Methylation of Aromatic Hydrocarbons by Dimethyl Sulfoxide in the Presence of Base[1]

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Received September 9, 1965

The methylsulfinyl carbanion ($CH_3SOCH_2^-$) is a unique methylating agent of the ylide type. Quinoline, isoquinoline, anthracene, phenanthrene, acridine, phenanthridine, and benzoxazole are converted to methyl derivatives by reaction with the methylsulfinylcarbanion in dimethyl sulfoxide solution at 70°.

The methylsulfinyl carbanion ($CH_3SOCH_2^-$)[2] is recognized to add to carbonyl[2-4] and olefinic[4] systems. We have found that the methylsulfinyl carbanion will also add to certain aromatic systems (AH) and that such additions can lead to the methylated aromatics in high yields.[5]

$$AH + CH_3SOCH_2^- \longrightarrow [AHCH_2SOCH_3]^- \longrightarrow ACH_3 + CH_3SO^-$$

This methylation reaction provides an explanation for the fact that many nitro aromatics not containing an acidic benzylic-type hydrogen atom slowly form the corresponding radical anions ($ArNO_2^{\cdot-}$) when dissolved in dimethyl sulfoxide (DMSO)–*t*-butyl alcohol mixtures (4:1) containing an excess of potassium *t*-butoxide.[6] Figure 1 shows the fully resolved 54-line e.s.r. spectrum of nitrobenzene radical anion formed in pure DMSO. The formation of nitrobenzene radical anion apparently involves the reduction of nitrobenzene by the transfer of one electron from some carbanion in the reaction mixture.[7] The donor may well be the *p*-nitrobenzyl anion since, when nitrobenzene in DMSO (80%)–*t*-butyl alcohol (20%)–potassium *t*-butoxide mixtures is shaken for an extended period of time in an oxygen atmosphere, the nitrobenzene is consumed and the major acidic product formed is a mixture of *o*- and *p*-nitrobenzoic acids. Under the reaction conditions *p*-nitrotoluene readily undergoes oxidation–reduction reactions yielding the *p*-nitrotoluene radical anion in the absence of oxygen.[6] In the presence of oxygen, *p*-nitrobenzoic acid is formed in high yield. The formation of nitrobenzoic acids and nitrobenzene radical anion during the initial stages of the reaction of nitrobenzene in basic DMSO solutions can be explained by

$$C_6H_5NO_2 + CH_3SOCH_2^- \longrightarrow o\text{- (or } p\text{-) } CH_3C_6H_4NO_2 + CH_3SO^-$$

$$NO_2C_6H_4CH_3 \rightleftharpoons NO_2C_6H_4CH_2^-$$

$$NO_2C_6H_4CH_2^- + C_6H_5NO_2 \text{ (excess)} \longrightarrow C_6H_5NO_2^{\cdot-} + NO_2C_6H_5CH_2\cdot$$

or by

$$CH_3C_6H_4NO_2 \xrightarrow{B^-} CH_3C_6H_4NO_2^{\cdot-} + \text{oxidation products}$$

$$CH_3C_6H_4NO_2^{\cdot-} + C_6H_5NO_2 \text{ (excess)} \longrightarrow C_6H_5NO_2^{\cdot-} + CH_3C_6H_4NO_2$$

Additional evidence for a methylation reaction by the methylsulfinyl carbanion is the observation that treatment of phenylglyoxal with a solution of potassium *t*-butoxide in DMSO spontaneously forms the radical anion of 1-phenylpropane-1,2-dione, $C_6H_5C(O\cdot)=C(O^-)CH_3$.[8] Under the reaction conditions, 1-phenylpropane-1,2-dione undergoes oxidation–reduction reactions to form the observed semidione.[9] The entire reaction sequence is reasonably formulated as

$$C_6H_5COCHO + CH_3SOCH_2^- \longrightarrow C_6H_5COCH(O^-)CH_2SOCH_3$$

$$C_6H_5COCH(O^-)CH_2SOCH_3 \longrightarrow [C_6H_5COC(OH)CH_2SOCH_3]^- \longrightarrow C_6H_5COC(OH)=CH_2 + CH_3SO^- \longrightarrow$$

$$C_6H_5COCOCH_3 \xrightarrow{B^-} C_6H_5COCOCH_2^-$$

$$C_6H_5COCOCH_2^- + C_6H_5COCOCH_3 \longrightarrow C_6H_5C(O\cdot)=C(O^-)CH_3 + C_6H_5COCOCH_2\cdot$$

$$C_6H_5COCOCH_2\cdot \longrightarrow \text{nonradical products}$$

Because of the oxidation–reduction reactions inherently connected with α-diketones and *o*- (or *p*-) nitrotoluene derivatives in basic solutions,[6] the methylation reaction was not unequivocally proven by the isolation of the presumed initial methylated species (*o*- and *p*-nitrotoluene, 1-phenylpropane-1,2-dione). We therefore decided to study other aromatic materials wherein anionic addition might be expected to occur readily, but the initial methylated species would be less susceptible to complicating side reactions involving electron transfer.

Benzene, pyridine, naphthalene, or thianaphthene do not react with the methylsulfinyl carbanion in DMSO solution during periods of several hours at 70°. However, quinoline and isoquinoline react readily at 70° to yield 4-methylquinoline (lepidine) and 1-methylisoquinoline in nearly quantitative yield. The products are in agreement with the calculated charge densities of these heterocyclic materials.[10]

Anthracene, phenanthrene, acridine, and phenanthridine react to form methylated derivatives readily. Phenazine fails to react at 70°. Anthracene forms 9-methyl- or 9,10-dimethylanthracene depending on conditions. Phenanthridine forms 6-methylphenan-

(1) Reactions of Resonance Stabilized Anions. XX. For Paper XIX, see E. R. Talaty and G. A. Russell, *J. Am. Chem. Soc.*, in press. This work was supported by a grant from The Army Office of Research (Durham).

(2) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962).

(3) G. A. Russell, E. G. Janzen, H. D. Becker, and F. Smentowski, *ibid.*, **84**, 2652 (1962); M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963).

(4) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963); **29**, 2699 (1964).

(5) See also (a) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *ibid.*, **30**, 3233 (1965); (b) V. J. Traynelis and J. V. McSweeney, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 125.

(6) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

(7) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

(8) G. A. Russell, R. D. Stephens, and E. R. Talaty, *Tetrahedron Letters*, 1139 (1965).

(9) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).

(10) D. A. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 2406 (1953).

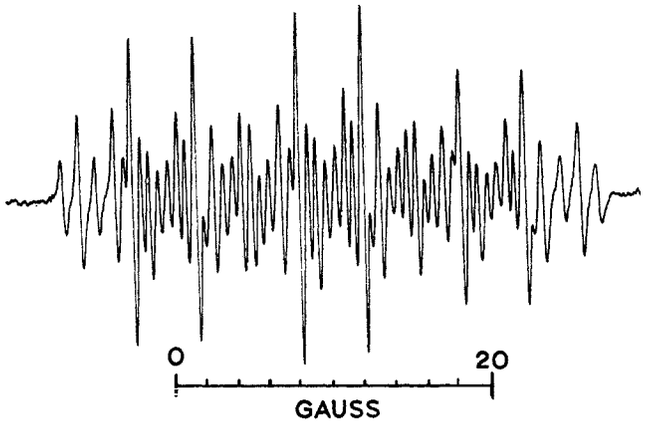
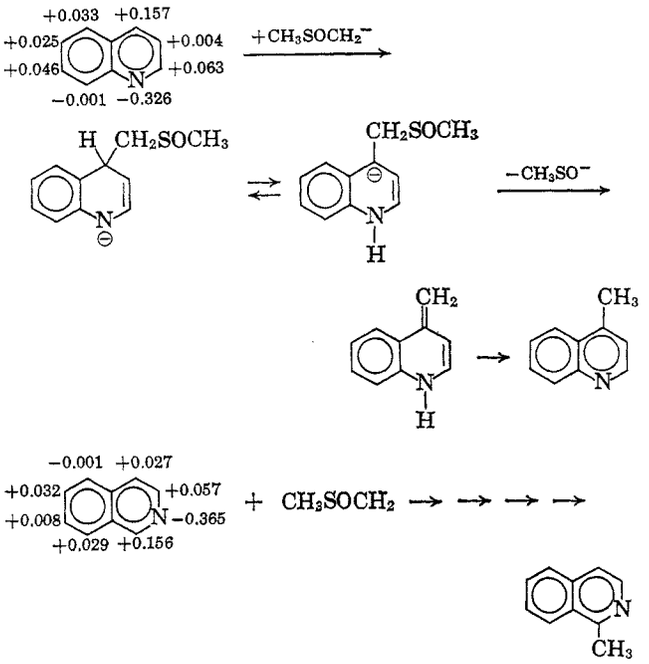
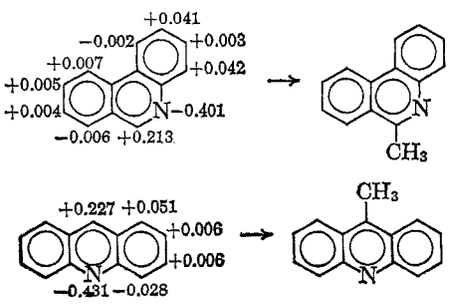


Figure 1.—First-derivative e.s.r. spectrum (~9.5 gigacycle/sec.) of nitrobenzene radical anion formed spontaneously from nitrobenzene in dimethyl sulfoxide solution containing potassium *t*-butoxide (0.10 *M*) at 25°. The 54-line spectrum is consistent with $a_m^H = 1.01$, $a_o^H = 3.39$, $a_p^H = 3.94$, and $a^N = 10.10$ gauss.



thridine in nearly quantitative yield. Phenanthrene and acridine yield their 9-methyl and 10-methyl derivatives, respectively.[11]



The methylation of anthracene has been studied most thoroughly because of the formation of mono- and dimethylated products and because of the presence of paramagnetic substances during the reaction. Table I summarizes the methylation conditions investigated.

(11) Charge densities given in ref. 10 and by H. C. Longuet-Higgins and C. A. Coulson, *J. Chem. Soc.*, 971 (1949).

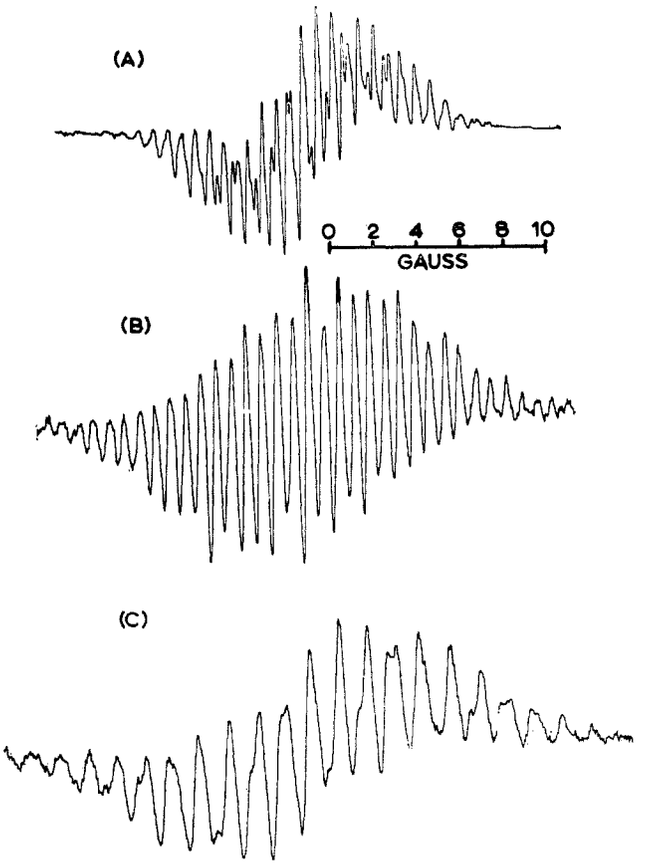


Figure 2.—First-derivative e.s.r. spectra (~9.5 gigacycle/sec.) in dimethyl sulfoxide solution at 25°: (a) observed immediately upon treatment of anthracene with the methylsulfinyl carbanion at 70°; (b) after 4 hr. at 70°; and (c) radical anion formed by treatment of 9,10-dimethylanthracene with the methylsulfinyl carbanion.

Treatment of naphthalene with basic solutions of DMSO fails to produce any e.s.r. signal. Phenanthrene yields a shortlived signal of low intensity under the methylation conditions. However, anthracene under methylation conditions yields a fairly intense e.s.r. signal that changes with time. Figure 2a gives the first derivative e.s.r. spectrum observed initially when anthracene (An) is allowed to react with the methylsulfinyl carbanion at 70°. The signal is also observed for reaction at 25° and is attributed to the anthracene radical anion, possibly formed *via* the following series of reactions.[12] As the methylation proceeds,

$$\mathrm{An} + \mathrm{CH_3SOCH_2^-} \longrightarrow \longrightarrow \mathrm{AnCH_3}$$
$$\mathrm{AnCH_3} + \mathrm{B^-} \rightleftharpoons \mathrm{AnCH_2^-}$$
$$\mathrm{AnCH_2^-} + \mathrm{An\ (excess)} \longrightarrow \mathrm{An^{\cdot-}} + \mathrm{AnCH_2\cdot}$$
$$\mathrm{AnCH_2\cdot} \longrightarrow \text{nonradical products}$$

the e.s.r. signal changes with loss of hyperfine structure. The over-all width of the signal also increases (Figure 2b). Figure 2c gives the e.s.r. signal observed when pure 9,10-dimethylanthracene is allowed to react with the methylsulfinyl carbanion at 70° and is attributed to the 9,10-dimethylanthracene radical anion. The results appear to be not inconsistent with the equilibrium

$$\mathrm{An^{\cdot-}} + (\mathrm{CH_3})_2\mathrm{An} \rightleftharpoons (\mathrm{CH_3})_2\mathrm{An^{\cdot-}} + \mathrm{An}$$

(12) The possibility that the donor anion is $[\mathrm{AnCH_2SOCH_3}]^-$ cannot be excluded.

TABLE I

METHYLATION PRODUCTS OF ANTHRACENE

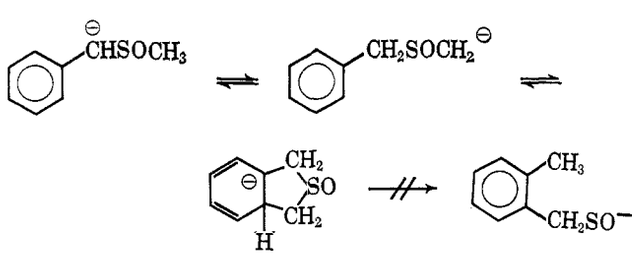
Solvent				Base	Product[a]	
DMSO, %	THF, %	Temp., °C.	Time, hr.	(ratio of B^-/anthracene)	9-Methyl	9,10-Dimethyl
80	20	25	8	NaH (4/1)	0	96
80	20	25	8	NaH (1/1)	33.5	7
80	20	70	2	*t*-BuOH (3/1)	42	2
100		70	2	*t*-BuOH (4.5/1)	67	..
100		70	2.5	*t*-BuOK (4.5/1)	74	4
100		70	4.5	*t*-BuOK (4.5/1)	63	34
80	20	25	20	NaH (10/1)	30[b]	
100		70	4	NaH (10/1)	93[b]	

[a] Determined by gas–liquid partition chromatography. [b] Methylation products of phenanthrene.

As the methylation proceeds, the intermediate radical anion changes from An^- to $AnCH_3^-$ to $An(CH_3)_2^-$ or to mixtures thereof. It does appear that the formation of radical anion is a side reaction and in no way connected with the ionic methylation reaction.

Benzoxazole was converted to its 2-methyl derivative in about 50% yield by reaction with the methylsulfinyl carbanion in DMSO at 70° for 4 hr. Reaction of benzofuran under these conditions yielded an essentially quantitative yield of *o*-hydroxyphenylacetylene.[13] Attempts to benzylate anthracene or phenanthrene with dibenzyl sulfoxide were unsuccessful owing to the formation of stilbene.[14]

We felt that a benzyl methyl sulfoxide might undergo a Sommelet–Hauser rearrangement in basic solution.[15] However, treatment of benzyl methyl sulfoxide with 1 molar equiv. of sodium hydride in refluxing tetrahydrofuran for 24 hr. yielded only unreacted starting material.



Methylation of aromatics by ylide-type reagents is not a general process except in the Sommelet–Hauser reaction.[5b,15] Under conditions wherein the methylsulfinyl carbanion gave high yields of methylanthracenes or methylphenanthrene, we were unable to detect more than traces of methylated derivatives by the use of equal molar mixtures of sodium hydride and trimethylsulfoxonium iodide, trimethylsulfonium iodide, or tetramethylammonium bromide in DMSO solution at 70°. The starting anthracene or phenanthrene was recovered unchanged.

Experimental Section[16]

Oxidation of Nitrobenzene in Dimethyl Sulfoxide Solution.—A solution of 20 ml. of DMSO, 5 ml. of *t*-butyl alcohol, 1.35 g. of potassium *t*-butoxide (0.48 *M*), and 0.31 ml. of nitrobenzene (0.12 *M*) was shaken in a creased flask in an oxygen atmosphere at 25° until the rate of oxygen absorption became quite slow (6 hr.). Analysis by g.l.p.c. (20% Carbowax, 148°) with chlorobenzene as an internal standard indicated a final concentration of nitrobenzene of 0.04 *M*. Hydrolysis of the oxidate with water followed by benzene extraction yielded an aqueous solution which upon acidification yielded an ether extract. Evaporation of the ether and sublimation at 145° (1 mm.) yielded a yellow solid, m.p. 145–170°. The sublimate was treated with an excess of diazomethane in ether solution, and the resulting methyl esters were analyzed by g.l.p.c. using a 20% Carbowax column at 135° and, independently, a 20% SE-30 column at 210°. The major components of the methylated sublimate were *o*- and *p*-nitrobenzoate methyl esters which had identical retention times with authentic samples on both columns employed.

Methylsulfinyl Carbanion ($CH_3SOCH_2^-$).—The methylsulfinyl carbanion was prepared in a nitrogen atmosphere either by dissolving potassium *t*-butoxide (Mine Safety Appliance Research Corp.) in DMSO or by reaction of sodium hydride (Metal Hydrides Corp.) which had been washed with Skellysolve B. The sodium hydride–DMSO mixture was stirred vigorously at 70° until the sodium hydride dissolved.

9-Methylanthracene.—To a solution of 3 g. of potassium *t*-butoxide dissolved in 75 ml. of DMSO at 70° under a nitrogen atmosphere was added 1 g. of anthracene dissolved in 75 ml. of warm DMSO. The reaction mixture was stirred for 2 hr. at 70° and treated with aqueous acid, and the resulting precipitate was filtered from a large excess of water. The precipitate was dissolved in chloroform; the chloroform solution was washed with water and dried with magnesium sulfate. Analysis of the chloroform solution indicated the presence of unreacted anthracene and 67% of 9-methylanthracene, based upon starting anthracene. 9-Methylanthracene and anthracene are not easily separated except by g.l.p.c.

9,10-Dimethylanthracene.—To a solution of 5.3 g. (0.22 moles) of sodium hydride in 75 ml. of DMSO at 25° was added 10 g. (0.056 moles) of anthracene (dissolved in a mixture of 85 ml. of DMSO and 40 ml. of THF) over a 5-min. period with rapid stirring. The reaction mixture was stirred for 8 hr. at 25°, and the product was isolated as described for 9-methylanthracene. The final chloroform solution contained no anthracene or 9-methylanthracene and was estimated to contain a 96% yield of 9,10-dimethylanthracene by g.l.p.c. using a 3% SE-30 column at 215°. Removal of the chloroform gave a yellow solid that was recrystallized from benzene to yield 9,10-dimethylanthracene, m.p. 182–183.5°, lit.[17] m.p. 180–182°.

9-Methylphenanthrene.—To a solution of 2.64 g. of sodium hydride (0.11 mole) in 100 ml. of DMSO at 70° was added 2 g. (0.011 mole) of phenanthrene in 50 ml. of DMSO. The solution was stirred for 4 hr. at 70° followed by the addition of 100 ml. of a 1:1 mixture of concentrated hydrochloric acid and water. The product was isolated as in the preparation of 9,10-dimethylanthracene. The crude solid was analyzed by g.l.p.c. in carbon tetrachloride which indicated a yield of 9-methylphenanthrene of 93% by use of a 3% SE-30 column at 189°. One recrystallization of the crude solid from methanol gave 1.88 g. of material, m.p. 80–84°. Two further recrystallizations from methanol yielded 1.64 g. (76%), m.p. 89–91°, lit.[18] m.p. 92–93°.

(13) *o*-Hydroxyphenylacetylene is also formed by the reaction of sodium in refluxing pyridine with benzofuran: Y. Odaira, *Bull. Chem. Soc. Japan*, **29**, 470 (1956).

(14) T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriescheim, *Proc. Chem. Soc.*, 137 (1963).

(15) S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

(16) All methylated derivatives had infrared and n.m.r. spectra consistent with the assigned structure. Their g.l.p.c. retention times were consistent with those of authentic samples. Melting and boiling points are uncorrected.

(17) G. M. Badger, F. Goulden, and F. L. Warren, *J. Chem. Soc.*, 18 (1941).

(18) E. J. Greenhow, D. McNeil, and E. N. White, *ibid.*, 986 (1952).

9-Methylacridine.—To a solution of 2.64 g. (0.11 mole) of sodium hydride in 125 ml. of DMSO at 70° was added 2 g. of acridine (0.011 mole) in 80 ml. of DMSO. The reaction mixture was stirred for 4 hr. at 70° under a nitrogen atmosphere followed by addition of 125 ml. of water. The reaction mixture was added to 1500 ml. of water which was extracted three times with chloroform to yield a yellow oil after removal of the chloroform. The yellow oil in chloroform as analyzed by g.l.p.c. on a 3% SE-30 column at 200° indicated a yield in excess of 98% of 9-methylacridine. Upon heating the yellow oil in a flask at 90° under high vacuum, yellow needles formed on walls of the flask. These were collected and resublimed at 93° and 1 mm. and recrystallized from Skellysolve B to yield yellow needles, m.p. 115–117°, lit.[19] m.p. 118–118.5°.

6-Methylphenanthridine.—To a solution of 2.64 g. (0.11 mole) of sodium hydride in DMSO at 70° was added 2 g. of phenanthridine (0.011 mole) in 60 ml. of DMSO. The reaction mixture was stirred for 4 hr. at 70° under a nitrogen atmosphere followed by the addition of 125 ml. of water. The reaction mixture was added to 1500 ml. of water which was extracted three times with chloroform. The chloroform extract yielded an oil which was analyzed by g.l.p.c. on a 3% SE-30 column at 200° to contain more than a 98% yield of 6-methylphenanthridine. The oil dissolved in Skellysolve B was passed through 50 g. of Woelm alumina, grade III. Crystallization of the eluent gave white crystals which were sublimed at 73° and 1 mm. The resulting needles had m.p. 84–85°, lit.[20] m.p. 85°.

1-Methylisoquinoline.—To a solution of 2.64 g. (0.11 mole) of sodium hydride in 100 ml. of DMSO at 70° was added 2.2 ml. of isoquinoline (0.019 mole) in 100 ml. of DMSO. The reaction mixture was stirred at 70° for 4 hr. under a nitrogen atmosphere, 100 ml. of water was added, and the reaction mixture was poured into 1500 ml. of water. The aqueous solution was extracted with benzene. Removal of the benzene yielded an oil which was analyzed by g.l.p.c. Analysis with a 3% SE-30 column at 140° indicated a quantitative yield of 1-methylisoquinoline. The oil distilled at 62–66° at 4 mm. and formed a picrate, m.p. 227°; the picrate of 1-methylisoquinoline is reported to melt at 225–228°.[21]

4-Methylquinoline.—4-Methylquinoline was prepared in 96% yield by a process similar to that employed in the synthesis of 1-methylisoquinoline. The resulting oil distilled at 60–65° at 4 mm. and formed a picrate, m.p. 212–216°, lit.[19] m.p. (picrate) 217°.

2-Methylbenzoxazole.—To a solution of 2.64 g. (0.11 mole) of sodium hydride in 125 ml. of DMSO at 70° was added 2.3 ml. of benzoxazole (0.021 mole). The solution was stirred for 4 hr. at 65° whence 125 ml. of water was added. The reaction mixture was poured into 1500 ml. of water which was extracted with ether. Evaporation of the ether left a crude oil which was analyzed on a 3% SE-30 column at 153°. The analysis indicated a 50% yield of 2-methylbenzoxazole.

***o*-Hydroxyphenylacetylene.**—When the methylation of benzofuran was attempted under the methylation conditions employed for quinoline and isoquinoline, the resulting product after distillation had a n.m.r. spectrum (60 Mc./sec.) with a sharp singlet (intensity 1.0) at 3.34 p.p.m. (relative to tetramethylsilane), a broadened singlet (intensity 1.02) at 4.07 p.p.m. that was exchangable with deuterium oxide, and a complex multiplet at 6.98 p.p.m. (intensity 4.35).

(19) O. Tsuge, M. Nishinohara, and N. Tashiro, *Bull. Chem. Soc. Japan*, **36**, 1477 (1963).

(20) C. L. Arcus and M. M. Coombs, *J. Chem. Soc.*, 4319 (1954).

(21) E. H. White and H. C. Dunathan, *J. Am. Chem. Soc.*, **78**, 6055 (1956).

1,2,4-Triazoles. XII. Derivatives of the s-Triazolo[4,3-*a*]pyridine Ring System[1a]

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Received June 8, 1965

Substituted *s*-triazolo[4,3-*a*]pyridines (**2**) containing alkyl, aryl, alkylaryl, heteryl, amino, hydroxyl, mercapto, and halogen substituents at position 3 have been synthesized in a study of the chemistry of this ring system, mainly by cyclization of 2-pyridylhydrazines (**1**) or their derivatives with appropriate reagents, and by modification of groups already present in the 3-position. Methyl substituents have also been placed at all peripheral carbon atoms. Di(3-*s*-triazolo[4,3-*a*]pyridyl)alkanes (**8**) and intermediate products have been obtained by the use of dicarboxylic acids, their anhydrides, or their esters in the above condensations. Substituents containing unsaturation or other functional groups can be introduced into position 3 of the bicyclic system by the use of the appropriate acid or ester. The structures of some interesting, substituted pyridines obtained as by-products in the reaction sequences are discussed.

The *s*-triazolo[4,3-*a*]pyridine ring system[2] (**2**) is one that has been known since 1903 but to which very meager attention has been paid.[3] Our interest in the possible aromatic character of fused ring systems with a nitrogen atom at the ring junction, such as has been shown in the case of the indolizine system, led us to investigate in detail the two possible isomeric *s*-triazolopyridines. In this communication, synthetic sequences used to obtain members of the *s*-triazolo[4,3-*a*]pyridine ring system (**2**) employed in our n.m.r. and other spectral studies, as well as other derivatives of interest, are described. The chemical characteristics of this nucleus and the spectral studies will be reported on in several forthcoming papers. The synthesis of members of the isomeric ring system, the *s*-triazolo[1,5-*a*]pyridine system, are described in a following paper.

Derivatives of similar fused ring systems have been shown to have interesting pharmacological properties,[4] especially in cancer chemotherapy,[5] and included in our study is the evaluation of these products for similar properties.

(1) (a) Support of this investigation by Public Health Service Research Grant CA-05973, 01-03, National Cancer Institute, is gratefully acknowledged. (b) To whom correspondence should be sent: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.

(2) A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd Ed., American Chemical Society, Washington, D. C., 1960, System No. 1094.

(3) W. Markwald and K. Rudzik, *Ber.*, **36**, 1111 (1903); R. G. Fargher and R. Furness, *J. Chem. Soc.*, 691 (1915); W. H. Mills and H. Schlinder, *ibid.*, 321 (1923); R. Graf, E. Pouzer-Lederer, V. Kopetz, R. Purket, and P. Laslo, *J. prakt. Chem.*, **138**, 244 (1933); D. S. Tarbell, C. W. Todd, M. C. Paulson, E. G. Lindstron, and V. P. Wystrack, *J. Am. Chem. Soc.*, **70**, 1381 (1948); J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 727 (1957); J. B. Bicking, U. S. Patent 3,050,525 (Aug. 21, 1962); *Chem. Abstr.*, **58**, 1480*e* (1963); R. Huisgen, H. J. Sturm, and M. Seidel, *Chem. Ber.*, **94**, 1555 (1961).

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(5) *E.g.*, Y. Makisumi, H. Kano, and S. Takahashi, Japanese Patent 9498 (July 27, 1962); *Chem. Abstr.*, **59**, 5178*e* (1963).