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*-acetamidophenyl,[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*-tohuenesulfonamide (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.

(11) R. S. Datta and H. K. Mitter, *J. Am. Chem. Soc.*, **41**, 2036 (1919).
(12) S. H. Dandegaonker and G. B. Desai; *Indian J. Chem.*, **1**, 298 (1963).
(13) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1951: (a) pp. 780–782; (b) p. 871.
(14) E. R. Huntress and F. H. Carten, *J. Am. Chem. Soc.*, **62**, 511 (1940).
(15) R. L. Shriner and R. W. Upson, *ibid.*, **63**, 2277 (1941).
(16) J. R. Stevens, K. Pfister, III, and F. J. Wolf, *ibid.*, **68**, 1635 (1946).

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

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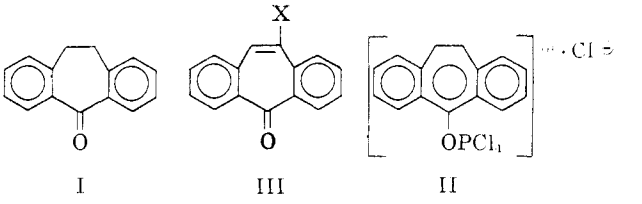
An efficient and novel conversion of 5H-dibenzo[*a*,*d*]-10,11-dihydrocyclohepten-5-one (I) to its 10,11-dehydro derivative III can be effected by PCl_5 in refluxing benzene. A red crystalline dibenzotropylium ion species formulated as II is formed as an intermediate.[1] The latter on decomposition with 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-dihydrocyclohepten-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*]cyclohepten-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. Shinga, *J. Pharm. Soc. Japan*, **82**, 191 (1962).

TABLE I

Aryloxyurea	Method	M.p., °C.	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
Phenoxyurea	A	119–120	$C_7H_8N_2O_2$	55.25	5.30	18.41	54.95	5.31	18.57
p-Tolyloxyurea	A	127–128	$C_8H_{10}N_2O_2$	57.82	6.07	16.86	57.62	6.12	16.64
m-Chlorophenoxyurea	A	121–122	$C_7H_7ClN_2O_2$[a]	45.05	3.78	15.02	45.39	4.06	15.40
1-*n*-Butyl-3-phenoxyurea	B	93–94	$C_{11}H_{16}N_2O_2$	63.44	7.74	13.45	63.17	7.93	13.50
1-*n*-Butyl-3-*p*-tolyloxyurea	B	87–88	$C_{12}H_{18}N_2O_2$	64.84	8.16	12.60	65.15	8.29	12.54
1-Allyl-3-phenoxyurea	B	105–106	$C_{10}H_{12}N_2O_2$	62.48	6.29	14.58	62.50	6.42	14.61
1-Phenoxy-3-phenylurea	B	154–155	$C_{13}H_{12}N_2O_2$	68.41	5.30	12.27	68.74	5.35	12.38
1-Cyclohexyl-3-phenoxyurea	B	139–140	$C_{13}H_{18}N_2O_2$	66.64	7.74	11.96	67.04	7.87	12.07
1-(2-Naphthyl)-3-phenoxyurea	B	158	$C_{17}H_{14}N_2O_2$	73.36	5.07	10.07	73.41	5.20	10.16

[a] *Anal.* Calcd.: Cl, 19.00. Found: Cl, 18.93.

Experimental Section[3]

***p*-Tolyloxyamine Hydrochloride.**—The method described Bumgardner and Lilly[4] for phenoxyamine was employed. A mixture of 33.6 g. (0.6 mole) of KOH, 63.8 g. (0.6 mole) of *p*-cresol, 420 ml. of water, and 200 ml. of methylcyclohexane was heated under reflux with stirring, and a solution of 17.0 g. (0.15 mole) of hydroxylamine-O-sulfonic acid in 40 ml. of water was added. After 10 min. the mixture was cooled, the layers were separated, and the aqueous phase was extracted with ether. The combined organic solutions were washed with 1 *N* NaOH and water and were dried ($MgSO_4$). The solution was acidified with ethanolic HCl and the solid which separated was collected. The product consisted of 1.9 g. (8%) of colorless plates, m.p. 96.5° dec.

***m*-Chlorophenoxyamine hydrochloride** colorless plates, m.p. 128–130° dec., was prepared in 2% yield from *m*-chlorophenol and hydroxylamine-O-sulfonic acid by the above method.

Aryloxyureas. Method A.—To a solution of 0.81 g. (0.01 mole) of KCNO in 5 ml. of water was added a solution of 0.01 mole of an aryloxyamine hydrochloride in 20 ml. of water. A solid rapidly separated. The mixture was stirred for 15 min. and filtered. The solid was recrystallized from hexane.

Method B.—A mixture of 0.01 mole of an aryloxyamine hydrochloride and 10 ml. of 1 *N* NaOH was extracted with ether, and the ether solution was dried briefly (K_2CO_3). Then, 0.011 mole of an organic isocyanate was added. After 1 hr. the solution was concentrated on a steam bath to an oil which crystallized upon cooling. The solid was recrystallized from hexane, benzene, or ethanol.

(3) Melting points were determined in a Hershberg apparatus and are uncorrected. Microanalyses were performed by Mr. L. M. Brancone and staff.

(4) C. L. Bumgardner and R. L. Lilly, *Chem. Ind.* (London), 559 (1962).

1-Acyl-1-alkoxy-3-(*p*-tolylsulfonyl)ureas[1]

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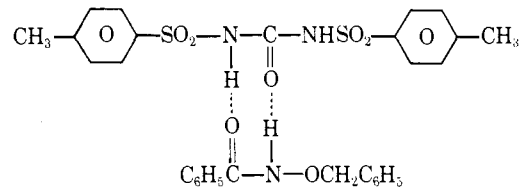
1-Alkyl-3-*p*-tolylsulfonylureas[3] and 1-alkoxy-3-*p*-tolylsulfonylureas[4] have been found to have hypoglycemic activity. On the basis of this, the preparation of 1-acyl-1-alkoxy-3-(*p*-tolylsulfonyl)ureas as possible hypoglycemic agents has been undertaken.

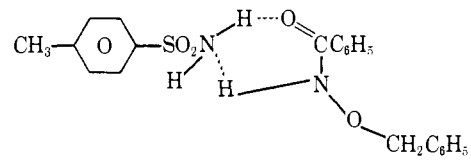
p-Toluenesulfonyl isocyanate, prepared by the method outlined by King,[5] was found to react with N-acetyl-O-*n*-propylhydroxylamine (Ia), N-acetyl-O-allylhydroxylamine (Ib), and N-carbethoxy-O-benzylhydroxylamine (Ic) to give the expected addition compounds. The only chemical property of these adducts that has been observed was their hydrolysis with boiling water to *p*-toluenesulfonamide and the N-acyl-O-alkylhydroxylamine.

RCONHR′

Ia, R = CH_3; R′ = *n*-C_3H_7
b, R = CH_3; R′ = CH_2=$CHCH_2$
c, R = OC_2H_5; R′ = $C_6H_5CH_2$
d, R = C_6H_5; R′ = $C_6H_5CH_2$



II



III

p-Toluenesulfonyl isocyanate failed to give an addition compound with N-benzoyl-O-benzylhydroxylamine (Id) under the same conditions used with the other hydroxylamines. Instead two complexes were isolated. The analysis of one showed it to be a hydrogen-bonded complex II, 1,3-bis-*p*-tolylsulfonylurea with Ia, and the other was a hydrogen-bonded complex III of *p*-toluenesulfonamide with Id. Our interpretation of the infrared spectrum[6] of the former complex led us to suggest structures II. The infrared spectrum of II in Nujol had NH at 3380 and 3220 and CO at 1740 and 1630 cm.$^{-1}$, while 1,3-bis(*p*-tolylsulfonyl)-urea and N-benzoyl-O-benzylhydroxylamine had NH 3295 and CO 1750, and NH 3297 and CO 1647 cm.$^{-1}$, respectively. The lowering of CO and NH absorption frequencies has been found in a number of urea inclusion products.[7,8]

Experimental Section[9]

1-Acetyl-1-propoxy-3-(*p*-tolylsulfonyl)urea.—A solution of 5.7 g. (0.029 mole) of *p*-toluenesulfonyl isocyanate and 3.39 g. (0.029 mole) of N-acetyl-O-*n*-propylhydroxylamine[10] was refluxed for 1 hr. The solvent was evaporated under reduced pressure on a water bath, and the residual oil was crystallized from ether–petroleum ether (b.p. 30–60°) to give white needles. A pure

(1) This investigation was supported by Research Grant E 4173 from the National Institutes of Allergy and Infectious Diseases, Public Health Service. Presented in part at the 19th Annual Northwest Regional Meeting of the American Chemical Society, Spokane, Wash., June 1964.

(2) Taken from the M. S. Thesis of J. D. McCown, University of Idaho, 1964.

(3) F. G. McMahon, Advances in Chemistry Series, No. 45, American Chemical Society, Washington, D. C., 1964, p. 102.

(4) Lucius and Bruning, Belgian Patent 603,268 (April 29, 1960).

(5) C. King, *J. Org. Chem.*, **25**, 352 (1960).

(6) All infrared spectra were run on a Perkin-Elmer 237 Infracord.

(7) A. R. Caniewski, V. Dabrowski, Z. Piasek, and T. Urbanski, *J. Chem. Soc.*, 2340 (1962).

(8) G. B. Barlow and P. J. Corish, *ibid.*, 1706 (1959).

(9) All melting points were determined using capillary tubes, 2 × 90 mm., in an A. H. Thomas melting points apparatus. The microanalyses were by Alfred Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr).

(10) J. H. Cooley, W. D. Bills, and J. R. Throckmorton, *J. Org. Chem.*, **25**, 1734 (1960).