on paper chromatography: solvent system A, R_f 0.77; solvent system B, R_f 0.52.

Anal. Calcd. for $C_{10}H_{16}O_6N_5P \cdot 0.5H_2O$: C, 37.30; H, 4.83; N, 19.74; P, 8.48; mol. wt., 344. Found: C, 37.30; H, 4.72; N, 19.87; P, 8.46; equiv. wt. (by ultraviolet-absorption measurements), 346.6.

Preparation of Adenosine-5′-ethylphosphonate (V, R = CH_2CH_3).—A solution of ethylphosphonic acid (4.6 g., 0.041 mole), isopropylideneadenosine (6.5 g., 0.031 mole), and dicyclohexylcarbodiimide (17.3 g., 0.084 mole) in 100 ml. of dry pyridine was allowed to stand overnight at 35° and the product was isolated as described for the preparation of adenosine-5′-methylphosphonate. After recrystallization from aqueous ethanol the crystalline product (4.7 g., 54%, m.p. 193–194°) showed a single spot upon paper chromatography: solvent system A, R_f 0.70; solvent system B, R_f 0.80.

Anal. Calcd. for $C_{11}H_{16}O_6N_5P \cdot 0.5H_2O$: C, 39.13; H, 5.20; N, 19.02; P, 8.41, mol. wt., 368.3. Found: C, 39.30; H, 5.46; N. 18.91; P, 8.32; equiv. wt. (by ultraviolet-absorption measurements), 361.4.

The Chemistry of Thioether-Substituted Hydroquinones and Quinones. III. An Unexpected Rearrangement of a Heterocyclic Group

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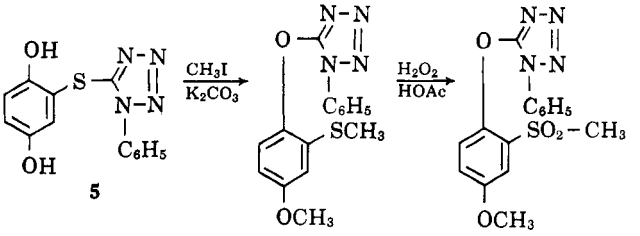
The structures of the methylation products of 1-phenyl-5-tetrazolyl thioether-substituted hydroquinones have been determined by n.m.r. studies. The structure was verified in one case by degradation and synthesis. A rearrangement of the tetrazole group from sulfur to oxygen was found to occur during the methylation.

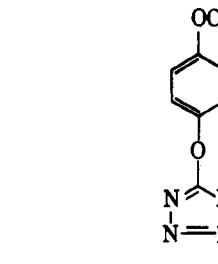
Discussion

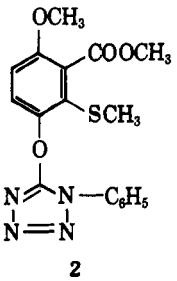
In the preceding paper[1] in this series concerned with the substituent effects in the 1,4-addition of 1-phenyl-5-mercaptotetrazole to monosubstituted quinones, it was necessary to methylate several of the resultant disubstituted hydroquinones so that the coupling constants of the hydroquinone ring protons could be determined. At first it was assumed that the expected dimethyl ethers had been obtained, but inspection of the n.m.r. spectra revealed that only one methoxyl group in the range τ 6.18–6.22 was present. However, another methyl group appeared in the range τ 7.55–7.82, suggesting the presence of an S–CH_3 group.

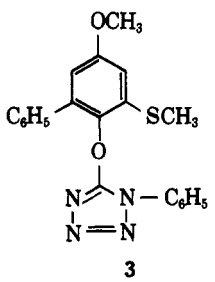
The four dimethyl derivatives, **1**, **2**, **3**, and **4**, reported previously,[1] all exhibited this S–CH_3 absorption. Inspection of the structure indicates that an unexpected rearrangement of the 1-phenyl-5-tetrazolyl group must have occurred. To elucidate this phenomenon, a simpler monothioether-substituted hydroquinone, 1′-phenyl-5′-tetrazolylthiohydroquinone[2] (**5**), was employed as a model for use in degradation studies. Methylation gave a dimethyl derivative whose n.m.r. spectrum exhibited one methoxyl at τ 6.18 and a three-proton peak at τ 7.60 indicative of an S–CH_3 group. Oxidation of this dimethyl derivative with peroxide in acetic acid produced the sulfone **7** which showed peaks in its n.m.r. spectrum at τ 6.17 and 6.76 assigned to methoxyl and methylsulfonyl, respectively. This sulfone was cleaved by strong alkali to give the tetrazole[3]

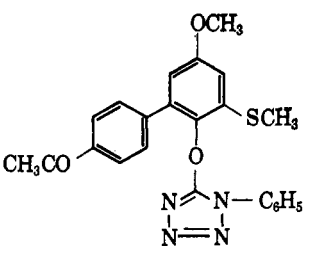


8 and the phenol **9**. The structure of **9** was confirmed by comparison with a sample synthesized by the sequence **11** → **12** → **13** → **14** → **9**. As further confirmation, the phenol **9** was allowed to react with 5-bromo-1-phenyltetrazole[4] (**10**) to produce the sulfone **7**, derived by oxidation from the original methylation product whose formula must be that represented by structure **6**. Since the methylation product **6** exhibited the S–CH_3 absorption and the sulfone **7** exhibited the









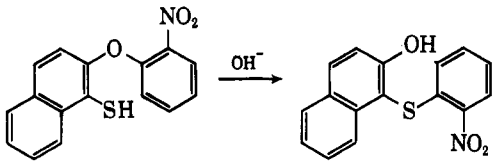
(1) H. S. Wilgus, III, E. Frauenglass, E. T. Jones, R. F. Porter, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 594 (1964).

(2) R. F. Porter, W. W. Rees, E. Frauenglass, H. S. Wilgus, III, G. H. Nawn, P. P. Chiesa, and J. W. Gates, Jr., *ibid.*, **29**, 588 (1964).

(3) (a) G. Heller and A. Siller, *J. prakt. Chem.*, [2] **123**, 257 (1929); (b) M. Freund and H. Hempel, *Ber.*, **28**, 74 (1895).

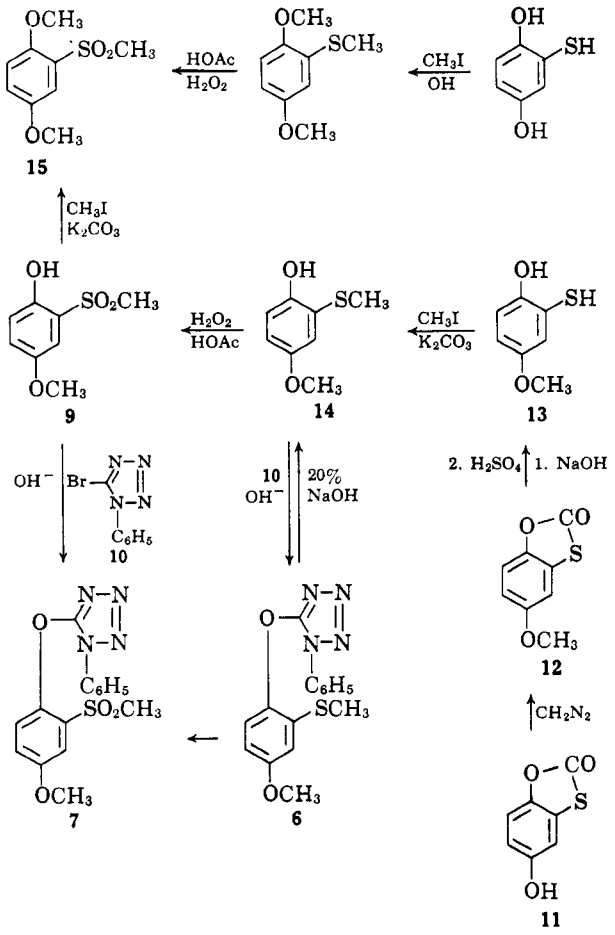
(4) R. Stolle and Fr. Henke-Stark, *J. prakt. chem.*, [2] **124**, 261 (1930).

$-SO_2-CH_3$ absorption, rearrangement had not occurred during oxidation but did occur during the methylation. This rearrangement is possibly related to the Smiles rearrangement[5] in which an activated aryl group migrates from oxygen to sulfur under the influence of



base. In the present case the rearrangement has been in the reverse direction and it appears that the alkylating agent is involved. Studies on the mechanism of the rearrangement are in progress. (See Chart I.)

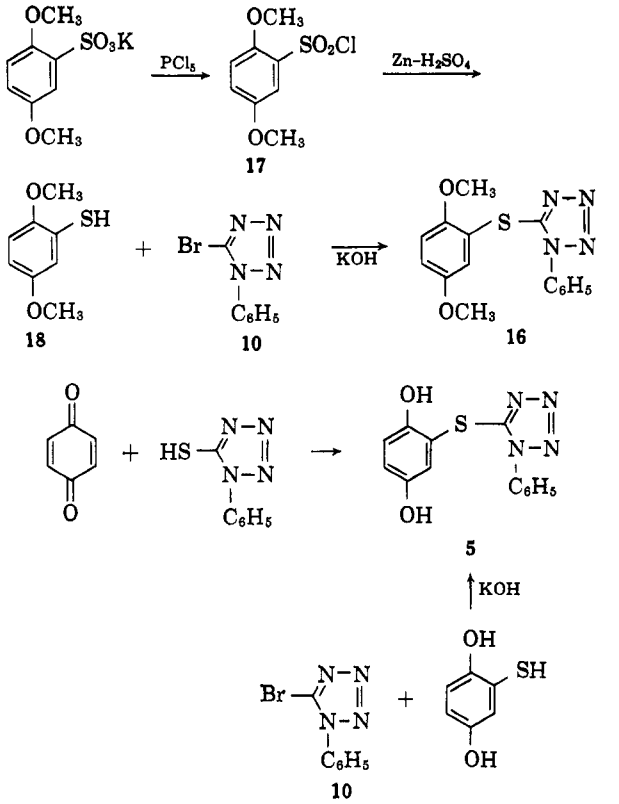
CHART I



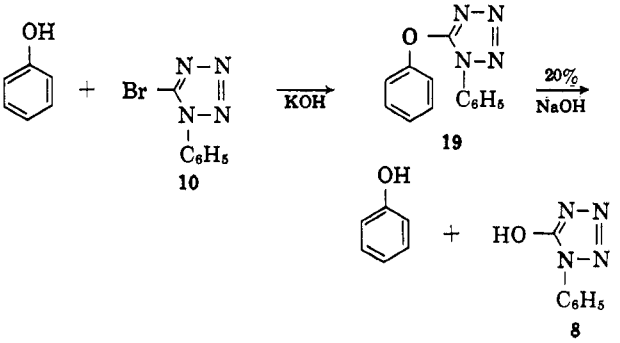
The structure of the methylation product **6** was also confirmed by reaction of 2-methylthio-4-methoxyphenol (**14**) with 5-bromo-1-phenyltetrazole (**10**).

The true dimethyl ether **16** was synthesized as indicated and shown to be different from the methylation product **6**. Compound **16** exhibited normal methoxyl absorption at τ 6.30 and 6.27 and showed no $-SCH_3$ at τ 7.60. The original hydroquinone **5** was also synthesized by an alternate route, thus confirming its identity and the original thioether structure. The reaction of mercaptohydroquinone[6] and 5-bromo-1-phenyltetrazole (**10**) produced the hydroquinone **5**.

(5) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 362 (1951).
(6) H. Burton and S. B. David, *J. Chem. Soc.*, 2193 (1952).



It is apparent that the strong alkaline cleavage reaction has not ruptured the sulfone linkage but has instead split the tetrazolyl ether linkage to produce **8** and **9**. The phenyl ether **19** of 5-hydroxy-1-phenyltetrazole (**8**) was prepared and subjected to a strong alkaline cleavage treatment to produce phenol and 5-hydroxy-1-phenyltetrazole (**8**). The cleavage of such a tetrazolyl ether is thus readily accomplished.



Experimental

The spectral measurements were made on a Perkin-Elmer Infracord spectrometer and on a Varian HR-60 instrument. Unless otherwise indicated, n.m.r. spectra were run in deuteriochloroform solution with tetramethylsilane as an internal reference. Melting points are uncorrected.

1′-Phenyl-5′-tetrazolylthiohydroquinone (5).—To a nitrogen-flushed system containing 1.12 g. of 5-bromo-1-phenyltetrazole[4] in 35 ml. of ethanol was added a nitrogen-flushed solution of 1.42 g. of mercaptohydroquinone[6] in 15 ml. of ethanol and 5 ml. of 1 *N* potassium hydroxide in ethanol. The solution was refluxed under nitrogen for 2.5 hr. and then the ethanol was removed on a rotary evaporator and the residue washed with chloroform and water. A single wash with ethanol gave 0.48 g. (34%), m.p. 201–203° dec. An infrared spectrum was identical with that of a sample obtained by the reaction of 1-phenyl-5-tetrazolylthiol with benzoquinone[1]; the mixture melting point was not depressed.

Dimethyl Derivative of 1′-Phenyl-5′-tetrazolylthiohydroquinone, 1-Methoxy-3-methylthio-4-[1′-phenyl-5′-tetrazolyloxy]benzene (6). Method A.—A solution of 14.3 g. of 1′-phenyl-5′-tetrazolylthiohydroquinone (**5**)[1] and 31.3 g. of methyl iodide in 400 ml. of dry acetone was refluxed for 8 hr. in the presence of 28 g. of anhydrous potassium carbonate. After this time, the solids were removed by filtration; the acetone solution was diluted with 200 ml. of water and evaporated until an oily precipitate appeared which solidified on chilling. This precipitate (14 g.), after two recrystallizations from alcohol, melted at 101–102°; yield, 12 g. (76%). The n.m.r. spectra showed peaks each corresponding to 3 protons at τ 6.18 and 7.60.

Anal. Calcd. for $C_{15}H_{14}N_4O_2S$: C, 57.3; H, 4.5; N, 17.8; S, 10.2. Found: C, 56.8; H, 4.5; N, 17.7; S, 10.5.

Method B.—A mixture of 2.7 g. of 4-methoxy-2-methylthiophenol (**14**) and 3.6 g. of 5-bromo-1-phenyltetrazole (**10**) in 32 ml. of 0.5 *N* ethanolic potassium hydroxide was boiled under reflux for 2 hr. After addition of benzene and water, the organic layer was separated, dried over sodium sulfate, and evaporated. The residual oil was crystallized from benzene–petroleum ether to give 2.1 g. (42%) of the phenoxytetrazole (**6**), m.p. 100–101°. Mixture melting point with the material from method A was 100–102°.

5-Methoxy-2-oxo-1,3-benzoxathiole (12).—A solution of 10.0 g. of 5-hydroxy-2-oxo-1,3-benzoxathiole[6] (**11**) in 400 ml. of ether was treated with 400 ml. of an ethereal solution containing *ca.* 11 g. of diazomethane. The resulting yellow solution was allowed to stand at room temperature for 4 days, at which time the excess diazomethane was destroyed with acetic acid. The ether solution was washed with 500 ml. of water, dried over sodium sulfate, and evaporated. The resulting solid was recrystallized from acetone–water to give 6.3 g. (58%) of crystals, m.p. 69–73°. One more recrystallization gave 6.1 g., m.p. 75–76.5°.

Anal. Calcd. for $C_8H_6O_3S$: C, 52.8; H, 3.3. Found: C, 52.7; H, 3.2.

2-Mercapto-4-methoxyphenol (13).—To 25 ml. of 2 *N* sodium hydroxide which had been deaerated with nitrogen was added 2.5 g. of 5-methoxy-2-oxo-1,3-benzoxathiole (**13**), and the resultant slurry was boiled under reflux for 1 hr. After cooling, the solution was acidified with 2 *N* sulfuric acid, saturated with sodium chloride, and extracted with ether. An oil was isolated which crystallized, giving 2 g. (93%) of the mercaptophenol **13**, m.p. 65–66°. Recrystallization from ether–cyclohexane did not raise the melting point.

Anal. Calcd. for $C_7H_8O_2S$: C, 53.7; H, 5.2; S, 20.6. Found: C, 53.3; H, 5.0; S, 20.4.

4-Methoxy-2-methylthiophenol (14). Method A.—A solution containing 1.2 g. of 2-mercapto-4-methoxyphenol (**13**) and 1.1 g. of methyl iodide in 25 ml. of dry acetone was boiled under reflux with 1.1 g. of anhydrous potassium carbonate for 3 hr. At the end of this time, the mixture was filtered, taken up in ether, and washed with water. The oil obtained from the ether layer crystallized after several days. After the solid had been washed with petroleum ether, 50 mg. of 4-methoxy-2-methylthiophenol (**14**) was obtained, m.p. 44–45°. A sample recrystallized for analysis had m.p. 47–47.5°. The n.m.r. spectrum showed peaks at τ 6.44 (OCH_3) and 7.82 (SCH_3).

Anal. Calcd. for $C_8H_{10}O_2S$: C, 56.5; H, 5.9; S, 18.8. Found: C, 56.1; H, 5.8; S, 18.8.

4-Methoxy-2-methylthiophenol (14), Cleavage of Compound 6. Method B.—A slurry containing 50 g. of **6**, 100 ml. of ethanol, and 400 ml. of a deaerated 20% sodium hydroxide solution was boiled under reflux for 1 hr., and at the end of this time the ethanol was removed by distillation. The solution was refluxed for an additional 18 hr., acidified with concentrated hydrochloric acid, and extracted with ether. The organic layer was washed with saturated potassium bicarbonate several times and dried over sodium sulfate, and the solvent was removed, leaving 28 g. of an oil. Repeated crystallization from ether–petroleum ether gave 9 g. (33%) of 4-methoxy-2-methylthiophenol (**14**), m.p. 47–47°, which was identical by mixture melting point (m.m.p. 44–46°) and infrared spectra with the material obtained by method A.

The combined aqueous bicarbonate layers were acidified and the white solid was collected. Recrystallization from ethanol gave 10 g. (39%) of 5-hydroxy-1-phenyltetrazole (**8**),[3] m.p. 187–188°, which was identified by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.

Sulfone of 6, 1-Methylsulfonyl-3-methoxy-6-[1′-phenyl-5′-tetrazolyloxy]benzene (7). Method A.—To a solution of 4.5 g. of the dimethyl derivative **6** in 100 ml. of glacial acetic acid 14.2 g. of 30% hydrogen peroxide was added and the resultant solution was heated for 6 hr. at 80°. At the end of this time the solution was evaporated under vacuum to a volume of 20 ml., diluted with alcohol, and chilled. A white powder, m.p. 138–140°, 4.3 g. (88%), was formed. After recrystallization from alcohol, it had m.p. 142–143°.

Anal. Calcd. for $C_{15}H_{14}N_4O_4S$: C, 52.0; H, 4.1; N, 16.2; S, 9.2. Found: C, 51.7; H, 3.8; N, 16.3; S, 9.2.

Method B.—To 2.25 g. of 5-bromo-1-phenyltetrazole in 35 ml. of boiling ethanol was added 2.02 g. of 2-methylsulfonyl-4-methoxyphenol (**9**) dissolved in 10 ml. of 1 *N* ethanolic potassium hydroxide. The resulting brown mixture was refluxed overnight and filtered, and the ethanol was removed on a rotary evaporator. The residue was taken up in chloroform and washed with 5% sodium hydroxide and then with water. After the solution had been dried over sodium sulfate, the chloroform was evaporated and the residue taken up in hot ethanol. A brown precipitate was formed upon cooling the solution and was removed by filtration. The mother liquors deposited 1.28 g. of white needles, m.p. 140–141°, with sintering at 138°. An infrared spectrum of this product was identical with that obtained in method A.

2-Methylsulfonyl-4-methoxyphenol (9). Method A.—A solution containing 1.5 g. of 4-methoxy-2-methylthiophenol (**14**) in 10 ml. of acetic acid was treated with 6 ml. of a 35% hydrogen peroxide solution and the mixture was heated on a steam bath for 2 hr. After addition of benzene and crushed ice, the organic layer was separated, washed with water, dried over sodium sulfate, and evaporated. The residual solid was recrystallized from benzene to give 1.3 g. (73%) of the sulfonyl compound **9**, m.p. 119–121°. A sample recrystallized for analysis had m.p. 122–123°. The n.m.r. spectrum showed two peaks, each corresponding to 3 protons, at τ 6.20 and 6.87.

Anal. Calcd. for $C_8H_{10}O_4S$: C, 47.5; H, 5.0; S, 15.8; OCH_3, 15.3. Found: C, 47.6; H, 5.0; S, 16.2; OCH_3, 15.1.

Cleavage of Compound 7. Method B.—A suspension of 26 g. of the methylation product **7** in 190 ml. of 20% sodium hydroxide solution to which 75 ml. of ethanol had been added was refluxed for 1 hr. until all the solid material had dissolved. The ethanol was then removed by distillation and refluxing was continued for 4 to 5 hr. At the end of this time the clear solution was cooled and acidified with concentrated hydrochloric acid, and the resultant slurry was exhaustively extracted with ether. After the combined ether extracts had been dried, they were evaporated to approximately 800 ml., at which point recrystallization started. The extracts were then shaken with two 200-ml. portions of saturated sodium bicarbonate solution, again dried, and then evaporated to dryness to yield 11 g. (66%) of material, m.p. 116–120°. Recrystallization from benzene or benzene–ligroin gave material **9**, m.p. 122–123°, which was identical by melting point, mixture melting point, and infrared spectrum with the material produced by method A.

Acidification of the combined bicarbonate washings and recrystallization of the collected precipitate gave 9.5 g. (71%) of 5-hydroxy-1-phenyltetrazole (**8**), m.p. 185–186°, which was identical by mixture melting point and infrared spectrum with the authentic sample.[3]

1,4-Dimethoxy-2-methylsulfonylbenzene (15). Method A.—A mixture of 2.8 g. of mercaptohydroquinone,[6] 16.5 g. of anhydrous potassium carbonate, and 21.5 g. of methyl iodide in 400 ml. of dry acetone was boiled under reflux for 18 hr. The solids were filtered and benzene and water were added to the filtrate. The organic layer was separated, dried over sodium sulfate, and evaporated. The oil residue, 6 g., was dissolved in 50 ml. of acetic acid and treated with 15 ml. of 35% hydrogen peroxide, and the resulting solution was boiled under reflux for 2 hr. The solution was poured over crushed ice and extracted with benzene. Evaporation of the benzene layer gave 4 g. (94%) of a solid, m.p. 77–78° (lit.[7] m.p. 77°).

Anal. Calcd. for $C_9H_{12}O_4S$: C, 50.0; H, 5.6. Found: C, 49.8; H, 5.4.

Method B.—A solution of 2 g. of 2-methanesulfonyl-4-methoxyphenol (**15**) obtained from the cleavage of **7** and 5 g. of methyl iodide in 100 ml. of dry acetone was refluxed for 18 hr. in the presence of 3 g. of anhydrous potassium carbonate. At the end of this time the solution was filtered and evaporated to dryness. The residual oil was crystallized from ethanol–water: yield, 1.85 g. (86%), m.p. 62–66°. Recrystallization from ethanol–water

(7) H. Burton and E. Hoggarth, *J. Chem. Soc.*, 14 (1945).

gave 1.2 g., m.p. 76–78°, which was identical by melting point, mixture melting point, and infrared spectrum with the material prepared by method A.

2,5-Dimethoxybenzenesulfonyl Chloride (17).—2,5-Dimethoxybenzenesulfonic acid was prepared by the method of Baker and Evans[8] and converted to its potassium salt. Interaction of the potassium salt with phosphorus pentachloride gave 2,5-dimethoxybenzenesulfonyl chloride which, after recrystallization from chloroform–petroleum ether (b.p. 60–80°), melted at 115–116°.

Anal. Calcd. for $C_8H_9ClO_4S$: C, 40.6; H, 3.8; S, 13.6. Found: C, 41.0; H, 4.1; S, 13.5.

2,5-Dimethoxybenzenethiol (18).—2,5-Dimethoxybenzenesulfonyl chloride was reduced with zinc and sulfuric acid as described[9] for the reduction of benzenesulfonyl chloride. The product had b.p. 142° at 18 mm. (lit.[7] b.p. 138–140° at 20 mm.).

2,5-Dimethoxy-1-(1′-phenyl-5′-tetrazolylthio)benzene (16).—A solution of 3.44 g. of 2,5-dimethoxybenzenethiol in 20 ml. of 1 *N* ethanolic potassium hydroxide was added to 4.5 g. of 5-bromo-1-phenyltetrazole in ethanol. The mixture was refluxed for 14 hr., cooled, and filtered to remove potassium bromide. The product (5.5 g., 88%) was recrystallized from ethanol, m.p. 116–117°.

Anal. Calcd. for $C_{15}H_{14}N_4O_2S$: C, 57.3; H, 4.5; N, 17.8. Found: C, 57.5; H, 4.3; N, 17.6.

5-Phenoxy-1-phenyltetrazole (19).—A mixture of 1.88 g. of phenol, 4.50 g. of 5-bromo-1-phenyltetrazole, 100 ml. of ethanol, and 20 ml. of 1 *N* potassium hydroxide in ethanol was refluxed overnight, the ethanol was evaporated, and the residue was extracted with chloroform. This solution was washed with cold 5% sodium hydroxide and then with water. The chloroform was removed by evaporation and the oil was dissolved in ether from which white crystals were obtained. Two recrystallizations from ethanol gave 0.95 g. (20%), m.p. 124.5–126.5°.

Anal. Calcd. for $C_{13}H_{10}N_4O$: C, 65.5; H, 4.2; N, 23.5. Found: C, 65.3; H, 4.3; N, 23.8.

Hydrolysis of 5-Phenoxy-1-phenyltetrazole (19).—A mixture of 0.66 g. of 5-phenoxy-1-phenyltetrazole (19) and 20 ml. of 1 *N* sodium hydroxide was refluxed overnight to give a solution. Filtration, followed by acidification with dilute hydrochloric acid, gave a white precipitate which was washed with water to remove the odor of phenol. The dried product weighed 0.35 g. (79%) and melted at 188–190°. An infrared spectrum of this compound was identical with that of a known sample of 5-hydroxy-1-phenyltetrazole (8).

Acknowledgment.—The authors gratefully acknowledge the assistance of Mr. C. M. Combs and Dr. J. K. O'Loane in the preparation and interpretation of the n.m.r. spectra.

(8) W. Baker and C. Evans, *J. Chem. Soc.*, 372 (1938).

(9) R. Adams and C. S. Marvel, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 504.

The Synthesis of a Pyrido[1,2-*a*]azepine. A New Heterocyclic System[1]

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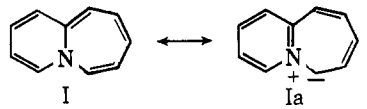
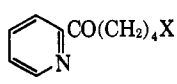
The cyclization of 2-(5′-ethoxyvaleryl)pyridine (II) gives the cyclic ketone (IV) which has been converted into the 9-bromo- and 9,9-dibromo-10,10-dihydroxypyridoazepinium salts (V and VI). Boiling acetic anhydride converted the dibromo compound (VI) into 10-acetoxy-9-bromo-6H-pyrido[1,2-*a*]azepinium bromide (IX) and bromination of this gave 7,9- dibromo-6H-pyrido[1,2-*a*]azepinium bromide (XII), converted by base into 7,9-dibromo-10-hydroxypyrido[1,2-*a*]azepine (XIII). The hydrogenations of the azepine (XIII) to a 2-pyridylpentanal acetal (XVI) and to the 10-hydroxytetrahydropyridoazepinium salt (XV) are described.

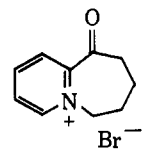
While the indolizine and quinolizinium systems are well known, and while there has been much recent interest in azepine chemistry, no attempts to prepare a pyrido[1,2-*a*]azepine system (I) have yet been reported. Although a fully aromatic form (with ten π-electrons and all atoms trigonal) cannot be achieved, some stabilization should be achieved by virtue of the carbon betaine structures (such as Ia) and still more stabilization was expected in the 6-, 8-, or 10-hydroxy systems. As we have previously devised a satisfactory method for the synthesis of a 1-hydroxyquinolizinium salt,[2] we decided to apply a modified version of this synthesis to the production of a 10-hydroxypyrido[1,2-*a*]azepine, thus obtaining the first member of this heterocyclic system.



I Ia



II, X = OC_2H_5
III, X = Br



IV

The starting material for the synthesis was the 2-pyridyl ketone (II) obtained from 2-cyanopyridine and 4-ethoxybutylmagnesium bromide. In the quinolizinium series the cyclization of a similar ketone was achieved by cleavage of the ether with hydrobromic acid and cyclization of the crude bromo ketone so obtained in refluxing chloroform. Only a poor yield of cyclic ketone (IV) was obtained in this manner, but the crude bromo ketone (III) was satisfactorily cyclized by heating without solvent to 130°. The infrared and ultraviolet absorption of the cyclic ketone (IV) were similar to those of 1-oxo-1,2,3,4-tetrahydroquinolizinium bromide,[3] notably in the position of the carbonyl stretching frequency at 1700 cm.$^{-1}$. Bromination of the cyclic ketone (IV) with bromine in concentrated hydrobromic acid proceeded readily, giving a mono- or dibromo product depending on the amount of bromine used. Neither brominated product showed more than vestigial carbonyl absorption in the infrared region and the ultraviolet spectra resemble that of a

(1) Presented before the Organic Chemical Division at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) A. Fezard and G. Jones, *J. Chem. Soc.*, 2203 (1963).

(3) E. E. Glover and G. Jones, *ibid.*, 1750 (1958). The quinolizinium bromide has λ_{max}^{EtOH} 2350 and 2750 Å. ($\log_{10}\epsilon$ 3.62 and 3.89); the shift of the second maximum to shorter wave length (2680 Å.) in the ketone (IV) is in accord with the known lowering of conjugation when a chromophore attached to an aromatic ring is contained in a fused seven-membered ring [for an example, see W. R. Remington, *J. Am. Chem. Soc.*, **67**, 1838 (1945), where the spectra of N-methyltetrahydroquinoline and N-methylhomotetrahydroquinoline are compared].