m.p. 149–50°; 4,6-dichloro-2-nitroaniline[11] (65%), brown long needles, m.p. 110–111°; 4,6-dichloro-*o*-phenylenediamine[12] ($SnCl_2$–HCl reduction, 36%; NaOH–Zn dust reduction in alcohol, 30%), colorless shining long needles from water, m.p. 59–60°; and *o*-toluene,[13a] *p*-toluene-, *p*-acetanidophenyl,[13a] *p*-aminophenyl,[13b] and *p*-bromophenylsulfonamides[14] were obtained by known procedures.

2,3-Dihydroxy-5,7-dichloroquinoxaline was obtained in excellent yield (86%) from the corresponding 4,6-dichloro-*o*-phenylenediamine and oxalic acid by the procedure of Shriner and Upson[15] as buff-colored shining leaflets; recrystallized from ethanol, m.p. 320°.

Anal. Calcd. for $C_8H_4Cl_2N_2O_2$: N, 12.13. Found: N, 12.17.

2,3,5,7-Tetrachloroquinoxaline.—2,3-Dihydroxy-5,7-dichloroquinoxaline, on heating with PCl_5 at 160° for 2 hr., was obtained by a procedure similar to that used by Stevens, *et al.*[16] It was converted in 52% yield to 2,3,5,7-tetrachloroquinoxaline, a pale brown solid; recrystallization from ethanol yielded colorless shining long needles, m.p. 114–115°.

Anal. Calcd. for $C_8H_2Cl_4N_2$: N, 10.45. Found: N, 10.20.

Example for Condensations. A. 2,3-Dichloroquinoxaline and Sulfonamide.—An intimate mixture of dichloroquinoxaline (2.0 g., 0.01 mole), *o*-toluenesulfonamide (1.77 g., 0.01 mole), K_2CO_3 (1.5 g.), KI (0.2 g.), and copper powder (0.1 g.) was heated slowly on an oil bath at 140–145°. The temperature of the bath was then raised to 180–185° and heating was continued for 7 hr. A white crystalline sublimate was noticed on the sides of the flask. The product was extracted with NaOH solution (10%, 50 ml.). The alkaline filtrate was acidified with dilute acetic acid. The precipitate thus obtained was filtered off, washed, and crystallized from acetic acid (Norit) to give 2-(*o*-methylbenzenesulfonamido)-3-chloroquinoxaline (3.02 g., 65.5%) as orange-yellow shining stout needles, m.p. 251–253°.

B. 2,3,5,7-Tetrachloroquinoxaline and Sulfonamide.—Tetrachloroquinoxaline (1.0 g., 0.0027 mole), *o*-toluenesulfonamide (0.638 g., 0.0027 mole), KI (0.5 g.), and copper powder (0.1 g.) were heated initially at 100–105° and then at 145–150° for 7 hr. A yellowish white sublimate was observed on the sides of flask. The product was cooled and extracted with water. The clear filtrate was acidified with glacial acetic acid. The precipitate was collected and crystallized from ethanol as green shining crystals.

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Transformation Products of 5H-Dibenzo[*a*,*d*]-10,11-dihydrocycloheptene-5-one

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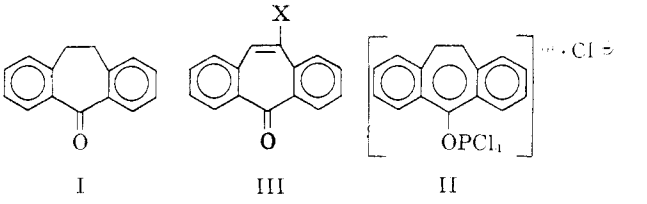
An efficient and novel conversion of 5H-dibenzo[*a*,*d*]-10,11-dihydrocycloheptene-5-one (I) to its 10,11-dehydro derivative III can be effected by PCl_5 in refluxing benzene. A red crystalline dibenzotropylium ion species formulated as II is formed as an intermediate.[1] The latter on decomposition with water yields III (X = H), whereas thermal decomposition affords the chloro derivative III (X = Cl).



I III II

(1) For another example of dibenzotropylium ion see G. Berti, *J. Org. Chem.*, **22**, 230 (1957).

Experimental Section[2]

Reaction of 5H-Dibenzo[*a*,*d*]-10,11-dihydrocycloheptene-5-one with Phosphorus Chlorides.—To a solution of 25.0 g. of dibenzo[*a*,*d*]cycloheptadien-5-one (I) in 2.5 ml. of $POCl_3$ and 50 ml. of dry benzene was added 75 g. of PCl_5 (3 equiv.) and the mixture was stirred under reflux for 2.5 hr. with protection from moisture. After *ca.* 15 min. a clear red solution resulted and a crystalline complex slowly separated accompanied by evolution of HCl. At the end of the reflux period (3 hr.), the reaction mixture was chilled to 10° and the dark red complex was isolated by filtration and washed twice with 25 ml. of dry benzene. The red complex (hygroscopic) was decomposed by portionwise addition (highly exothermic reaction) to a vigorously stirred solution of 300 ml. of 5:1 methanol–water. The complex was added at such a rate as to maintain gentle ebullition. The aqueous methanol solution of the product was allowed to cool slowly with stirring and was finally chilled to 10°. The crystalline product was isolated by filtration, sucked dry on the filter, washed with 50 ml. of water, and air dried; yield, 20.2 g. of dibenzo[*a*,*d*]cycloheptatrien-5-one (III, X = H); colorless needles, m.p. 84–86° (micro hot stage). From the mother liquors there was obtained, after recrystallization from methanol, an additional 1.0 g. of III (X = H), nearly colorless needles, m.p. 82–85° (micro hot stage), total yield 21.2 g. (85%). This material was found to be identical with authentic III (X = H).[3]

10-Chloro-5H-Dibenzo[*a*,*d*]cycloheptene-5-one (III, X = Cl).—A 0.5-g. sample of the crystalline red complex obtained from the reaction of I with PCl_5 was heated for 1 hr. at 100° *in vacuo* (~30-mm. water pump). The cooled reaction residue on trituration with acetic acid deposited III (X = Cl) which melted after recrystallization from methanol at 125–126.5°. λ_{max} (isooctane) 252 mμ (ε 1358) and 303 mμ (ε 540). The n.m.r. spectrum is in agreement with structure III (X = Cl).

Anal. Calcd. for $C_{15}H_9ClO$: C, 74.85; H, 3.77; Cl, 14.73. Found: C, 74.84; H, 3.79; Cl, 14.83.

(2) Melting points were taken on a micro hot stage and are corrected. Ultraviolet spectra were measured on a Cary recording spectrophotometer.
(3) W. Treibs and H. J. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951).

The Synthesis of Aryloxyureas

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Sulfonylureas have won wide acceptance in the treatment of maturity-onset diabetes.[1] Recently a sulfenylurea has been reported[2] to produce hypoglycemia in rabbits. In this communication, we describe the synthesis of nine aryloxyureas, a class of compounds which may be considered to be analogs of sulfonylureas.

The aryloxyureas were prepared by the reaction of an aryloxyamine hydrochloride and potassium cyanate or an organic isocyanate and are crystalline solids which are readily soluble in dilute aqueous sodium carbonate (see Table I).

(1) W. C. Cutting, "Handbook of Pharmacology," Appleton-Century-Crofts, New York, N. Y., 1964, p. 374.
(2) Y. Nitta, N. Ando, Y. Ikeda, M. Koiyumi, and A. Shioga, *J. Pharm. Soc. Japan*, **82**, 191 (1962).