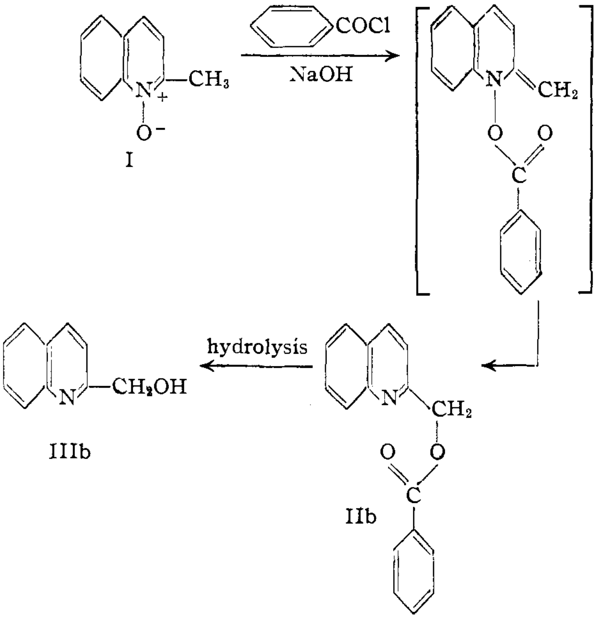
found to be identical with that formed directly from quinaldine oxide and benzoyl chloride. Reaction with rearrangement thus occurs when quinaldine oxide is treated with benzoyl chloride. The subsequent formation of IIIb from IIb is the result of simple hydrolysis.



I

IIIb

IIb

In isolating IIb, Henze acidified the benzoylation product with hydrochloric acid, purified the hydrochloride, and then liberated IIb with alkali. It was possible that the acidification transformed initially-formed IIa to IIb. An experiment avoiding acidification was therefore performed. The product isolated directly from the alkaline benzoylation mixture proved to be identical with that obtained *via* the hydrochloride.

A simplified method for the preparation and purification of quinaldine oxide hydrate is described.

Experimental[4]

Quinaldine Oxide Hydrate.—To 20 g. of freshly distilled quinaldine was added 22 g. of 30% aqueous hydrogen peroxide and 60 ml. of acetic acid. The solution was heated at 55° for 20 hours. It was then cooled in ice and slowly treated with a solution of 80 g. of potassium hydroxide in 100 ml. of water. Quinaldine oxide hydrate separated as a dark oil and soon solidified. It was filtered and the filtrate was extracted with 30 ml. of chloroform. The chloroform was evaporated from the extract and the residue was combined with the main product and added to 300 ml. of benzene. The mixture was distilled until water no longer came over with the benzene. The light yellow benzene solution was then decanted from dark brown insoluble materials, cooled, and stirred with a few ml. of water. The quinaldine oxide hydrate, which separated as almost colorless needles, was filtered and dried to give 16.2 g. of product, m.p. 75–76°. Recrystallization from water raised the m.p. to 77–78°.

2-Quinolinemethyl Benzoate.—To 0.5 g. of 2-quinolinemethanol was added 20 ml. of water, 2 ml. of 10% aqueous sodium hydroxide and 0.5 g. of benzoyl chloride. The mixture was stirred until the pale yellow oil solidified. The product was filtered and recrystallized from aqueous methanol to form clusters of almost colorless plates, m.p. 52–53°. The infrared spectrum and m.p. of the compound were identical with those of the product obtained from the reaction of quinaldine oxide hydrate with benzoyl chloride. There was no depression of m.p. upon admixture of the two samples.

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[4] It was reported[1] that the debenzoylated compound, now formulated as IIIb, gives a red color with ferric chloride in the alcoholic solution. In the present work, a yellow precipitate, but no red color, was observed. In other experiments, the results reported by Henze were obtained.

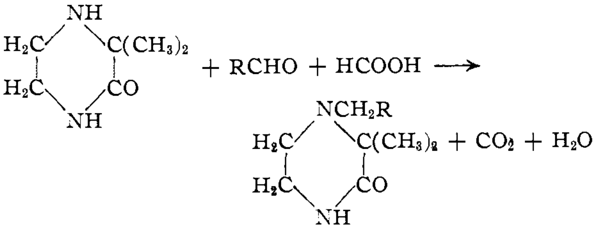
Leuckart Alkylation of 2-Piperazinones[1]

BY PHILIP RUBY AND PETER L. DEBENNEVILLE

RECEIVED FEBRUARY 20, 1953

The availability of 2-piperazinones by a new method developed in these laboratories,[2] suggested the possibility of alkylation on the amine nitrogens under Leuckart conditions. In this way, the amide nitrogen could be the site for a desired methylolation reaction without the complication of resin formation from the secondary amino group.

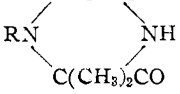
The alkylation may be illustrated by the series of compounds prepared from 3,3-dimethyl-2-piperazinone.[3]



Data for these reactions are given in Table I. Reaction proceeded smoothly at temperatures of 100–130°, resulting in good yields when aldehydes were used. Ketones failed to react even at high temperatures, and in all three cases tried, 4-formyl-2-piperazinone was the only product. The failure of ketones to react can probably be ascribed to the methyl groups in the 3-position, as well as to the fact that the piperazinone is a secondary amine. It has been noted that in the sequence ammonia, methylamine and dimethylamine, yields of 78,

TABLE I

ALKYLATED 3,3-DIMETHYL-2-PIPERAZINONES



R	Yield, %	M.p., °C.[a]	Empirical formula	Nitrogen,[b] % Calcd.	Found
Methyl	72	131–132	$C_7H_{14}N_2O$	19.7	19.2
Ethyl	27	164–165	$C_8H_{16}N_2O$	17.9	17.6
Isobutyl	60	136–138	$C_{10}H_{20}N_2O$	15.2	15.1
p-Chlorobenzyl	56	201–203	$C_{13}H_{17}N_2OCl$	11.1[c]	11.0[c]
3,4-Methylenedioxybenzyl[d]	35	190–193	$C_{14}H_{18}N_2O_3$	10.6	10.5
3,5,5-Trimethylhexyl	73	99–100	$C_{15}H_{30}N_2O$	11.1	11.2

[a] Uncorrected. [b] Kjeldahl method. [c] Calcd. for $C_{13}H_{17}N_2OCl$: Cl, 14.0. Found: Cl, 13.7. [d] From piperonal.

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[1] Communications should be directed to Peter L. deBenneville, Rohm & Haas Co., 5000 Richmond St., Philadelphia, Pa.

[2] V. T. Elkind, J. S. Strong and W. E. Craig, private communication.

[3] S. R. Aspinall, THIS JOURNAL, 62, 1203 (1940).

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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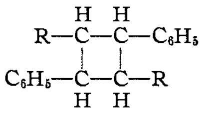
The Structure of a Photodimer of Dibenzalacetone

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

RECEIVED JANUARY 26, 1953

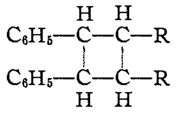
Two different dimers have been reported as irradiation products of dibenzalacetone. One of these (m.p. 245°) was obtained in 90% yield from a reaction of dibenzalacetone in glacial acetic acid which contained uranyl chloride. It was assigned structure I.[1] The other substance, formed by the action of 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.



$$\begin{array}{l} \quad\;\;\mathrm{H\;\;H} \\ \mathrm{R{-}C{-}C{-}C_6H_5} \\ \quad\;\;|\;\;\;| \\ \mathrm{C_6H_5{-}C{-}C{-}R} \\ \quad\;\;\mathrm{H\;\;H} \end{array}$$

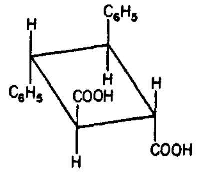
I



$$\begin{array}{l} \qquad\;\;\mathrm{H\;\;H} \\ \mathrm{C_6H_5{-}C{-}C{-}R} \\ \qquad\;\;|\;\;\;| \\ \mathrm{C_6H_5{-}C{-}C{-}R} \\ \qquad\;\;\mathrm{H\;\;H} \end{array}$$

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).