96–97°)[10]; ultraviolet spectrum (methanol): λ_{max} 266 mμ (8030), 212 mμ (9450).

The dimethyl ester had a m.p. of 118–119°.

Anal. Calcd. for $C_{10}H_{13}NO_4$ (211.21): C, 56.86; H, 6.20; N, 6.63. Found: C, 56.65; H, 6.26; N, 6.59.

2-Methylpyrrole-3,4-dicarboxylic acid. Trimethyl 2-methylpyrrole-1,3,4-tricarboxylate (1.3 g., 0.0051 mole) yielded 0.7 g. (81%) of a light grey powder, m.p. 230–234° dec. (reported m.p. 236–237° dec.)[11]; ultraviolet spectrum (methanol): λ_{max} 261 mμ (6730), 242 mμ (5300), 208 mμ (9820).

The diethyl ester had a m.p. of 121° (reported m.p. 124–125°)[11]; ultraviolet spectrum (methanol): λ_{max} 260 mμ (7240), 212 mμ (9450).

The dimethyl ester had a m.p. of 159°.

Anal. Calcd. for $C_9H_{11}NO_4$ (197.19): C, 54.82; H, 5.62; N, 7.10. Found: C, 54.75; H, 5.58; N, 7.13.

Pyrrole-3,4-dicarboxylic acid. Trimethylpyrrole-1,3,4-tricarboxylate (2.1 g., 0.0087 mole) yielded 1.1 g. (80%) of a light-gray powder m.p. 290–297° dec. (reported m.p. 290–292° dec.)[11]; ultraviolet spectrum (methanol): λ_{max} 258 mμ (5610), 244 mμ (5800), 210 mμ (7480).

The diethyl ester had a m.p. of 151–152° (reported m.p. 153–155°)[11]; ultraviolet spectrum (methanol): λ_{max} 253 mμ (7550), 206 mμ (10,350).

The dimethyl ester had a m.p. of 241–242° (reported m.p. 244°).[5]

Acknowledgment. The author is indebted to E. I. du Pont de Nemours and Co. for a Postgraduate Teaching Assistant Award and to Professor G. L. Closs for his encouragement and interest in this work.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF CHICAGO
CHICAGO 37, ILL.

[11] E. C. Kornfeld and R. G. Jones, *J. Org. Chem.*, **19**, 1671 (1954).

The Reaction of Dihalonortricyclenes with Magnesium, Lithium, and Phenyllithium

HARRY W. JOHNSON, JR., AND PETER N. LANDERMAN

Received March 30, 1960

Elimination-rearrangement reactions have been reported by Schubert[1] with open chain dihalides and 1,1-bishalomethyl cyclic compounds and iodide. Applequist[2,3] found somewhat similar reactions in the reactions of 9-bromoanthracene photodimer. Wiberg[4] used a ring-bridging dehydrohalogenation in the cyclobutane series (though it is probably best considered an active methylene displacement type reaction). The present note reports the formation of bicycloheptadiene from the reaction of 3,5-dibromo- and diiodonortricyclenes with magnesium, lithium and phenyllithium; the reaction involves 1,4 elimination of halogen with cleavage of the cyclopropane ring.

The preparation of 3,5-dibromonortricyclene[5,6] and 3,5-diiodonortricyclene[7] was accomplished in the usual manner by reaction of bicycloheptadiene with halogen. Olefinic products which accompany the nortricyclenes were removed by reaction with permanganate.[8] Winstein has shown that the dibromonortricyclene produced in this manner is a mixture of *cis*- and trans isomers.[8] The diiodonortricyclene was shown to have the indicated ring structure by hydrogenation over platinum in alcoholic potassium hydroxide to yield nortricyclene. It was presumed that the diiodonortricyclene was also a mixture of *cis* and *trans* isomers, but no separation was attempted.

Reaction of diiodonortricyclene with magnesium in ether gave 75% of bicycloheptadiene which was identified by vapor phase chromatography and infrared spectrum. One g.-atom of magnesium was required per mole of dihalide. The reaction of diiodonortricyclene with lithium in ether or with phenyllithium in ether also led to bicycloheptadiene in 70% and 73% yields, respectively. Iodobenzene was present in the reaction mixture from phenyllithium. Reaction of dibromonortricyclene with magnesium or lithium in ether also gave bicycloheptadiene, though in somewhat lower yields (49% and 43% respectively).

The mechanism of the elimination appears to involve attack at one halogen by the metal (or phenyllithium) to yield the product directly or else to yield a monometallated product which subsequently loses halide. Applequist[2] found that monometallated compound with an appreciable lifetime appeared to form from 9-bromoanthracene photodimer, since the intermediate apparently could be partitioned to form mixtures of three products.

In view of the report of Winstein[8] concerning the possible toxicity of this series of compounds, work has been discontinued with them. Contact of diiodonortricyclene with the hands led to severe, though painless, blistering.

EXPERIMENTAL

Diiodonortricyclene.[7] A solution of 127 g. of iodine (0.5 mole) in 500 ml. of ether was added to a solution of 46 g. of bicycloheptadiene[9] (0.5 mole) in ether with stirring. The color of iodine persisted after addition of 460 ml. of the iodine solution, and addition was stopped. The ether solution was washed with 20% sodium bisulfite solution (3 × 100 ml.) and water, and the solvent was evaporated at reduced pressure. The residue was treated with saturated potassium permanganate solution until the violet color

---

[1] W. M. Schubert and S. M. Leahy, Jr., *J. Am. Chem. Soc.*, **79**, 381 (1957).

[2] D. E. Applequist, R. L. Little, E. C. Friedrich, and R. E. Wall, *J. Am. Chem. Soc.*, **81**, 452 (1959).

[3] The authors are indebted to Prof. F. D. Greene, M.I.T., for pointing out ref. 1 and 2.

[4] K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).

[5] S. Winstein and M. Shatavsky, *Chemistry and Industry*, **56** (1956).

[6] L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).

[7] Brit. Patent **717,010**; *Chem. Abstr.*, **49**, 15970 (1955).

[8] S. Winstein, *J. Am. Chem. Soc.*, **83**, 1516 (1961).

[9] Gift of the Shell Oil Co., b.p. 88–89; n_D^{25} 1.4675.

persisted for 10 min. The mixture was acidified (sulfuric acid), and sodium bisulfite was added to dissolve the manganese dioxide. The suspension was extracted with ether; the ether was dried with sodium sulfate and evaporated at room temperature using a water aspirator. The residue was distilled using a falling film molecular still at 100° (0.01 mm.). The product was stored over copper wire in an evacuated (10^{-4} mm.) sealed off container for approximately 2 weeks. After this treatment the colorless oil could be handled in air for reasonable periods of time without darkening. The product was distilled:

Fraction	Wt. (G.)	n_D^{25}	B.P. (1.5 Mm.)
1	20	1.6295	Less than 105°
2	20	1.6596	105–110
3	70	1.6695	110–112
4	80	1.6709	112–113
5	70	1.6705	112–113

Attempts to distill the product prior to the treatment with copper wire led to extensive decomposition and the formation of black tar in the column.

Anal. Calcd. for $C_7H_8I_2$: C, 24.3; H, 2.3; I, 73.4; mol. wt., 346. Found: C, 24.8; H, 2.6; I, 72.9; mol. wt., 352, 354 (cryoscopic in benzene).

Diiodonortricyclene should be handled with caution; it appeared to be a powerful, though painless, blistering agent.

Diiodonortricyclene (1.00 g., 0.00289 mole) was reduced over prereduced platinum oxide in 75 ml. of 1*M* methanolic potassium hydroxide; 135 ml. (96% of 2 moles) of hydrogen was absorbed slowly at 25° and 1 atm. The suspension was filtered, and the filtrate was extracted with pentane. The pentane was washed with water, dilute sodium bisulfite solution, and water. After drying (sodium sulfate), the solution was distilled through a concentric rod column to yield nortricyclene, b.p. 108–110°; m.p. 55–56°. The infrared spectrum agreed with that of an authentic sample.

Reaction of diiodonortricyclene with magnesium, lithium, and phenyllithium. To a suspension of 1.41 g. (0.058 g.-atom) of magnesium in dry ether was added slowly 10.0 g. of diiodo compound (0.029 mole). After spontaneous reaction ceased, the mixture was refluxed for 30 min. Water was added to the mixture and the layers were separated. The ether layer was dried (sodium sulfate) and distilled to yield 2 g. (75%) of bicycloheptadiene, b.p. 88–90°. The bicycloheptadiene was identified by retention time on a silicone rubber column and by comparison of its infrared spectrum with that of an authentic sample. From the original hydrolysis mixture 0.80 g. of magnesium metal (56%) was recovered.

The reaction of 0.42 g. of lithium wire in ether with 10 g. of diiodonortricyclene gave 1.90 g. (70%) of bicycloheptadiene. Phenyllithium (0.06 mole) and 10.0 g. of diiodo compound likewise yielded 1.95 g. of bicycloheptadiene (73%). Iodobenzene was present in the distillation residue (infrared spectrum of vapor phase chromatography fraction).

Reaction of dibromonortricyclene with magnesium and lithium. Dibromonortricyclene (b.p. 72–75° (1.7 mm.); n_D^{25} 1.5770) was prepared from bicycloheptadiene and bromine in carbon tetrachloride[5,6,8]; olefins were removed with permanganate. A solution of 10.0 g. of dibromonortricyclene in ether was allowed to react with 1.93 g. of magnesium. When the reaction ceased, the suspension was refluxed for 20 min. Water was added (a precipitate formed which dissolved on the addition of more water), and the layers were separated. The ether layer was dried (sodium sulfate) and distilled to yield 1.8 g. of bicycloheptadiene (49%). The use of lithium wire in ether gave 45% bicycloheptadiene from dibromonortricyclene. The infrared spectra of the samples of bicycloheptadiene were identical with that of an authentic sample.

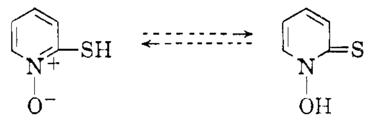
Department of Chemistry
University of California
Riverside, Calif.

S-Alkoxymethyl and S-Alkylmercaptomethyl Derivatives of 2-Pyridinethiol 1-Oxide

R. E. McClure and Alexander Ross[1]

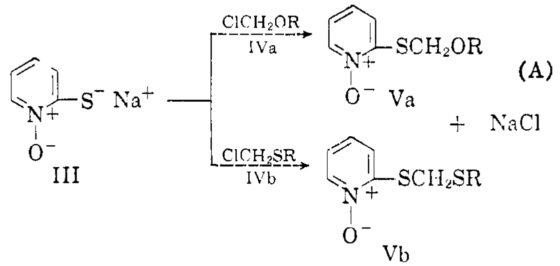
Received March 15, 1961

2-Pyridinethiol 1-oxide (I), (also known as 1-hydroxypyridine-2-thione from its tautomeric form, II) has demonstrated strong bactericidal and fungicidal properties,[2] as have a number of its derivatives.[3a] In the process of studying some of the physical and biocidal properties of this interesting structure, we have synthesized a series of previously unreported alkoxymethyl (Va) and alkylmercaptomethyl derivatives (Vb).[3b]



I II

Method. Two general procedures were used. The first method involved the reaction of the sodium salt of 2-pyridinethiol 1-oxide, III, with a chloromethyl alkyl ether (IVa) or thio ether (IVb) as in reaction (A). Inert solvents were used.



(A)

Dioxane was first tried because of its fair solvent power on the sodium salt (III). It was later abandoned because its low volatility and tenacity for water caused difficulties in the purification and crystallization of the products. Acetone or 1,2-dimethoxyethane were found to work well. Although the sodium mercaptide (III) was only

---

[1] Present address: Metal and Thermit Corp., Research Laboratories, Rahway, N. J., to whom requests for reprints should be sent.

[2] E. Shaw, J. Bernstein, K. Losee, and W. Lott, *J. Am. Chem. Soc.*, 72, 4362 (1950).

(3a) U. S. Patents; 2,686,786; 2,734,903; 2,742,393; 2,742,476; 2,745,826; 2,678,116; 2,809,971; 2,826,585; 2,826,586; 2,922,790; 2,922,791; 2,922,792; 2,922,793; 2,940,978. (3b) U. S. Patent 2,932,647 to Jack Rockett (Olin Mathieson Chemical Corp.).