53 and 0% are obtained in the Leuckart reaction with laurophenone.[4]

Experimental

Formaldehyde and paraldehyde were used in the form of their revertible polymers as described below. Other aldehydes were commercial products, used without purification. The yields, given in Table I, are crude yields. The preparation of 4-*p*-chlorobenzyl-2-piperazinone described below is typical.

3,3-Dimethyl-2-piperazinone[3] was prepared by the method of Elkind, Strong and Craig.[2] Formic acid was 98% commercial grade.

3,3,4-Trimethyl-2-piperazinone.—To a mixture of 3,3-dimethyl-2-piperazinone (128 g., 1 mole) and paraformaldehyde (35 g., 1.1 moles), heated with stirring on the steam-bath under reflux, formic acid (57.5 g., 1.25 moles) was added dropwise. The paraformaldehyde went into solution and CO_2 was evolved copiously. After further heating for 2.5 hours on the steam-bath, reaction was complete. The solid product distilled from a Claisen flask at 160–170° at 26 mm. to yield 131 g. of colorless crystals, melting at 100–110°. After recrystallization from isopropyl alcohol, a yield of 102 g. (72%) melting at 128–130° was obtained. Further recrystallization raised the melting point to 131–132°.

3,3-Dimethyl-4-ethyl-2-piperazinone.—A mixture of paraldehyde (9.7 g., 0.22 mole), 3,3-dimethyl-2-piperazinone (25.6 g., 0.2 mole), formic acid (11.5 g., 0.25 mole), and 0.7 ml. of 37% HCl was heated at 125–130° for 29 hours. The solid obtained on cooling was recrystallized twice from isopropyl alcohol and then from benzene to give 6.9 g. (22%) of alkylated product melting at 164–165°. A small amount of product (5%) was recovered from the mother liquors.

3,3-Dimethyl-4-*p*-chlorobenzyl-2-piperazinone.—A mixture of *p*-chlorobenzaldehyde (62 g., 0.44 mole), 3,3-dimethyl-2-piperazinone (51.2 g., 0.4 mole) and formic acid (23 g., 0.5 mole) was heated at reflux for 8 hours. The product solidified on cooling and was recrystallized from isopropyl alcohol to yield 53 g. (56%) of colorless crystals melting at 201–203°.

Failure of Ketones to React in the Leuckart Reaction.—A mixture of 3,3-dimethyl-2-piperazinone (51.2 g., 0.4 mole), cyclohexanone (43.1 g., 0.44 mole) and formic acid (23 g., 0.5 mole) was heated at reflux for 54 hr. The solid produced was recrystallized from ethanol and then from benzene. There was obtained 22.4 g. of colorless crystalline product, which melted at 170–172°. This proved on analysis to be 4-formyl-3,3-dimethyl-2-piperazinone in 36% yield. Calcd. for $C_7H_{12}N_2O_2$: N, 17.9. Found: N, 17.8.

The same product, compared by mixed melting point, was obtained from similar reactions of acetone (52% yield) and acetophenone (62.5% yield). This formyl derivative was heated for 10 hr. with acetophenone at 200°, and then for 9 hours additional in the presence of an equivalent quantity of formic acid at 200°. No CO_2 was evolved and the formyl derivative was recovered.

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[4] F. S. Crossley and M. L. Moore, *J. Org. Chem.*, **9**, 529 (1944).

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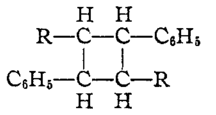
The Structure of a Photodimer of Dibenzalacetone

BY G. W. RECKTENWALD, J. N. PITTS, JR., AND R. L. LETSINGER

RECEIVED JANUARY 26, 1953

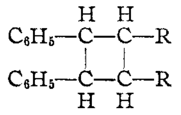
Two different dimers have been reported as irradiation products of dibenzalacetone. One of these (m.p. 245°) was obtained in 90% yield from a reaction of dibenzalacetone in glacial acetic acid which contained uranyl chloride. It was assigned structure I.[1] The other substance, formed by the action of sunlight on dibenzalacetone in ethanol, was obtained in a crude state only (m.p. 125–135°). It was shown to be a dimer but was not further characterized.[2]

By irradiating dibenzalacetone in an isopropyl alcohol–benzene solution with ultraviolet light, we obtained in 30% yield a dimeric product which melted at 139.5–140°. The dimer precipitated from this particular solvent system during the course of the reaction in a relatively pure state. It seems likely that the substance previously reported to melt at 125–135° was principally this substance. As the dimer was an unsaturated ketone which yielded δ-truxinic acid (III) on oxidation with neutral potassium permanganate, it must have structure II. The configuration probably also corresponds to that of δ-truxinic acid; however, since the possibility of izomerization among the different truxinic acid type compounds under the conditions of the oxidation has not been eliminated, such an assignment cannot be made unequivocally.



$$\begin{array}{c} \text{H}\quad\text{H} \\ \text{R—C—C—C}_6\text{H}_5 \\ |\quad\ | \\ \text{C}_6\text{H}_5\text{—C—C—R} \\ \text{H}\quad\text{H} \end{array}$$

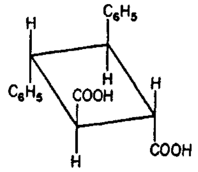
I



$$\begin{array}{c} \text{H}\quad\text{H} \\ \text{C}_6\text{H}_5\text{—C—C—R} \\ |\quad\ | \\ \text{C}_6\text{H}_5\text{—C—C—R} \\ \text{H}\quad\text{H} \end{array}$$

II

R is $C_6H_5CH{=}CHCO-$



III

In only a few cases have dimers been isolated from reactions in which α,β-unsaturated acids or carbonyl compounds are irradiated in solution in an organic solvent. Generally, under these conditions, the compounds either are only isomerized or else form resins.[3] In the other cases where dimerization in solution did occur and the structures of the products were investigated (methyl benzalpyruvate,[4] benzalacetophenone[5] and benzal-*p*-methylacetophenone[5]) the dimers were also found to be of the truxinic type. On the other hand, the photodimer obtained from an acetic acid solution of 2-cinnamylidene-2-phenylacetonitrile[6] was a truxillic type compound.

Experimental

A mixture of 20 g. of dibenzalacetone, 30 cc. of thiophene-free benzene and 90 cc. of isopropyl alcohol was irradiated for 90 hours with the light from a Hanovia type SH quartz–mercury arc. A Pyrex plate was used as a filter to absorb short wave length radiations. Throughout this period a nitrogen atmosphere was maintained above the reactants, which were mixed by a magnetic stirrer. The mixture was allowed to warm up from the heat of the lamp until all of the benzalacetone had dissolved (eight hours); thereafter the temperature was maintained at about 25° by cooling the solution with a cold finger condenser. A white precipitate began to form after approximately 60 hours of irradiation. At the completion of the reaction the precipitate was filtered and washed with cold ethyl ether; yield 6.1

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[1] P. Praetorius and F. Korn, *Ber.*, **43**, 2744 (1910).

[2] G. Ciamician and P. Silber, *ibid.*, **42**, 1386 (1909).

[3] C. Ellis and A. B. Wells, "The Chemical Action of Ultraviolet Rays," Reinhold Publ. Corp., New York, N. Y., 1941, pp. 482–493. A. Mustafa, *Chem. Revs.*, **51**, 1 (1952). Most of the photodimers which have been isolated were obtained from reactions in which the dry solid or aqueous suspensions of the solids were irradiated. Both truxinic and truxillic type compounds are formed under these conditions.

[4] M. Reimer, THIS JOURNAL, **46**, 783 (1924).

[5] H. Stobbe and K. Bremer, *J. prakt. Chem.*, **123**, 1 (1929).

[6] H. Stobbe and F. Kuhrman, *Ber.*, **58**, 85 (1925).

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°.[7] The melting points of the other truxinic acids are: β, 209–210°; ξ, 239°; nev, 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 epi, 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.

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

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The Reaction of Amine Oxides with Aqueous Potassium Dichromate

BY PAUL J. SCHEUER, WALTER I. KIMOTO AND KIICHI OHINATA

RECEIVED JANUARY 14, 1953

When Freund and Speyer[1] 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 Fischer[2] 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 Robinson[3] 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 Brehm[4] nor Scheuer[5] 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 Scheuer[5] to be 18-oxostrychnine.[7]

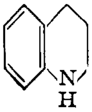
This research was undertaken to determine whether the production of a lactam from an amine oxide might be of general applicability. For an initial approach kairoline-N-oxide (N-methyl-1,2,3,4-tetrahydroquinoline-N-oxide) was chosen as the starting material, for it is readily accessible and all of the 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°.

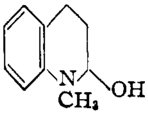
Preparation of kairoline-N-oxide by the elegant method used by Brehm[6] in the strychnine series proved unsatisfactory. Considerable amounts of starting material remained unreacted. This may be explained by the difference in basic strength between strychnine and alkyl-substituted anilines.[10] For the 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 *p*H values yielded, beside intractable tars, only one product, a colorless crystalline solid, m.p. 163–164°. This compound was shown to be identical with hydrocarbostyril (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.

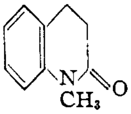
Reasoning from the results obtained by earlier workers, one may conclude that the following structures represent possible reaction products.



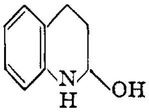
I



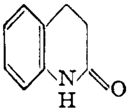
II



III



IV



V

If the reaction had followed the course of the original Freund and Speyer[1] reaction with *chromate*, compound I would have been the product. Compound II should have resulted by analogy with the work of Bailey and Robinson[3] and compound IV if

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[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).

[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. Häfliger, *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.*, **385**, 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).