necked adaptor for gas inlet and condenser. The system was evacuated to 1 mm. and refilled with dry nitrogen three times. After flushing the system for 30 min. with a slow stream of nitrogen (which was continued during the reaction), the flask was immersed in a Woods' metal bath which was preheated to 200–210°. After 0.5–1 hr. at this temperature, the red mixture was allowed to cool, then boiled with several portions of anhydrous ether to remove the phthalan from the solid residue. The combined etheral extracts were dried over anhydrous magnesium sulfate. Removal of the solvent afforded an oil which was treated as described below.

The oil obtained from 85.9 g. (0.224 mole) of methiodide Ia was distilled to give 33.3 g. (76%) of 1-phenylphthalan (IIa), b.p. 108–110° (0.05 mm.), lit.[6] b.p. 127–129° (0.03 mm.). This product was stored under nitrogen to prevent slow decomposition.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.44; H, 6.30.

The oil obtained from 13.8 g. (0.03 mole) of methiodide Ib crystallized when the last trace of solvent was removed *in vacuo*. The solid was recrystallized from acetone (cooled in Dry Ice) to give 4.6 g. (56%) of 1,1-diphenylphthalan (IIb), m.p. 99–100.5°, lit.[9] m.p. 95.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.07; H, 5.88.

A sample of the solid residue left after the ethereal extractions of the reaction product was warmed with 6 *M* sodium hydroxide to evolve trimethylamine, which was bubbled through ethanolic picric acid to give the yellow picrate of this amine, m.p. 224–226°, after recrystallization from ethanol. This melting point was not depressed on admixture with an authentic sample of the picrate.

Oxidations of phthalans IIa and IIb were effected by treatment of refluxing mixtures of 0.5-g. samples of each in 25 ml. of 1 *M* sodium hydroxide with 1-g. portions of potassium permanganate until the purple persisted. After refluxing for 6 hr., ethanol was added, the suspension filtered, and the filtrate acidified. The mixture was extracted with ether, and the solvent removed from the dried ethereal extracts. The residue from the experiment with IIa was recrystallized from water–ethanol to give *o*-benzoylbenzoic acid, m.p. 128–130°, undepressed on admixture with an authentic sample. The residue from the experiment with IIb was recrystallized from hexane to give 3,3-diphenylphthalide, m.p. 116–117°, undepressed on admixture with an authentic sample.[13] The two products were further identified by comparison of their infrared spectra with the spectra of the authentic samples.

Reaction of Carbinol Quaternary Hydroxide with Alkali.—A solution of 9.16 g. (0.025 mole) of methiodide Ia in 250 ml. of hot water was treated with 11.2 g. (0.05 mole) of silver oxide, and the resulting carbinol quaternary hydroxide treated (after filtration) with 35 g. of sodium hydroxide essentially as described previously.[8] After refluxing until trimethylamine ceased to be evolved (3 hr.), the reaction mixture was cooled, diluted with water, and extracted with ether. The solvent was removed from the dried ethereal solution and the oily residue distilled *in vacuo* to give 2.4 g. (49%) of a mixture of phthalan IIa and ketone V, b.p. 108–110° (0.05 mm.). The infrared spectrum of the mixture showed peaks at 1031 and 1019 cm.$^{-1}$ for a cyclic ether and a strong peak at 1637 cm.$^{-1}$ for a carbonyl group.[14] A vapor phase chromatogram of the mixture showed two peaks (approximate ratio, 7:3), the retention times of which corresponded to those of IIa and V,[15] respectively. A solution of a sample of the mixture in 95% ethanol was treated with 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylhydrazone of ketone V, m.p. 179–189°, undepressed on admixture with an authentic sample, m.p. 181–189°. The infrared spectra of the two samples were identical.

The stability of phthalan IIa in refluxing 50% sodium hydroxide was demonstrated by the observation that no ketone V was obtained after 4 hr. refluxing. Recovery IIa (90%) was identified by boiling point, v.p.c., and n.m.r. spectrum.

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[13] F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 3364 (1962).

[14] See ref. 4, p. 132.

[15] Authentic ketone V, b.p. 110–113° (0.6 mm.), was prepared in 83% yield from *o*-tolyl chloride and benzene by means of aluminum chloride as described previously [H. Goldschmidt and H. Stoker, *Ber.*, **24**, 2805 (1891)].

Additional Rearrangements of 5-Phenyl-1,4-benzodiazepines

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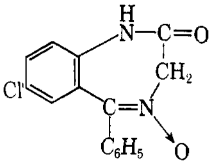
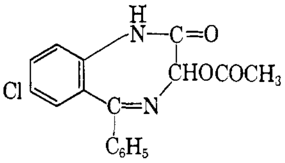
7-Chloro-5-phenyl-1,3-dihydro-2H-1,4-benzodiazepin-2-one 4-oxide (I) has been shown to undergo a Polonovski-type rearrangement upon treatment with acetic anhydride to afford 3-acetoxy-7-chloro-5-phenyl-1,3-dihydro-2H-1,4-benzodiazepin-2-one (II).[1] The acetyl group of II has been removed, leaving an isomer of I (III).[2] In studying the scope of this rearrangement, I was treated with *p*-toluenesulfonyl chloride and with phosphorus oxychloride. The product (IV), obtained in either case, was isomeric with I but was not III; neither was it 7-chloro-5-phenyl-4,5-dihydro-2H-1,4-benzodiazepine-2,3(1H)-dione nor 6-chloro-4-phenyl-3,4-dihydroquinazoline-2-carboxylic acid, two other isomers of I that were prepared earlier.[1]

Compound IV, m.p. 255–257°, absorbed in the infrared at 3.15 and at 6.01 μ suggesting the persistence of NH and C=O in the product. The n.m.r. spectrum showed a singlet (2H) at δ 4.56.[3] The reaction conditions suggested the possibility of a Beckmann-type rearrangement. The expected product (*trans* shift) of such a rearrangement is 4-benzoyl-6-chloro-3,4-dihydroquinoxalin-2(1H)-one, a structure consistent with the physical data.


I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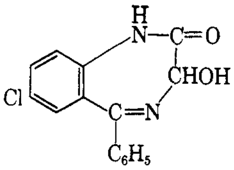
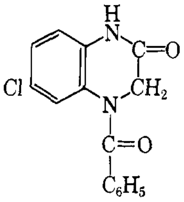

III


IV

Compound IV was hydrolyzed with hot sodium hydroxide removing the benzoyl group and affording the known 6-chloro-3,4-dihydroquinoxalin-2(1H)-one.[4] Catalytic dechlorination of IV resulted in 4-benzoyl-3,4-dihydroquinoxalin-2-(1H)-one, identical with an authentic sample made from 3,4-dihydroquinoxalin-2(1H)-one by benzoylation.[5] The structure of IV was thus established.

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[1] S. C. Bell and S. J. Childress, *J. Org. Chem.*, **27**, 1691 (1962).

[2] Compound III has been assigned the generic name oxazepam.

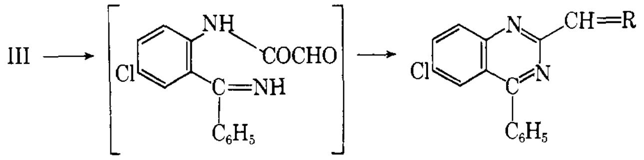
[3] N.m.r. measurements were made in deuteriochloroform (tetramethylsilane) with a Varian A-60 spectrometer.

[4] A. F. Crowther, F. H. S. Curd, D. G. Davey, and G. J. Stacy, *J. Chem. Soc.*, 1260 (1949).

[5] S. Motylewski, *Ber.*, **41**, 800 (1908).

Walker[6] recently has described a treatment of the oxime of 2-benzoyl-4-chlorooxaniloyl chloride with phosphorus oxychloride to afford 6-chloro-4-phenylquinazolin-2(1H)-one. Since the properties ascribed to this compound differed from those of a preparation made in this laboratory by two independent methods,[7] it seemed more likely to us that a Beckmann rearrangement had taken place, *followed* by cyclization and decarboxylation to give 6-chloro-3-phenylquinazolin-4-(3H)-one (V). In order to test this hypothesis, 5-chloroanthranilic acid was fused with formanilide to yield V in an unambiguous way. Compound V melted at 182–184° and absorbed in the infrared at 5.97, 6.20, and 6.28 μ (Nujol). Walker gave m.p. 185° and infrared bands at 5.97, 6.20, and 6.26 μ.

In addition to those reported earlier,[1] still another rearrangement has been observed with III. Heating in acetic acid afforded 6-chloro-4-phenylquinazoline-2-carboxaldehyde (VI). Compound VI with hydrazine gave a hydrazone (VII) that was also obtainable directly from hydrazine and III. Methylamine was observed also to bring about this ring contraction leading to the methylimine (VIII) of the aldehyde. The structure of VI was proved easily by elemental analysis, positive Tollens test, and infrared and n.m.r. data (5.81 μ; δ = 10.1 p.p.m.), as well as its oxidation to the known 6-chloro-4-phenylquinazoline-2-carboxylic acid.[8]



VI, R = O
VII, R = NNH_2
VIII, R = NCH_3

Experimental[9]

4-Benzoyl-6-chloro-3,4-dihydroquinoxalin-2-(1H)-one (IV).—A mixture of 5.0 g. of I, 15 ml. of phosphorus oxychloride, and 50 ml. of chloroform was heated under reflux for 0.5 hr. until the solid had dissolved. The resultant dark reaction mixture was concentrated to dryness *in vacuo*. The residue was recrystallized from acetonitrile to afford 1.3 g. of IV, m.p. 255–257°; λ_{max}^{KBr} 3.15, 6.01 μ; δ = 4.56 p.p.m. (s, 2H).

Anal. Calcd. for $C_{15}H_{11}ClN_2O_2$: C, 62.81; H, 3.81; Cl, 12.37; N, 9.77. Found: C, 62.34; H, 3.85; Cl, 12.30; N, 9.87.

Hydrolysis of IV in refluxing 4 *N* sodium hydroxide for 10 min., followed by acidification, gave 6-chloro-3,4-dihydroquinoxalin-2(1H)-one, m.p. 180–182°. Crowther, *et al.*,[4] reported m.p. 184°.

Compound IV (0.3 g.) in 10 ml. of ethanol containing 0.5 ml. of 4 *N* sodium hydroxide was hydrogenated in the presence of palladium–charcoal (5%). After filtering from the catalyst, the solution was diluted to precipitate 4-benzoyl-3,4-dihydroquinoxalin-2(1H)-one, m.p. 204–206°. There was no depression upon mixing with a sample prepared according to the procedure of Motylewski.[5]

6-Chloro-3-phenylquinazolin-4(3H)-one (V).—A mixture of 17.5 g. of 5-chloroanthranilic acid and 12.1 g. of formanilide was fused at 130–150° for 15 min. The melt, which solidified on cooling, was dissolved in alcohol and the resultant solution was diluted with water. The precipitate so obtained was collected and recrystallized from ethanol to give 3 g. of V, m.p. 182–184°; λ_{max}^{Nujol} 5.97, 6.20, 6.28 μ.

Anal. Calcd. for $C_{14}H_9ClN_2O$: C, 65.50; H, 3.53; Cl, 13.82. Found: C, 65.58; H, 3.80; Cl, 14.00.

6-Chloro-4-phenylquinazoline-2-carboxaldehyde (VI).—A mixture of 10.0 g. of III and 100 ml. of acetic acid was heated under reflux for 10 min., then cooled, and diluted with water. The resultant precipitate was recrystallized from an alcohol–water mixture, then hexane, and finally acetonitrile. Compound VI (6 g.) was obtained as a light yellow solid, m.p. 176–178°; λ_{max}^{KBr} 5.81 μ; δ = 10.1 p.p.m. (s, 1H).

Anal. Calcd. for $C_{15}H_9ClN_2O$: C, 67.04; H, 3.38; Cl, 13.20; N, 10.43. Found: C, 67.01; H, 3.36; Cl, 13.12; N, 10.38.

Alkaline oxidation of VI with dilute potassium permanganate afforded 6-chloro-4-phenylquinazoline-2-carboxylic acid, m.p. 212–214°, identical with an authentic sample.[8]

6-Chloro-4-phenylquinazoline-2-carboxaldehyde Hydrazone (VII).—A solution of 1.5 g. of III, 50 ml. of ethanol, and 3.0 ml. of hydrazine hydrate (85%) was heated under reflux for 0.5 hr. Upon cooling 0.8 g. of product was collected. Recrystallization from isopropyl alcohol gave VII, m.p. 166–167°. An identical compound was prepared by treating VI with hydrazine.

Anal. Calcd. for $C_{15}H_{11}ClN_4$: C, 63.88; H, 3.93; Cl, 12.57; N, 19.86. Found: C, 63.72; H, 3.72; Cl, 13.00; N, 19.90.

6-Chloro-4-phenylquinazoline-2-carboxaldehyde Methylimine (VIII).—A mixture of 3.0 g. of III, 50 ml. of ethanol, and 15 ml. of 30% aqueous methylamine that had refluxed for 1 hr. was diluted with 100 ml. of water. The precipitate was collected and recrystallized from cyclohexane. There was obtained 1.7 g. of VIII, m.p. 153–154°.

Anal. Calcd. for $C_{16}H_{12}ClN_3$: C, 68.20; H, 4.29; Cl, 12.59; N, 14.91. Found: C, 68.27; H, 4.20; Cl, 12.60; N, 15.18.

Acknowledgment.—We are indebted to Dr. Gordon Ellis for the microanalyses, to Mr. Bruce Hofmann for the infrared data, and to Dr. C. A. Hetzel for the n.m.r. spectra.

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[6] G. N. Walker, *J. Org. Chem.*, **27**, 1929 (1962).

[7] T. S. Sulkowski and S. J. Childress, *ibid.*, **27**, 4424 (1962).

[8] S. C. Bell, C. Gochman, and . J. Childress, *ibid.*, **28**, 3010 (1963).

[9] The melting points are uncorrected.

Electron Spin Resonance Spectra of the Negative Ions of Phenothiazine and Some of Its Derivatives[1]

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Continuing earlier work on thiazine and oxazine dye radicals,[2] we have obtained well-resolved spectra of phenothiazine, 3,7-diaminophenothiazine (Lauth's violet), 3,7-bis(dimethylamino)phenothiazine (methylene blue), and 7-dimethylaminophenothiazin-3-one (methylene violet).

Previously[2] the radicals were produced in various alkaline and acid solutions. The four spectra discussed later were obtained from radicals produced in *p*-dioxane with the sodium mirror technique at room temperature. The hyperfine structure lines observed had an average width of 0.07 gauss. A section of the spectrum of Lauth's violet between the central line and one outer component of the central nitrogen triplet is shown in Fig. 1. This section is typical for all spectra recorded.

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(1) Work supported by the (U. S.) National Science Foundation, the Research Corporation, and by the Rockefeller Fund of the School of Arts and Sciences of the American University of Beirut.

(2) F. W. Heineken, M. Bruin, and F. Bruin, *J. Chem. Phys.*, **37**, 1497 (1962).