1,5-Bis(p-toluenesulfonyl)-3,7-Dihydroxyoctahydro-1,5-diazocine

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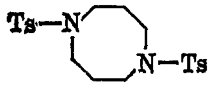
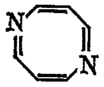
The synthesis, structure determination, and probable mode of formation of *cis*- and *trans*-1,5-bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine is described.

The classical synthesis of N-*p*-toluenesulfonylazetidines[1] involves the condensation of 1,3-dihalopropanes in the presence of base with *p*-toluenesulfonamide. One of the by-products of this reaction is the corresponding dimeric condensation product, 1,5-bis-(*p*-toluenesulfonyl)octahydro-1,5-diazocine (I). The chemistry of octahydro-1,5-diazocines is predominantly limited to cases of 1,5 disubstitution by alkyl or ω-substituted alkyl groups. Excluding the few instances of the octahydrodiazocine being fused to another ring system, the only positions substituted otherwise are represented by several 1,5-dialkyl- or 1,5-diaryl-3,7-dihydroxy[2] and 3,7-dialkyl-3,7-dinitro[3] derivatives.


I

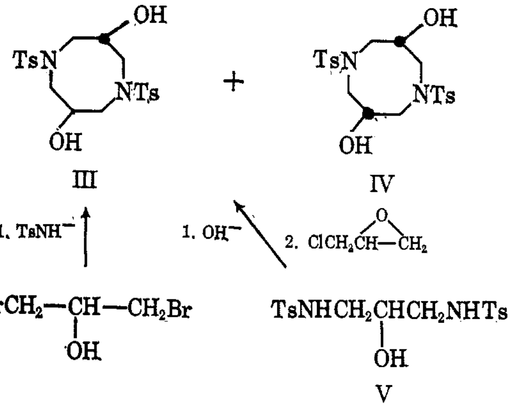

II

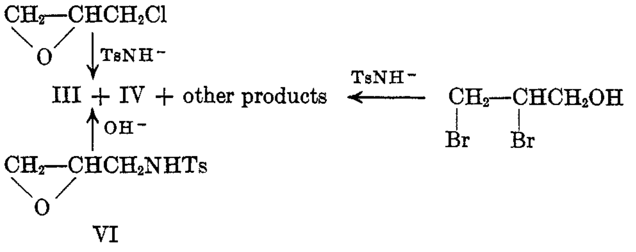
In order to prepare, ultimately, 1,5-diazocine (1,5-diazacyclooctatetraene) (II), it became necessary to develop a synthesis of properly substituted octahydro-1,5-diazocines. The synthesis of these compounds by modifying the classical azetidine synthesis appeared to present a reasonable starting point.

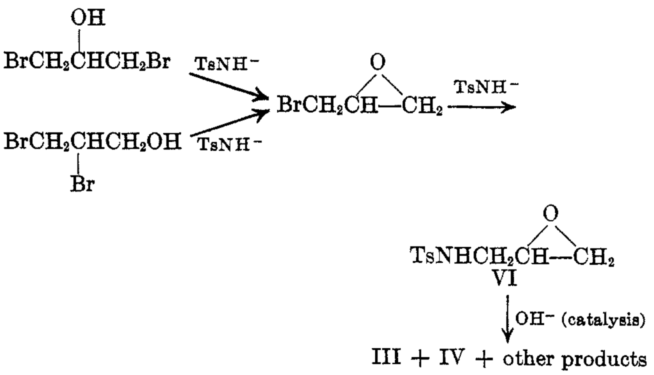
We have found that the condensation of 1,3-dibromo-2-propanol with *p*-toluenesulfonamide anion, followed by the addition of a second mole of base, yields a material of molecular formula $C_{20}H_{26}N_2O_6S_2$ in 13% yield. While numerous crystallizations did not alter the melting point of this material, thin layer chromatography did conclusively demonstrate that it is a two-component mixture. Silica gel chromatography readily separated this mixture into its pure components, each of which had an analysis for $C_{20}H_{26}N_2O_6S_2$. Both of these compounds readily form diacetates, showing the presence of two hydroxyl groups.

It is well known[4] that the hydrogen α to the hydroxyl group in secondary alcohols is shifted paramagnetically by 1.0–1.15 p.p.m. upon acetylation. A two-proton multiplet present in the alcohols is shifted paramagnetically by 1.01 p.p.m. in the diacetyl derivatives. This strongly suggests the presence of two secondary hydroxyl groups in each of the two isomeric condensation products.

The n.m.r. spectra of the diacetyl derivatives, tabulated in the Experimental Section, lead us to suggest that we are dealing with the *cis* and *trans* isomers of 1,5-bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine (III and IV). Conclusive proof of this structure assignment is found in the formation of the same mixture of diols from the condensation of 1,3-bis(*p*-toluenesulfonamido)-2-propanol (V) with epichlorohydrin. The same mixture of diols is also obtained (in essentially the same yields) from 2,3-dibromopropanol, epichlorohydrin,[5] or the epoxide VI by the reactions shown. These syntheses and the isolation of free *p*-toluenesulfonamide from the reaction mixture of 1,3-dibromo-2-propanol and 1 mole of *p*-toluenesulfonamide anion suggest that the major reaction sequence might well be the following. Since some of compound V has also been isolated from the reaction mixture of the 1,3-dibromo-2-propanol condensation, the condensation of this compound with epibromohydrin might also contribute to the formation of the two diols III and IV.







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[1] W. Marckwald, *Ber.*, **31**, 3265 (1898).

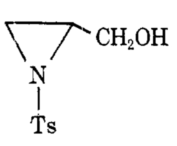
[2] V. R. Gaertner, *Tetrahedron Letters*, 141 (1964).

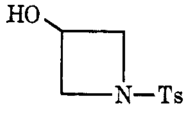
[3] R. Kolinsky, H. Piotrowska, and T. Urbanski, *J. Chem. Soc.*, 2319 (1958).

[4] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, p. 55.

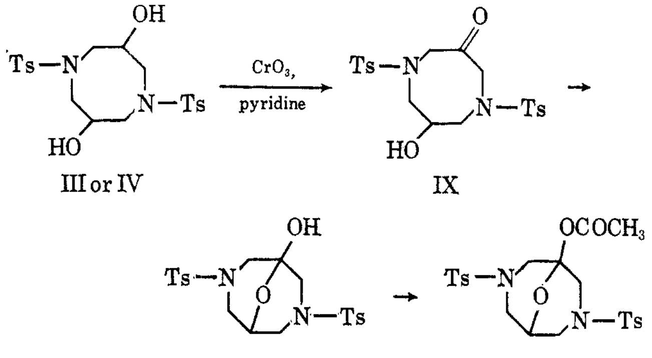
[5] M. Cohen [*Ind. Eng. Chem.*, **47**, 2095 (1955)] obtained polymers from epichlorohydrin and *p*-toluenesulfonamide in the presence of concentrated base. A patent (U. S. Patent 2,643,244) for the preparation of these polymers was issued to J. K. Simons.

One would anticipate that another reaction product would be the aziridine VII, as well as the azetidinol VIII formed by attack of the anion of VI on the epoxide linkage. We are currently analyzing the reaction mixture, which contains large amounts of polymeric materials, for the presence of these compounds.


VII


VIII

Chromic anhydride oxidation of either diol yields a compound, $C_{20}H_{24}N_2O_6S_2$. That this material does not contain a carbonyl group is shown by the absence of any absorption in the carbonyl region (5.75–6.10 μ) of its infrared spectrum. The formation of a monoacetate suggests that the compound is a hemiketal. The formation of this ketal could occur by oxidation of one of the hydroxyl groups in either one of the isomeric diols, followed by transannular ketalization, to give X.



III or IV IX X XI

The n.m.r. spectrum of X should exhibit a four-proton AB pattern owing to the four methylene group protons adjacent to the carbon atom bearing the hydroxyl group, and an A_2B_2X system for the remaining ring protons. These features are indeed visible in the spectrum of this compound (in CF_3CO_2D). The four-proton AB pattern has a coupling constant of 12 c.p.s., with the resonance positions of H_A at τ 6.10 and H_B at τ 7.27. The AB protons of the expected A_2B_2X system have a coupling constant of 14 c.p.s. (H_A at τ 5.69, H_B at τ 7.02). The protons at τ 7.02 show additional splitting (J = 2 c.p.s.) owing to the proton on the carbon atom bearing the oxygen bridge. The expected one-proton multiplet is partially hidden by the proton at τ 6.10, but its presence is clearly discernible from the integration. The aromatic protons and the aromatic methyl groups are at essentially the same chemical shift positions as those of the diols III and IV.

The n.m.r. spectrum of the acetylated hemiketal in deuteriotrifluoroacetic acid further confirms the assigned structure. The acetyl methyl protons absorb at τ 7.88. The protons of the AB pattern (J = 12 c.p.s.) absorb at τ 6.08 and 7.06, respectively. The AB protons of the expected A_2B_2X pattern appear at τ 5.47 and 6.96, respectively (J = 11 c.p.s.). The proton resonating at τ 6.96 shows additional splitting (J = 2.5 c.p.s.) owing to coupling with the remaining ring protons (multiplet at τ 5.58).

Unfortunately, the low solubility of the diols III and IV in nonpolar solvents precludes a complete infrared study to determine the presence of *inter- vs. intra*molecular hydrogen bonding. Consequently, no decision can be made as to the stereochemistry of the diols III and IV.

An X-ray crystallographic structure determination of the diols III and IV is in progress, the results of which will be reported by Dr. A. Clearfield of this department.

Experimental Section[6]

cis- **and** *trans-***1,5-Bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine (III and IV) from 1,3-Dibromo-2-propanol.**—1,3-Dibromo-2-propanol (43.6 g., 0.2 mole) was added with vigorous stirring to a solution of 34.2 g. (0.2 mole) of *p*-toluenesulfonamide and 11.2 g. (0.2 mole) of potassium hydroxide pellets in 400 ml. of 95% ethanol. The mixture was neutral after heating to reflux, and potassium bromide had precipitated. Another 5.6 g. of potassium hydroxide in ethanol was added with stirring and refluxing. After 30 min., the mixture was again neutral and a final 5.6 g. of potassium hydroxide in ethanol was added. After refluxing for 1 hr., the now neutral mixture was filtered. The solid obtained was washed with four 20-ml. portions of ethanol and the combined filtrate and washings were evaporated to give an oily solid which was crystallized from ethanol–water to give short prisms, 3.5 g. (m.p. 200.5–202°).

A second crop of crystals was obtained: m.p. 188–192°, 2.6 g.; total yield, 6.1 g. (13.3%). An analytical sample melted at 203–204°.

Anal. Calcd. for $C_{20}H_{26}N_2O_6S_2$: C, 52.84; H, 5.76; N, 6.16; mol. wt., 455. Found: C, 52.80, 52.58; H, 5.83, 5.82; N, 6.00, 6.01; mol. wt. (Rast), 458.

Thin layer chromatography on silica gel G, using a 1:1 (v./v.) mixture of benzene–ethyl acetate as the developing solvent, showed the material to be a two-compound mixture (made visible with I_2 vapors). A typical set of R_f values for this mixture is 0.66 and 0.72.

Separation of the ***cis*** **and** ***trans*** **Isomers of 1,5-Bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine (III and IV).**—The mixture of diols (3.300 g.) was dissolved in methanol, and after addition of 20 g. of silica gel, the mixture was evaporated to dryness and placed on a silica gel column (1650 g. of grade 923, Grace Davison Co. silica gel). The column was eluted with benzene–ethyl acetate (3:2) and 10-ml. fractions were collected. Intermittent t.l.c. analysis of the eluate permitted the fractions listed in Table I. After crystallization from absolute ethanol, fraction B yielded two crops of crystals: (1) 635 mg., m.p. 221.5–222.5°, R_f 0.74; (2) 128 mg., m.p. 223–224°, R_f 0.73. Crystallization of fraction E gave (1) 938 mg., m.p. 208–209°, R_f 0.68; (2) 207 mg., m.p. 207–209.5°, R_f 0.65. [*Anal.* Calcd. for $C_{20}H_{26}N_2O_6S_2$: C, 52.84; H, 5.76; N, 6.16, mol. wt., 455. Found (for isomer melting at 222–223°): C; 52.99; H, 5.95; N, 5.52; mol. wt., 516. Found (for isomer melting at 210–211°): C, 53.32; H, 6.03; N, 5.79; mol. wt., 513.] The n.m.r. spectra are given in Table II.

TABLE I

Fraction	Wt., mg.	Comments
A, 1–340	191	
B, 341–486	882	Pure high R_f isomer
C, 487–520	249	Mixture of isomers
D, 521–560	301	Low R_f isomer contaminated with high R_f isomer
E, 561–881	1346	Pure low R_f isomer

Diols III and IV from Epichlorohydrin.—A mixture of 171 g. (1.0 mole) of recrystallized *p*-toluenesulfonamide, 56.0 g. (1.0 mole) of potassium hydroxide pellets, and 3 l. of methanol was

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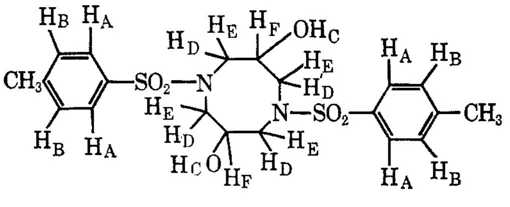
[6] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Robertson Laboratories, Florham Park, N. J. N.m.r. spectra were obtained on a Varian A-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer. The melting points reported are capillary melting points and are not corrected.

TABLE II

N.M.R. SPECTRA[a]



III and IV

Position (τ)	Number of H	Multiplicity	J, c.p.s.	Assignment
		"Low-Melting" Diol IV		
2.22	4	AB pattern	8	H_A
2.58	4			H_B
4.74	2	2	4	H_C (D_2O exchangeable)
6.28	6	2 (broad)	...	H_E (or H_D)
7.17	4	Ill-defined multiplet	...	H_E (or H_D)
7.62	6	1	...	$-CH_3$
		"High-Melting" Diol IV		
2.22	4	AB pattern	8	H_A
2.58	4			H_B
4.90	2	2	5	H_C (D_2O exchangeable)
6.20	2	Broad multiplet	...	H_F
6.87	8	2 (broad)	...	H_D and H_E
7.62	6	1	...	$-CH_3$

[a] Spectra are in DMSO-d_6 (25 mg./0.5 ml.).

warmed slightly to effect solution and 100 g. (1.1 mole) of epichlorohydrin was added rapidly with vigorous stirring. After stirring and refluxing for 5 hr., the mixture was almost neutral to pH paper and contained much precipitated potassium chloride. The solvent was removed and the resulting oily mass was swirled with 350 ml. of ether, and the precipitated solid was collected, washed with additional ether and 600 ml. of water, and dried. Crystallization from ethanol-water gave 26.5 g. of short prisms (m.p. 202–204°). The infrared absorption spectrum was identical with that of the material obtained from 1,3-dibromo-2-propanol.

The combined ether washings deposited additional product after standing for several days. This was recrystallized to yield 2.0 g. (m.p. 198–200°): total yield, 28.5 g. (12.6%). The ether washings (10% of the total) were concentrated by removal of the ether *in vacuo*, to yield 20.5 g. of a colorless oil. The oil was then dissolved in 200 ml. of chloroform and the resulting solution was washed with two 100-ml. portions of 5% aqueous sodium hydroxide. The combined aqueous extracts were acidified with dilute nitric acid, and extracted with two 100-ml. portions of chloroform. The dried (anhydrous Na_2CO_3) chloroform solution was concentrated to 100 ml., and 100 ml. of dry ether was added. This solution was then chilled overnight, and the precipitated solid was collected. Recrystallization from benzene–chloroform yielded 1.3 g. of 1,3-bis(*p*-toluenesulfonamido)-2-propanol (V), m.p. 143.5–145.0°.

Anal. Calcd. for $C_{17}H_{22}N_2O_5S_2$: C, 50.91; H, 5.21; N, 6.90. Found: C, 51.23; H, 5.36; N, 7.03.

The n.m.r. spectrum of this compound is in agreement with the assigned structure [two aromatic methyl groups, τ 7.58; eight aromatic protons (AB system), J_{AB} = 8.5 c.p.s., τ 2.62 and 2.25; one-proton quintet, J = 5.0 c.p.s., τ 6.00; and four-proton doublet, J = 5 c.p.s., τ 6.92; solvent, deuteriotrifluoroacetic acid].

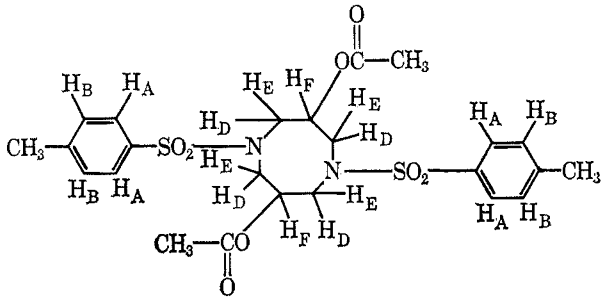
Diols III and IV from V and Epichlorohydrin.—A solution of 120 mg. (1.30 mmoles) of epichlorohydrin in 10 ml. of methanol was added with swirling to a solution of 87 mg. of potassium hydroxide and 510 mg. (1.28 mmoles) of V in 15 ml. of methanol. The solution was refluxed for 9 hr., diluted with an equal volume of water, and left standing overnight. The crystals which separated weighed 184 mg. (31%), m.p. 196–199.5°. The infrared spectrum of this material was identical with that of III and IV obtained from 1,3-dibromo-2-propanol.

Diols III and IV from 2,3-Dibromo-1-propanol.—The same procedure was used as in the case of 1,3-dibromo-2-propanol. When 0.5 mole of reactants was employed, 13.4 g. (11.8%) of III and IV was obtained.

Reaction of 1,3-Dibromo-2-propanol with *p*-Toluenesulfonamide Anion.—To a refluxing solution of 10.9 g. (0.05 mole) of 1,3-dibromo-2-propanol in 30 ml. of methanol was added a solution of 8.6 g. (0.05 mole) of *p*-toluenesulfonamide and 2.8 g. (0.05 mole) of potassium hydroxide pellets in 70 ml. of methanol (addition time 2 hr.). After refluxing for an additional 1 hr., the now neutral methanolic solution was decanted from precipitated potassium bromide, the solid was washed with additional methanol, the combined methanolic solutions were evaporated, and the methanol was replaced with water. Chilling the aqueous solution caused the crystallization of white plates, m.p. 129–131°. A mixture melting point with *p*-toluenesulfonamide was 132–135°. Dry weight of recovered starting material was 7.3 g. (85%).

TABLE III

N.M.R. SPECTRA[a]



Position, τ	Number of H	Multiplicity	J, c.p.s.	Assignment
		Diacetyl Derivative of Low-Melting Diol		
2.30	4	AB pattern	8	H_A
2.67	4		8	H_B
4.76[b]	2	Quintet	5	H_F
6.46	8	AB pattern	5	H_D and H_E
6.55				
7.57	6	1	...	Tolyl methyl
7.88	6	1	...	Acetyl methyl
		Diacetyl Derivative of High-Melting Diol		
2.25	4		8	H_A
2.60	4	AB pattern	8	H_B
4.76[b]	2	Quintet	5.5	H_F
6.52	8	Doublet	5.5	H_D and H_E
7.53	6	1	...	Tolyl methyl
7.88	6	1	...	Acetyl methyl

[a] Spectra are in deuteriochloroform. [b] τ 5.27 and 5.19 for the derivatives from the low-melting and high-melting diols were determined in DMSO-d_6 (25 mg./0.5 ml.).

N-(2,3-Epoxypropyl)-*p*-toluenesulfonamide (VI).—N-Allyl-*p*-toluenesulfonamide[7] (9.6 g., 0.045 mole) was dissolved in 150 ml. of moist chloroform containing 6.8 g. (0.050 mole) of perbenzoic acid,[8] and the solution was kept in an icebox for 48 hr. It was then washed successively with four 100-ml. portions of 5% sodium carbonate and 100 ml. of saturated salt solution, dried over sodium sulfate, filtered, and evaporated. The colorless oil so obtained solidified when chilled and was crystallized from ether–hexane to yield 5.0 g. (48%) of colorless plates (m.p. 65–67°). An analytical sample melted at 66.5–68°.

Anal. Calcd. for $C_{10}H_{13}NO_3S$: C, 52.85; H, 5.77; N, 6.16; mol. wt., 227.3. Found: C, 53.01; H, 5.69; N, 6.36; mol. wt., 234.

Base-Catalyzed Rearrangement of VI.—To 1.55 g. of VI in 20 ml. of methanol was added 3 drops of saturated methanolic potassium hydroxide. The solution was refluxed for 5 hr. and cooled. The short prisms which separated weighed 0.21 g. (13.8% of III and IV) and melted at 195–199°. A mixture melting point with III and IV obtained from 1,3-dibromo-2-propanol showed no depression. The infrared spectrum of this compound was identical with that of III and IV. The residue obtained by evaporation of the filtrate was a base-insoluble colorless oil which has not been identified. This compound could possibly be the aziridine VII or the azetidine VIII.

Preparation of *cis*- and *trans*-1,5-Bis(*p*-toluenesulfonyl)-3,7-diacetoxyoctahydro-1,5-diazocine form the Diols III and IV.—The low-melting diol (51.5 mg., 0.113 mmole), 0.30 ml. of acetic anhydride, and 0.60 ml. of pyridine were allowed to react at room temperature for 24 hr. After most of the pyridine and

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(7) V. A. Portnyagina, *Ukr. Khim. Zh.*, **25**, 102 (1959); *Chem. Abstr.*, **53**, 19953*d* (1958).

(8) A. H. Blatt, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

acetic anhydride was removed *in vacuo*, the residue was washed with water. Crystallization from absolute ethanol gave 41.1 mg. of the diacetate, m.p. 213–214°.

Anal. Calcd. for $C_{24}H_{30}N_2O_8S_2$: C, 53.52; H, 5.61; N, 5.20. Found: C, 53.40; H, 5.70; N, 5.07.

The high-melting diol, when treated as above, gave a diacetate which melted at 203°. The n.m.r. spectra of the diacetates are given in Table III.

Anal. Found: C, 53.31; H, 5.77; N, 4.96.

Oxidation of *cis*- and *trans*-1,5-Bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine with Chromic Anhydride.—Chromic anhydride (4.53 g., 45.6 mmoles) was added to 46 ml. of pyridine with stirring at 15–20°. The mixture of diols III and IV (6.86 g., 15.1 mmoles) in 69 ml. of pyridine was then added. After standing at room temperature for 21 hr., the reaction mixture was poured into 300 ml. of water. The mixture was extracted three times with 200-ml. portions of chloroform. After the combined extracts were dried over anhydrous sodium carbonate and the chloroform was removed *in vacuo*, 7.75 g. of a dark brown solid was obtained.

The crude product was chromatographed on an alumina column. Elution with chloroform gave starting material but further elution with chloroform–absolute ethanol (4:1) gave 3.15 g. (46%) of product melting at 216–217°. An analytically pure sample melted at 217°. Treatment of each of the pure diols III and IV, as above, yielded similar results, although it was observed that the low-melting diol had reacted less completely under identical reaction conditions. T.l.c. R_f values were the same for the products of each oxidation.

Anal. Calcd. for $C_{20}H_{24}N_2O_6S_2$: C, 53.08; H, 5.35; N, 6.19. Found: C, 53.08; H, 5.20; N, 6.05.

Preparation of the Monoacetate XI of the Hemiketal from *cis*- and *trans*-1,5-Bis(*p*-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine.—The hemiketal (51.7 mg., 0.114 mmole) from the low-melting diol was heated in a solution of 0.5 ml. of acetic anhydride and 1.0 ml. of pyridine at 75° for 7 hr. The pyridine and excess acetic anhydride were removed under vacuum, and the residue was washed once with 10 ml. of water. The white solid (45.8 mg.) was crystallized from acetone to give 21.9 mg. (39%) of a product melting at 253–253.5°.

Similar treatment of the hemiketal (60.7 mg., 0.134 mmole) from the high-melting diol produced 66.1 mg. of crude solid which, crystallized from acetone, gave 41.1 mg. (62%) of a product melting at 254–254.5°. A mixture melting point of both acetates was 252.5–253.5°. A portion of the monoacetate recrystallized from methylene chloride furnished an analytical sample, which melted at 252°.

Anal. Calcd. for $C_{22}H_{26}N_2O_7S_2$: C, 53.42; H, 5.30; N, 5.66. Found: C, 53.02; H, 5.35; N, 5.86.

Acknowledgment.—This investigation was supported in part by a research grant (CA-07917-01) from the National Cancer Institute, Public Health Service.

The Oxidation–Reduction Reaction of Hydrazinofluoro Aromatic Compounds. II.[1] 4,4′-Dihydrazinooctafluorobiphenyl, a Route to Tetrasubstituted Hexafluorobiphenyls

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The oxidation–reduction reaction of 4,4′-dihydrazinooctafluorobiphenyl, in ethanolic sodium ethoxide, affords 2,2′,3,3′,6,6′-hexafluorobiphenyl, which has been employed in the synthesis of hexafluorobiphenyl-3,3′,4,4′-tetracarboxylic acid through stepwise metalation procedures.

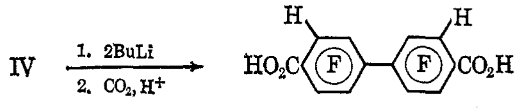
The use of alkoxide as the reagent in the oxidation–reduction reactions of hydrazinofluoro aromatic compounds provides homogeneous reaction conditions which greatly accelerate the rate of reaction in comparison with those reactions previously run as slurries in 3 *N* sodium hydroxide.[1] Thus, 4,4′-dihydrazinooctafluorobiphenyl (I) undergoes rapid oxidation–reduction on reaction with 2 moles of sodium ethoxide in ethanol (see Scheme I).

The oxidation–reduction reaction has been proposed to proceed through quinoid tautomerization, with the reaction course governed by the relative leaving abilities of the *para* or *ortho* substituents. In this case, selective displacement of the *o*-fluorine, by 1,4-dehydrohalogenation of the *o*-quinoid tautomer II occurs in preference to displacement of a fluoro aromatic anion from a *p*-quinoid tautomer. Spontaneous decomposition of the diimide III and repetition of the reaction on the other aromatic nucleus affords the observed major product, 2,2′,3,3′,6,6′-hexafluorobiphenyl (IV).

The crude product, obtained in quantitative yield, has been shown by vapor phase chromatography to be a mixture of the hexafluorobiphenyl IV (92.4%), 2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl (0.6%), and what is believed to be 2,2′,3,3′,5,6,6′-heptafluorobiphenyl (6.9%). It was anticipated that the latter two byproducts would be encountered by means of a previously mentioned[1] nonquinoid mechanism.

The reactive nature of the 2,2′-positions of fluorinated biphenyl systems was observed when 4 moles or more of sodium ethoxide was employed in this reaction. Nucleophilic attack at the sterically hindered 2,2′-positions of the hexafluorobiphenyl IV yielded the diethoxytetrafluorobiphenyl V. Conversion to 2,2′-dihydroxy-3,3′,6,6′-tetrafluorobiphenyl (VI), by reaction with aluminum chloride, was accomplished for the purpose of further characterization of the diethoxytetrafluorobiphenyl V.

In analogy with the facile reaction of *n*-butyllithium with the aromatic proton of highly fluorinated benzene compounds reported by us earlier,[3] the aromatic protons of the hexafluorobiphenyl IV readily underwent



VII, 83%

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(1) Part I: D. G. Holland, G. J. Moore, and C. Tamborski, *J. Org. Chem.*, **29**, 3042 (1964).

(2) Presented, in part, at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(3) (a) R. J. Harper, Jr., E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, **29**, 2385 (1964); (b) G. Baum and C. Tamborski, *Chem. Ind.* (London), 1949 (1964).