The Preparation of $H_2NCONHPO(OC_4H_9)_2$.—Analogous treatment of 0.3 mole of chlorourea and 0.3 mole of tri-*n*-butylphosphite produced after recrystallization from 30 parts of ethanol 36 g. of long white needles, melting at 175–176°.

Anal. Calcd. for $C_9H_{21}N_2O_4P$: C, 42.85; H, 8.39; N, 11.10. Found: C, 43.08; H, 8.40; N, 10.92.

The Preparation of $H_2NCONHP(C_6H_5)_3$ Cl.—A solution of 0.1 mole (26.2 g.) of triphenylphosphine in 150 ml. of acetonitrile (or tetrahydrofuran) is dropped into a stirred solution of 0.1 mole (9.4 g.) of chlorourea in 150 ml. of acetonitrile. The temperature of the reaction mixture is maintained at 10–15° by external cooling. After completion of addition the temperature is lowered to 0° for 5 hr. The precipitate is collected, washed with cold acetonitrile, and dried under vacuum. The filtrate is combined with the wash liquor, concentrated under vacuum to 50-ml. volume, and diluted with 100 ml. of acetone. After standing for 24 hr., the insoluble portion is separated by filtration, washed with cold acetonitrile, and added to the first crop. Recrystallization from absolute ethanol yields 15 g. of compact crystals melting at 194–195°.

Anal. Calcd. for $C_{19}H_{18}ClN_2OP$: C, 63.96; H, 5.08; Cl, 9.93; N, 7.85. Found: C, 63.78; H, 5.08; Cl, 9.36; N, 7.55.

Sulfostyril (2,1-Benzothiazine 2,2-Dioxide). I. Preparation and Reactions of 3,4-Dihydrosulfostyril

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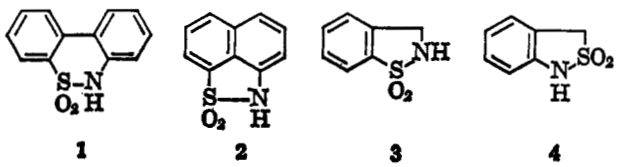
3,4-Dihydrosulfostyril was synthesized as a potential intermediate to the hitherto unknown parent aromatic sultam, sulfostyril (**5**). The reactions and properties of dihydrosulfostyril are described. N-Bromosuccinimide in dimethylformamide proved to be a very convenient nuclear-brominating agent.

The preparation and properties of aliphatic sultams have been investigated well[1,2]; however, there has been little reported on aromatic sultams. At the time this work was initiated, the only aromatic sultams known were the completely aromatic derivatives [diphenylenesultam (**1**)[1] and 1,8-naphthosultam (**2**)[1]] and the



1 **2** **3** **4**

sulfonyl analog of isooxindole (**3**).[1,3] After the present work had been completed, the preparation of **4**, the sulfonyl analog of oxindole, was reported.[4]

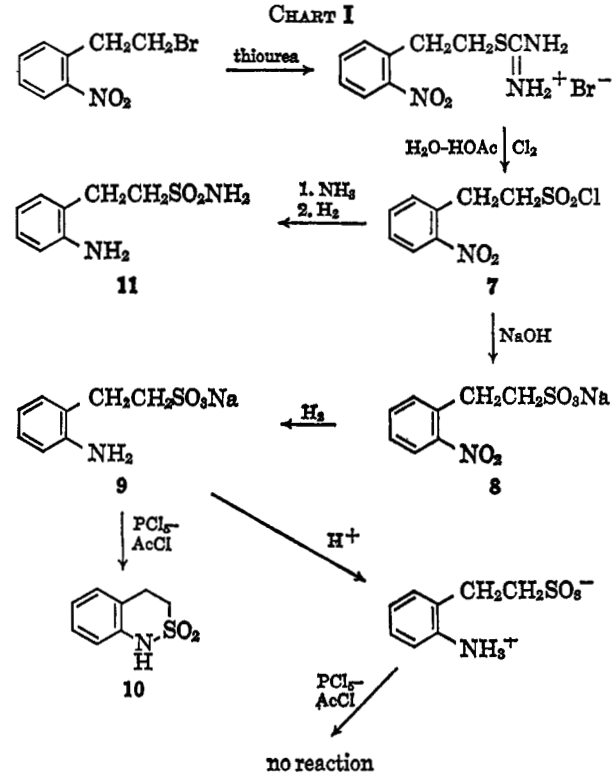
We were interested in preparing the remaining member of the aromatic sultam series, sulfostyril (**5**),[5] in

5 **6**

order to compare the physical and chemical properties of it and its derivatives with those of carbostyril (**6**).

In this paper, we describe the synthesis of dihydrosulfostyril (**10**), originally intended to serve (*via* dehydrogenation) as the immediate precursor of **5**.

CHART I



The synthesis of dihydrosulfostyril (**10**) is outlined in Chart I. 2-Nitrophenethyl bromide was converted in two steps to the sulfonyl chloride, **7**. Alkaline hydrolysis gave the sodium sulfonate **8**[6] which was readily catalytically reduced to the amine **9**. Acidification of an aqueous solution of **9** gave the very insoluble zwitterion. This zwitterion could not be converted to the desired sultam by heating (it decomposed), and was recovered unchanged from treatment with phosphorus pentachloride, phosphorus oxychloride, acetyl chloride, or mixtures of these reagents. However, trituration

(1) A. Mustafa, *Chem. Rev.*, **54**, 206 (1954), and A. Mustafa, "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1960, p. 183.

(2) W. F. Erman and H. C. Kretschmar, *J. Org. Chem.*, **26**, 4841 (1961), and references cited therein.

(3) Compound **3** has been called "benzyl sultam," but this ambiguous name should be avoided since it could also refer to compound **4**.

(4) J. F. Bunnett, T. Kato, R. R. Flynn, and J. A. Skorcz, *J. Org. Chem.*, **28**, 1 (1963).

(5) Compound **5** can be systematically named as 2,1-benzothiazine 2,2-dioxide or, less satisfactorily, as *o*-aminostyrene-β-sulfonic acid sultam; for convenience, we prefer the name "sulfostyril," by analogy with the name "carbostyril" used for compound **6**.

(6) Compound **8** was also prepared in one step by the reaction of *o*-nitrophenethyl bromide with sodium sulfite; however, the yield of **8** by this route was very low.

CHART II

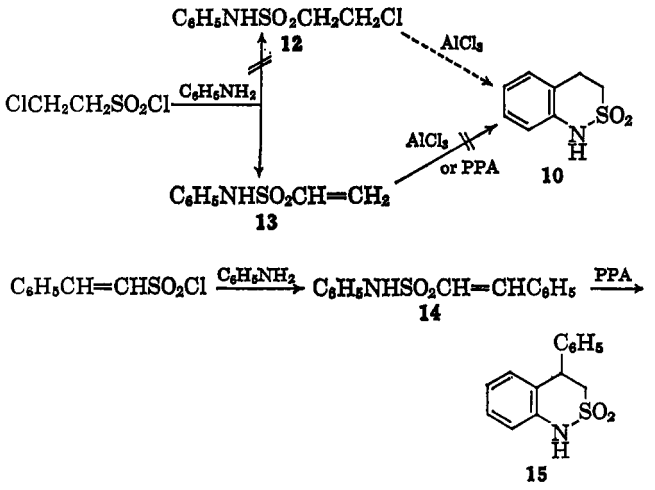
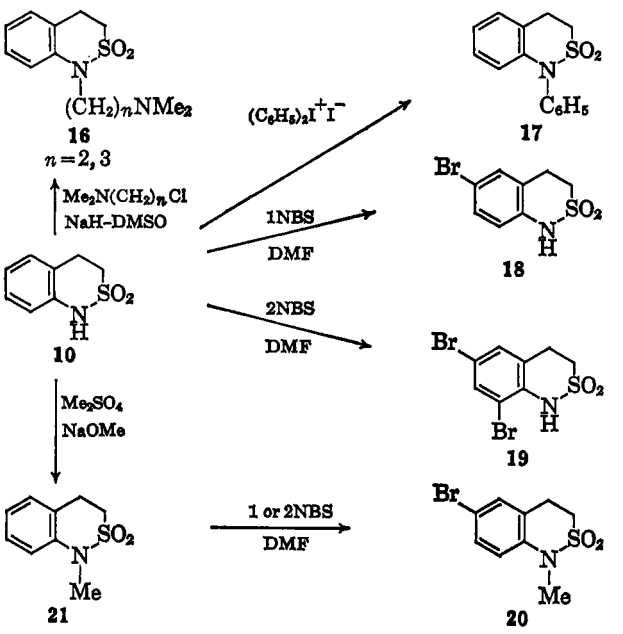


CHART III



of **9** with these reagents gave 3,4-dihydrosulfostyril, **10**.[7]

Attempts to convert **7** directly to dihydrosulfostyril by reduction were unsuccessful. Catalytic reduction failed, and chemical reducing agents led either to hydrolysis or reduction of the sulfonyl chloride. An attempt to convert **7** to a sulfonic ester (for use as a protecting group) by stirring with ethanol gave, instead, a good yield of the sulfonic acid. This was readily reduced to the zwitterion.

Compound **7** was converted to *o*-aminophenethylsulfonamide (**11**), but all attempts to cyclize this to **10** failed.[8]

When sodium *o*-aminobenzyl sulfonate, prepared from *o*-nitrobenzyl chloride by a sequence analogous to that illustrated in Chart I, was treated with various acid chlorides, no cyclic product (**4**) could be isolated.

Attempts were made to prepare N-phenyl-2-chloroethanesulfonamide (**12**), with the objective of cyclizing it to dihydrosulfostyril[9] (Chart II). Even under the most carefully controlled conditions, however, the reaction of 2-chloroethanesulfonyl chloride (**12**) with aniline gave only ethylenesulfonanilide (**13**). The olefin could not be converted to the chloride **12** by reaction with hydrogen chloride, nor could it be cyclized directly to **10**. When the olefin was suitably activated, as in the case of styrenesulfonanilide (**14**) we were able to carry out the cyclization smoothly to give 4-phenyl-3,4-dihydrosulfostyril (**15**). Certain reactions of dihydrosulfostyril are shown in Chart III.

Dihydrosulfostyril (**10**) is readily soluble in aqueous base. The sodium salt prepared using sodium methoxide in benzene or DMF was readily alkylated in high yield with methyl sulfate and arylated with diphenyliodonium iodide to give the N-methyl and N-phenyl derivatives (compounds **21** and **17**). The dimethylaminoethyl and -propyl derivatives (**16**, n = 2 and 3) could not be prepared using this same system. However, when sodium hydride in dimethyl sulfoxide was used, these were obtained in moderate yields.

Dihydrosulfostyril proved to be extraordinarily heat stable, even at temperatures of 250°. All attempts to dehydrogenate it to sulfostyril failed.

Dihydrosulfostyril was treated with N-bromosuccinimide (NBS) in dimethylformamide in the hope that bromination might take place on the benzylic carbon to give the 4-bromo derivative which could then be dehydrohalogenated to sulfostyril. A spontaneous exothermic reaction occurred and a mono- or dibromo derivative (depending on the amount of NBS used) separated. N-Methyldihydrosulfostyril (**21**) with NBS gave only a monobromo product. The bromo compounds were inert to vigorous treatment with alkali or alcoholic silver nitrate, and n.m.r. confirmed the fact that substitution had not occurred in the hetero ring. The monobromo products are probably the 6- and the dibromo compounds the 6,8-substituted structures (**18**, **19**, and **20**) by analogy with the results, described below, obtained on treatment of *dihydrocarbostyril* with NBS.

When 3,4-dihydrocarbostyril was treated with NBS under the same conditions, 6-bromo- and 6,8-dibromo-3,4-dihydrocarbostyrils[10] were obtained in good yields. The system N-bromosuccinimide in dimethylformamide is a very convenient one for mono- or dibrominating carbostyrils, oxindoles, and other anilides. Addition of a peroxide had no effect on the course of the reaction.

Since the conversion of dihydrosulfostyril to sulfostyril did not look promising, alternate routes to the latter compound were investigated. The successful synthesis of sulfostyril will be described in part II of this series.[11]

(7) After this work had been completed, G. R. Collins [*J. Org. Chem.*, **29**, 1688 (1964)] described the synthesis of a polycyclic analogue of dihydrosulfostyril by reaction of N-sulfinylaniline with norbornene and then oxidation of the resulting hexahydrodibenzo[1,2]thiazine oxide. These authors point out, however, that the norbornenes are unique for this reaction and that other olefins do not work, so dihydrosulfostyril could not have been prepared by their procedure.

(8) Other reactions of compound **11**, showing its resistance to cyclization reactions, are described by B. Loev and M. F. Kormendy [*Can. J. Chem.*, **42**, 176 (1964)].

(9) Cyclization of 2-chloropropionanilides provides an excellent synthesis of dihydrocarbostyrils: F. Mayer, L. van Zütphen, and H. Phillips, *Ber.*, **60**, 858 (1927).

(10) These compounds, made by a different route, have been described by H. Ugeda [*J. Chem. Soc., Japan Pure Chem. Sect.*, **64**, 61 (1943)].

(11) B. Loev and K. M. Snader, to be published.

Experimental[12]

2-(*o*-Nitrophenyl)ethanesulfonyl Chloride (7).—A mixture of 0.1 mole of 2-(*o*-nitrophenyl)ethyl bromide, 0.11 mole of thiourea, and 100 ml. of alcohol was heated at reflux for 1 hr. The solution was concentrated *in vacuo* until a solid started to separate and was then cooled, and the thiuronium bromide that precipitated was filtered (99% yield, m.p. 147–149°). This salt (0.1 mole) was dissolved in 250 ml. of 50% aqueous acetic acid, and the solution was maintained at 15° while chlorine gas was passed into the solution for 1.5 hr. The sulfonyl chloride separated and was filtered and washed with cold water (70% yield). A sample was recrystallized from isopropyl ether for analysis (m.p. 70–71°).

Anal. Calcd. for $C_8H_8ClNO_4S$: C, 38.48; H, 3.23; N, 5.61. Found: C, 38.59; H, 3.40; N, 5.67.

2-(*o*-Aminophenyl)ethanesulfonic Acid.—(a) The sulfonyl chloride **7**, 12.5 g., was suspended in ethanol and refluxed for several hours. The resulting solution was concentrated *in vacuo*, giving an orange, strongly acidic, water-soluble oil, 2-(*o*-nitrophenyl)ethanesulfonic acid. The oil was dissolved in water and hydrogenated using 10% palladium-on-carbon catalyst at 50 p.s.i.g., then the catalyst was filtered, and the filtrate was concentrated *in vacuo*, giving 9.0 g. (90%) of the product (m.p. 285° dec.). (b) The sulfonyl chloride **7**, 25 g., was stirred with 100 ml. of 10% sodium hydroxide; after a few minutes it dissolved with the evolution of heat. The compound was reduced in 5 min. using 10% palladium-on-carbon catalyst and 50 p.s.i.g. hydrogen. The catalyst was removed by filtration, and the solution was evaporated to dryness, giving a 94% yield of the sodium salt of 2-(*o*-aminophenyl)ethanesulfonic acid. A sample of the salt was dissolved in water; on acidification, the zwitterion of the product precipitated (m.p. 284° dec.); the infrared spectrum of the product was identical with that of the material prepared by method a. A small sample was recrystallized from hot water for analysis.

Anal. Calcd. for $C_8H_{11}NO_3S$: C, 37.7; H, 5.47. Found: C, 37.8; H, 5.71.

3,4-Dihydrosulfostyril (10).—The dried sodium salt, prepared as described under b above, was finely powdered, and then 33.4 g. was stirred with 80 ml. of acetyl chloride. To this mixture was then added 41.6 g. of phosphorus pentachloride and the mixture was heated, with stirring, on a steam bath for 15 min. Volatile materials were then removed *in vacuo*, and the residue was stirred with cold water. When the mild exothermic reaction subsided, the suspension was heated, with stirring, for 1 hr. on the steam bath; then it was cooled and filtered giving 11.5 g. of product (m.p. 151–153°). The filtrate could be evaporated to dryness and recycled through the same procedure again. In each cycle, approximately a 40% conversion was obtained. A sample of dihydrosulfostyril was recrystallized from ethyl acetate–pentane for analysis (m.p. 154–155°; λ_{max} 3.05, 6.71, 7.61, 7.77, 8.64, 8.89, 10.68, and 13.12 μ).

Anal. Calcd. for $C_8H_9NO_2S$: C, 52.44; H, 4.95; N, 7.64. Found: C, 52.55; H, 4.94; N, 7.48.

3,4-Dihydrosulfostyril was recovered almost quantitatively from attempts to dehydrogenate it by refluxing with 10% palladium-on-carbon catalyst in *p*-cymene or quinoline, with selenium dioxide in dioxane, or by heating with sulfur or selenium at 250°.

2-(*o*-Aminophenyl)ethanesulfonamide (11).—Ammonia was bubbled through a cold solution of **7** in ether until precipitation of ammonium chloride ceased (20 min.). The solvent was removed *in vacuo*, and the residue was treated with water and the resulting precipitate of 2-(*o*-nitrophenyl)ethanesulfonamide was filtered and recrystallized from alcohol (5.3 g., m.p. 123–126°). This was dissolved in alcohol and reduced at 50 p.s.i.g. using 5% palladium-on-carbon catalyst. After filtering off the catalyst and concentrating the filtrate to dryness, the solid residue was recrystallized from alcohol–pentane (3.1 g., m.p. 126–128°). Mixture melting point determination with the nitro precursor gave a large depression.

Anal. Calcd. for $C_8H_{12}N_2O_2S$: C, 47.98; H, 6.04; N, 13.99. Found: C, 48.26; H, 6.23; N, 13.83.

A sample of **11**, heated at 250° for 0.5 hr., was recovered unchanged.

Ethylenesulfonanilide (13).—The literature procedure[13] was modified slightly. A solution of 1 mole of aniline in 100 ml. of acetone was slowly added to a solution of 0.5 mole of 2-chloroethanesulfonyl chloride in 200 ml. of acetone, with stirring, maintaining the solution at 10–12°. At the end of the addition, the suspension was stirred for 1 hr., then concentrated *in vacuo*, keeping the pot temperature below 30°. The residue was stirred with 3 *N* hydrochloric acid, extracted with methylene chloride, and the organic layer was dried and concentrated *in vacuo*. The residual oil was molecularly distilled, giving a 40% yield of a yellow oil that crystallized. The product was recrystallized from toluene–pentane, m.p. 64–67° (lit.[13] m.p. 66–67°). The infrared spectrum of this material was essentially identical with that of the original crude oil, indicating that the dehydrohalogenation had occurred during the reaction, and not during the work-up.

Variations in the reaction involved the use of greater and lesser amounts of aniline, addition of other acid acceptors, the use of other solvents, and lower temperatures. The results were always the same.

4-Phenyl-3,4-dihydrosulfostyril (15).—A suspension of 5 g. (0.019 mole) of styrenesulfonanilide[14] in 100 g. of polyphosphoric acid was heated with stirring. At 110° the suspension appeared to transpose, and the liquid turned green. The mixture was maintained at 130° for 10 min., then cooled and poured into water. An oil separated and soon crystallized. The solid was extracted with hot cyclohexane, and the insoluble material, 3.8 g., was then recrystallized from ethanol–water (m.p. 160–161°). It was purified by sublimation at 150° (0.1 mm.) in order to remove the pink color (m.p. 161–162°, 2.8 g.).

Anal. Calcd. for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.72; H, 5.02; N, 5.37.

N-Methyl-3,4-dihydrosulfostyril (21).—Sodium methoxide (0.022 mole) was slowly added to a solution of 4 g. (0.022 mole) sulfostyril in DMF. The resulting suspension was heated on a steam bath for 15 min., then 6 ml. of dimethyl sulfate was added, whereupon the solid dissolved. The solution was heated at reflux for 2 hr., then concentrated *in vacuo*. The residual oil was stirred with water, and a solid separated and was filtered and dried (3.55 g., m.p. 80–82°). A sample was recrystallized for analysis from ethyl acetate–pentane and melted at 80–82°.

Anal. Calcd. for $C_9H_{11}NO_2S$: C, 54.80; H, 5.60; N, 7.10. Found: C, 55.04; H, 5.61; N, 6.84.

N-Phenyl-3,4-dihydrosulfostyril (17).—Cuprous chloride (0.2 g.) was added to a mixture of 4.9 g. (0.027 mole) of dihydrosulfostyril, 16 g. (0.04 mole) of diphenyliodonium iodide (Aldrich Chemical Co.), and 1.44 g. (0.027 mole) of sodium methoxide in 100 ml. of methanol. The mixture was refluxed for 2.5 days, then the yellow solution was cooled and filtered from the small amount of high-melting solid. The filtrate was concentrated *in vacuo*, and the residue was dissolved in methylene chloride and extracted with dilute sodium hydroxide solution. The organic layer was dried and concentrated, leaving as residue 4 g. of an oil that slowly crystallized and was recrystallized from 2-propanol (2.2 g., m.p. 121–123°).

Anal. Calcd. for $C_{14}H_{13}NO_2S$: C, 64.84; H, 5.05; N, 5.40. Found: C, 64.76; H, 5.05; N, 5.07.

N-(2-Dimethylaminoethyl)-3,4-dihydrosulfostyril (16, *n* = 2).—A solution of dimethylaminoethyl chloride in benzene was prepared by dissolving the hydrochloride (8.21 g., 0.057 mole) in 10 ml. of water, cooling, adding 50 ml. of benzene and, slowly, 6 ml. of 40% sodium hydroxide solution. The organic layer was separated and dried. This solution was added, with stirring, to a solution prepared by adding 1.1 g. of 55% sodium hydride dispersed in mineral oil to 4.3 g. (0.0235 mole) of dihydrosulfostyril in 50 ml. of dry dimethyl sulfoxide. After the addition of the chloride solution, the mixture was heated at reflux for 21 hr., then the benzene was distilled off, and 150 ml. of water was added. The resulting cloudy solution was extracted with ether, and the ethereal solution was dried and concentrated leaving 5.0 g. of an oil. This was dissolved again in ether and converted to the hydrochloride by addition of ethereal hydrogen chloride. The hygroscopic salt was twice recrystallized from alcohol (m.p. 130–136°, 2.2 g.). After drying *in vacuo* at 60° the melting point rose to 152–154°.

Anal. Calcd. for $C_{12}H_{19}ClN_2O_2S$: C, 49.56; H, 6.59; N, 9.63. Found: C, 49.71; H, 6.44; N, 9.70.

N-(3-Dimethylaminopropyl)-3,4-dihydrosulfostyril (16, *n* = 3).—In a similar manner to that described above, 4.0 g. (0.022 mole) of dihydrosulfostyril was treated successively with 1.1 g. of

(12) All melting points are corrected. Analyses were performed by the analytical department of these laboratories.

(13) A. A. Goldberg, *J. Chem. Soc.*, 464 (1945).

(14) F. G. Bordwell, *et al.*, *J. Am. Chem. Soc.*, **68**, 139 (1946).

55% sodium hydride dispersed in mineral oil, and then with 6.56 g. (0.0543 mole) of dimethylaminopropyl chloride. After the same type of work-up, there was obtained 6.5 g. of an oil which was converted to a hydrochloride and recrystallized from alcohol (3.2 g., m.p. 138–142°). After drying, the melting point rose to 157–158.5°.

Anal. Calcd. for $C_{13}H_{21}ClN_2O_2S$: C, 51.22; H, 6.94; N, 9.19. Found: C, 51.31; H, 7.02; N, 8.87.

6-Bromo-3,4-dihydrosulfostyril (Probable Structure) (18).—A solution of 0.27 g. (0.0015 mole) of N-bromosuccinimide in a small amount of DMF was added to a suspension of dihydrosulfostyril in DMF. Heat was evolved, and the solution turned yellow. After 5 min., the solution was diluted with water, and the product precipitated (m.p. 175–180°, 0.3 g.). A sample recrystallized from ethyl acetate–pentane melted at 183–186°.

Anal. Calcd. for $C_8H_8BrNO_2S$: C, 36.8; H, 3.06; N, 5.34. Found: C, 36.9; H, 3.02; N, 5.25.

6,8-Dibromo-3,4-dihydrosulfostyril (Probable Structure) (19).—A solution of 3.56 g. (0.02 mole) of N-bromosuccinimide in DMF was treated with 1.85 g. (0.01 mole) of dihydrosulfostyril in a manner similar to that described above. Dilution of the reaction mixture with water gave the dibromide; after recrystallization from ethyl acetate–pentane, there was obtained 1.7 g. of product (m.p. 191–193°; mixture melting point with monobromide, 140–160°).

Anal. Calcd. for $C_8H_7Br_2NO_2S$: C, 28.18; H, 2.06; N, 4.11. Found: C, 28.51; H, 2.18; N, 4.03.

In some instances when the bromination was carried out, a mixture of mono- and dibromo products was obtained, m.p. 150–170°. These could be separated by chromatography over alumina, using 1:1 benzene–ethyl acetate. The monobromo compound was eluted first.

6-Bromo-*N*-methyl-3,4-dihydrosulfostyril (Probable Structure) (20).—A mixture of 3.9 g. (0.02 mole) of N-methyldihydrosulfostyril and 3.6 g. (0.02 mole) of N-bromosuccinimide was stirred with 15 ml. of DMF. The solids slowly dissolved, and heat was evolved. The reddish brown solution was heated for 5 min. on the steam bath, then was diluted with water and the resulting precipitate was recrystallized from ethyl acetate–pentane (3.6 g., m.p. 109–111°). When a 100% excess of N-bromosuccinimide was used, again only the monobromide was obtained, in high yield.

Anal. Calcd. for $C_9H_{10}BrNO_2S$: C, 39.15; H, 3.63; N, 5.08. Found: C, 39.28; H, 3.63; N, 5.48.

6-Bromo-3,4-dihydrocarbostyril.—Solutions of 7.35 g. (0.05 mole) of 3,4-dihydrocarbostyril in warm DMF and 8.9 g. (0.05 mole) of N-bromosuccinimide in DMF were mixed and heated on a steam bath for 5 min. The solution was cooled and diluted with water, and the solid that separated was filtered and recrystallized from alcohol (5.2 g., m.p. 170–172°, lit.[10] m.p. 170–171°).

6,8-Dibromo-3,4-dihydrocarbostyril.—Dihydrocarbostyril (0.75 g., 0.005 mole) was brominated with 1.8 g. (0.01 mole) of N-bromosuccinimide in the same manner as described above. From this reaction there was obtained, after one recrystallization from ethanol, 0.65 g. of product (m.p. 144–146°, lit.[10] m.p. 147–148°).

Acknowledgment.—We wish to thank Dr. James W. Wilson for many helpful discussions, and Mr. Irving Fried for technical assistance.

Substituted Perinaphthenyl Anion Radicals[1]

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2,3-Dihydroperinaphthen-$\Delta^{1\alpha}$-malononitrile, 2,3-dihydroperinaphthen-$\Delta^{1\alpha}$-ethyl cyanoacetate, and 2-3-dihydroperinaphthen-$\Delta^{1\alpha}$-cyanoacetamide have been synthesized. Organic bases catalyze the dehydrogenation of these compounds to the corresponding cyanomethylene perinaphthenes. The anion radical of perinaphthen-$\Delta^{1\alpha}$-malononitrile was obtained by reaction with metallic sodium in tetrahydrofuran (THF). Its e.s.r. spectrum closely resembles that of radicals generated during the dehydrogenation reaction, for which a mechanism involving electron-transfer steps is proposed.

Abstraction of a hydrogen atom, a hydride ion, or a proton from the methylene group of perinaphthene generates the corresponding free radical, carbonium ion, or carbanion, respectively. The symmetry and extensive conjugation of these species imply considerable stability,[2] which is borne out by the successful generation of all three systems.[3–5] Structural consideration indicates that a substituted perinaphthenyl radical anion should be accessible from a perinaphthene derivative in which the methylenic hydrogens are replaced by an exocyclic double bond. If the substituents of this double bond are highly electronegative, the negative charge can be stabilized external to the ring system, while the electron is delocalized within the ring system. Cyanomethyleneperinaphthenes constitute appropriate precursors of this type. In this paper we describe the synthesis of perinaphthen-$\Delta^{1\alpha}$-malononitrile and perinaphthen-$\Delta^{1\alpha}$-ethyl cyanoacetate, and the generation of corresponding radical anions.

(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; Abstract, p. 84S.
(2) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2184 (1952).
(3) D. H. Reid, *Tetrahedron*, **3**, 339 (1958).
(4) R. Petit, *J. Am. Chem. Soc.*, **82**, 1972 (1960).
(5) (a) F. C. Stehling and K. W. Bartz, *J. Chem. Phys.*, **34**, 1976 (1961); (b) J. E. Bennett, *Proc. Chem. Soc.*, 144 (1961).

Results and Discussions

The dihydrocyanomethylene derivatives were prepared from perinaphthanone (**1**) by the Cope modification of the Knoevenagel condensation. Malononitrile gave 2,3-dihydroperinaphthen-$\Delta^{1\alpha}$-malononitrile (**2a**) in approximately 50% yield. It was necessary to establish that the product indeed had the structure of **2a**, and not that of the tautomer **3a**. The compound **3a**, by analogy with perinaphthene, would be expected to provide the corresponding free radical by reaction with oxygen. E.s.r. measurements in oxygen-saturated ethanolic solutions at room temperature showed no evidence of radical formation. Further proof of structure **2a** comes from the n.m.r. spectrum. This shows absorption at 3.23–3.37 p.p.m. (3.8 protons), which can be assigned to the methylenic groups, and a complex multiplet (5.83 protons) centered at 7.98 p.p.m., which is due to the aromatic hydrogen atoms.

Compounds **2b** and **2c** were prepared in a similar manner, but in somewhat lower yields.

The dehydrogenation of compound **2a** was attempted by several methods. Refluxing its solution in several solvents with chloranil or dichlorodicyanoquinone (DDQ) was unsuccessful. Bromination with N-bromosuccinimide gave a product which could not be