ treated the N-oxide of codeine-sulfonic acid with potassium chromate in aqueous solution, they obtained formaldehyde and a substance which upon desulfonation was believed to be isomeric with morphine. Diels and Fischer² repeated this work and recognized Freund and Speyer's product to be norcodeine. They further showed that the reaction could be applied to codeine-N-oxide itself.

Bailey and Robinson³ recently realized that this little-known method might be applied to prepare pseudo-strychnine from strychnine-N-oxide, a tertiary amine which cannot be demethylated. This proved to be the case.

Neither Brehm⁴ nor Scheuer⁵ were able to isolate pseudostrychnine or any other product from this reaction. Brehm,⁶ however, succeeded in preparing pseudo-strychnine by treating strychnine-N-oxide with potassium dichromate instead of chromate. He also isolated a neutral by-product, oxostrychnine, which was shown by Scheuer⁵ to be 18-oxostrychnine.⁷

This research was undertaken to determine whether the production of a lactam from an amine oxide might be of general applicability. For an

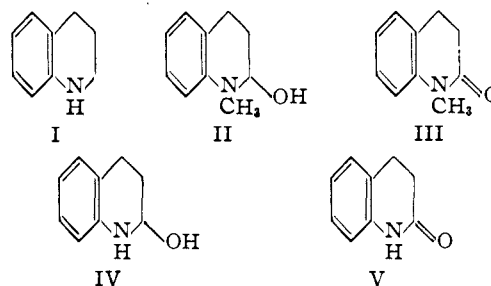
initial approach kairoline-N-oxide (N-methyl-1,2,3,4-tetrahydroquinoline-N-oxide) was chosen as the starting material, for it is readily accessible and all of the expected reaction products are easily characterized.

After considerable experimentation with other routes of approach it was found that kairoline could best be prepared by the methylation of commercial tetrahydroquinoline with dimethyl sulfate according to the general procedure of Gilman and Banner^{8,9} in about 50% yield. The colorless oil formed a yellow picrate, m.p. 121°.

Preparation of kairoline-N-oxide by the elegant method used by Brehm⁶ in the strychnine series proved unsatisfactory. Considerable amounts of starting material remained unreacted. This may be explained by the difference in basic strength between strychnine and alkyl-substituted anilines.¹⁰ For the relatively weak base kairoline longer reaction times proved necessary as, e.g., in the earlier work of Meisenheimer and Dodonow.¹³ No attempt was made to isolate the hygroscopic solid which was identified by its yellow picrate melting at 122–123° into a green liquid.

The crude kairoline-N-oxide was immediately subjected to the reaction with potassium dichromate. In a series of experiments the best conditions were found to be brief reaction times and catalytic amounts (one mole per cent.) of dichromate at 65°. Ether extraction of the reaction mixture at acidic, basic and neutral pH values yielded, beside intractable tars, only one product, a colorless crystalline solid, m.p. 163–164°. This compound was shown to be identical with hydrocarbostyryl (2-oxo-1,2,3,4-tetrahydroquinoline), m.p. 167–167.5°, which was prepared from aniline.^{14,15} The two compounds when mixed melted at 164–167° and had identical infrared spectra.

Reasoning from the results obtained by earlier workers, one may conclude that the following structures represent possible reaction products.



If the reaction had followed the course of the original Freund and Speyer¹ reaction with chromate, compound I would have been the product. Compound II should have resulted by analogy with the work of Bailey and Robinson³ and compound IV if

(8) H. Gilman and I. Banner, *ibid.*, **62**, 345 (1940).

(9) After completion of this work another report (S. Hünig, *Ber.*, **85**, 1056 (1952)) on successful N-methylation of aromatic amines with dimethyl sulfate was received.

(10) Strychnine, $pK_b = 6.63^{11}$; dimethylaniline, $pK_b = 9.62^{12}$.

(11) V. Prelog and O. Häfiger, *Helv. Chim. Acta*, **32**, 1851 (1949).

(12) L. F. Fieser and M. Fieser, "Organic Chemistry," Second Edition, D. C. Heath and Co., Inc., Boston, Mass., 1950, p. 635.

(13) J. Meisenheimer and J. Dodonow, *Ann.*, **365**, 134 (1911).

(14) P. A. S. Smith and T. Y. Yu, *This Journal*, **74**, 1096 (1952).

(15) F. Mayer, L. van Zuetphen and H. Phillips, *Ber.*, **60**, 858 (1927).

(1) M. Freund and E. Speyer, *Ber.*, **44**, 2339 (1911).
(2) O. Diels and E. Fischer, *ibid.*, **47**, 2043 (1914); **49**, 1721 (1916).
(3) A. S. Bailey and R. Robinson, *J. Chem. Soc.*, 703 (1948).
(4) W. J. Brehm, private communication.
(5) P. J. Scheuer, Ph.D. thesis, Harvard, 1950.
(6) W. J. Brehm, Ph.D. thesis, Harvard, 1948.
(7) (a) The numbering system suggested by Woodward and Brehm^{7b} is used; (b) R. B. Woodward and W. J. Brehm, *This Journal*, **70**, 2107 (1948).

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 oxostrychnine (*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 oxostrychnine.⁵

Experimental Part^{16,17}

Kairolinone from 1,2,3,4-Tetrahydroquinoline.—Following the procedure of Gilman and Banner⁹ 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°¹⁸ and 136–137°¹⁹).

Anal. Calcd. for C₁₆H₁₆N₄O₇: 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.¹³ 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°¹³).

Anal. Calcd. for C₁₆H₁₆N₄O₈: 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 K₂Cr₂O₇ 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 Na₂SO₄ 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–H₂O the colorless needles melted at 163–164°.

Anal. Calcd. for C₉H₉NO: 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.²⁰ six-membered lactam band at 5.98 μ . The tarry residue was dissolved in 1 M HCl and on cooling was made basic with 6 M NH₄OH. Several ether extractions furnished only films of brown oil which could not be identified.

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

propionyl chloride (Eastman Kodak Co., White Label); m.p. of product recrystallized from MeOH 117–119° (reported¹⁶ 119°).

Hydrocarbostyryl.—The anilide was cyclized with AlCl₃ without solvent as described by Mayer, *et al.*,¹⁶ and obtained as gray needles, m.p. 140–155°. After 5 recrystallizations from dilute MeOH, m.p. 167.0–167.5° (reported¹⁶ 163°). Mixed m.p. with the product from the dichromate reaction was 164–167°.

Anal. Calcd. for C₉H₉NO: 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 μ .

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Cleavage of 3-Bromo-2,2-dimethyl-1-propanol by Base¹

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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 Philip³ and by Fonteyne and Ticket⁴ 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),⁵ 1,1-dimethyltrimethylene oxide (43% from 4-chloro-2-methyl-2-butanol)³ and 2,2-bis-(bromomethyl)-trimethylene oxide (79% from pentaerythryl tribromide).⁶

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 Kofler 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.