

bridges are essentially in agreement with values found for the three asymmetric basal carbonyl bridges in the $[\text{Fe}_6(\text{CO})_{13}^{2-}]$ dianion ($\text{Fe}-\text{C} = 1.82$ and 2.28 \AA).⁹

The central carbon atom is, within the limits of experimental error, equidistant from the six iron atoms, individual distances being $\text{Fe}(1)-\text{C}(11) = \text{Fe}(1')-\text{C}(11) = 1.89$ (4), $\text{Fe}(2)-\text{C}(11) = 1.97$ (4), $\text{Fe}(3)-\text{C}(11) = 1.93$ (4), $\text{Fe}(4)-\text{C}(11) = 1.84$ (4), and $\text{Fe}(5)-\text{C}(11) = 1.82$ (4) \AA .

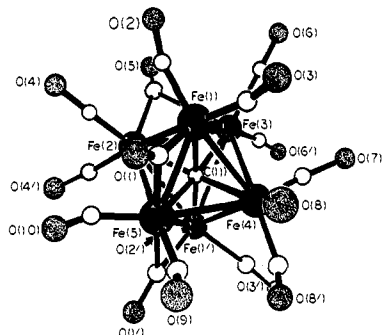


Figure 1. Stereochemistry of the $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$ ion. Note that the terminal carbonyl group defined by $\text{C}(2')-\text{O}(2')$, which is linked to $\text{Fe}(1')$, is hidden beneath $\text{Fe}(5)$. The anion has a mirror plane passing through $\text{Fe}(2)$, $\text{Fe}(3)$, $\text{Fe}(4)$, and $\text{Fe}(5)$. Individual iron-iron distances within the two crystallographically independent units are: $\text{Fe}(1)-\text{Fe}(2)$, 2.706 (9) and 2.688 (9); $\text{Fe}(1)-\text{Fe}(3)$, 2.682 (9) and 2.695 (9); $\text{Fe}(1)-\text{Fe}(4)$, 2.699 (9) and 2.654 (9); $\text{Fe}(1)-\text{Fe}(5)$, 2.632 (10) and 2.621 (9); $\text{Fe}(2)-\text{Fe}(3)$, 2.609 (10) and 2.553 (10); $\text{Fe}(3)-\text{Fe}(4)$, 2.743 (10) and 2.729 (10); $\text{Fe}(4)-\text{Fe}(5)$, 2.682 (11) and 2.646 (10); $\text{Fe}(5)-\text{Fe}(2)$, 2.662 (11) and 2.725 (10) \AA .

The only previously known iron carbonyl carbide species is $\text{Fe}_5(\text{CO})_{13}\text{C}$.¹⁰ As with this former compound, $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$ exhibits considerable thermal stability and also a degree of stability toward aerobic oxidation (the solid is only partially decomposed after exposure to air for 3 days) not shared by the simple iron carbonyl anions.

The $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$ anion is evidently closely related to the only other known molecular carbides, $\text{Ru}_6(\text{CO})_{17}\text{C}^{4a,c}$ and $\text{Ru}_6(\text{CO})_{14}\text{C}(\text{arene})$,^{4a,b} but it is the first known *anionic* carbido-carbonyl complex of any metal. Its high stability suggests that it may be possible to prepare an extended range of carbido-carbonyl complexes, and we may predict the series $\text{Fe}_6(\text{CO})_{17}\text{C}$, $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$, $[\text{Fe}_6(\text{CO})_{15}\text{C}^{4-}]$ by analogy with the known series¹ based on $\text{Co}_6(\text{CO})_{16}$. Acidification of $[\text{Fe}_6(\text{CO})_{16}^{2-}]$ does, in fact, yield a black crystalline complex which is soluble in petroleum ether ($30-60^\circ$) and is almost certainly a neutral carbido-carbonyl [ir ν_{CO} 2050 (s), 2032 (s), 2011 (m), 1989 (m) cm^{-1} (*n*-hexane solution) or 2096 (sh), 2065 (sh), 2030 (s), 2001 (m), 1988 (m), 1960 (sh), 1834 (m) cm^{-1} (KBr disk)].

The crystal structure of this neutral species, as well as further reactions of the $[\text{Fe}_6(\text{CO})_{16}\text{C}^{2-}]$ dianion, is currently under investigation in these laboratories.

(9) R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 4847 (1966).

(10) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *ibid.*, **84**, 4633 (1962).

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP-26293 to M. R. C.)

(11) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

Melvyn R. Churchill,*¹¹ John Wormald
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

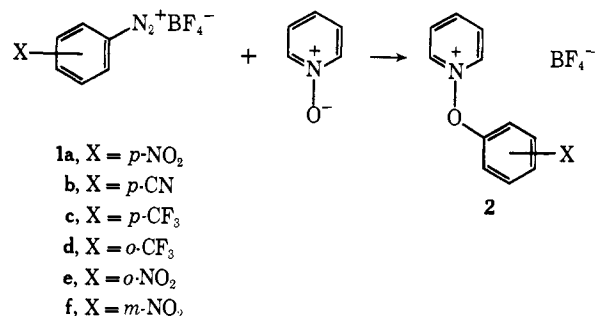
John Knight, Martin J. Mays
University Chemical Laboratory
Cambridge, CB2 1EW, England
Received March 13, 1971

N-Aryloxy-pyridinium Salts and Their Base-Catalyzed Rearrangement

Sir:

The chemistry of *N*-alkoxy-pyridinium salts is well documented.¹ In contrast, the *N*-aryloxy compounds are not known. We now report a convenient one-step synthesis of such compounds and a novel molecular rearrangement which they undergo.

The diazonium tetrafluoroborate (1) of an aromatic amine bearing an electron-withdrawing substituent is added to a solution of pyridine 1-oxide in acetonitrile and the solution is either stirred at room temperature for 24 hr or warmed gently. The product, 2, usually precipitates and more is recovered by evaporation of the solvent. Yields are in the range 24-70%.



The structures of the products 2 were established by spectroscopic methods and microanalysis, as illustrated for *N*-*p*-nitrophenoxypyridinium tetrafluoroborate (2a): mp 157.5-159°; ir 1390, 1090 cm^{-1} (BF_4^-);² λ_{max} 260 nm; ϵ 14,000; nmr [acetone-*d*₆] δ 9.65 (2 H, d, $J_{2,3} = J_{5,6} = 6$ Hz, H-2,6), 9.00 (1 H, t, $J_{3,4} = J_{4,5} = 7$ Hz, H-4), 8.56 (2 H, d of d, H-3,5), 8.39 (2 H, d, $J_{\text{ortho}} = 9$ Hz, phenyl meta hydrogens), and 7.50 (2 H, d, $J_{\text{ortho}} = 9$ Hz, phenyl ortho hydrogens); mass spectrum m/e 216 (M^+), 186 ($\text{M}^+ - \text{NO}$), 170 ($\text{M}^+ - \text{NO}_2$), 139 ($\text{NO}_2\text{C}_6\text{H}_4\text{OH}^+$), 79 ($\text{C}_5\text{H}_5\text{N}^+$, base peak). *Anal.* Calcd for $\text{C}_{11}\text{H}_9\text{BF}_4\text{N}_2\text{O}$: C, 43.46; H, 2.98; F, 24.99; N, 9.22. Found: C, 43.35; H, 3.09; F, 24.66; N, 9.31. 2b (X = *p*-CN), mp 214-215°, 2c (X = *p*-CF₃), mp 135-136°, 2d (X = *o*-CF₃), mp 169-170°, 2e (X = *o*-NO₂), mp 161-162°, and 2f (X = *m*-NO₂), mp 148-149°, were similarly prepared and characterized. If X is not electron withdrawing then the only products are those formed by the attack of the phenyl cation upon acetonitrile to give a nitrilium salt

(1) E. Ochiai, "Aromatic Amine Oxides," Elsevier, Amsterdam, 1967, p 178.

(2) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1967.

which, in turn, reacts with pyridine 1-oxide to give 2-acylaminopyridines.³

Heterocyclic tertiary amine *N*-oxides⁴ and ylides⁵ are known to undergo interesting photodecompositions and -rearrangements, and recently Mee, Heseltine, and Taylor⁶ have reported that the photolysis of *N*-methoxyphenanthridinium perchlorate yields methoxyl radicals which can substitute into an aromatic nucleus. It was our hope that photolysis of **2** would take a different course and lead to pyridine and $\text{XC}_6\text{H}_4\text{O}^+$ which would be isoelectronic with the corresponding nitrene. To our surprise, **2a** proved to be stable to irradiation in acetonitrile using 2537- or 3000-Å light. Photolysis of **2a** in acetonitrile containing some 1,4-dimethoxybenzene at 2537 Å gave a trace of *p*-nitrophenol, the salt being recovered almost quantitatively. On the other hand, the *o*-CF₃ salt (**2d**) did undergo photolysis and the nature of the products formed from it and other salts will be described in a future paper. The salts are also thermally stable and may be recovered unchanged after boiling in acetonitrile for prolonged periods.

On the other hand, we have discovered a new base-catalyzed rearrangement of compounds **2**. Treatment of **2a** in hot acetonitrile solution either with potassium phenoxide or with triethylamine gave 2-(2-hydroxy-5-nitrophenyl)pyridine (**3a**): mp 216–217° (65%); $\nu_{\text{max}}^{\text{KB}}$ 2600 (–N⁺H=); $\lambda_{\text{max}}^{\text{MeCN}}$ 249, 287, and 323 m μ ; ϵ 14,000, 16,700, 12,000; *m/e* 216 (M⁺), 200 (M⁺ – O), 186 (M⁺ – NO), 170 (M⁺ – NO₂), 142 (M⁺ – NO₂ – CO); $\delta_{\text{TMS}}^{\text{CF}_3\text{CO}_2\text{H}}$ 8.93–8.67 (m, 5 H), 8.0 (1 H, t, *J* = 7 Hz), 7.37 (1 H, d, *J* = 10 Hz). An authentic sample of **3a** was synthesized by the Gomberg–Hey arylation of pyridine with the diazonium salt from 2-amino-4-nitroanisole, fractional crystallization of the products to give 2-(2-methoxy-5-nitrophenyl)pyridine,⁷ followed by demethylation with hot HBr to give **3a**, identical in all respects with the rearrangement product. Similarly, other 2-(2-hydroxyphenyl)pyridines were obtained in good yield from **2b–f**. Interestingly, **3a–e** exhibit no O–H stretching band in the infrared (or only a very weak broad band), but do show a broad –N⁺H= band at *ca.* 2600 cm^{–1}, indicating that, in the solid state at least, they exist in the zwitterionic form **4**.

A possible mechanism for the rearrangement involves base-catalyzed proton abstraction from the 2 position of the pyridine ring⁸ followed by nucleophilic attack at the ortho position of the benzene ring, though other pathways are conceivable (see scheme).

The scope of this O-arylation, the chemical reactions and photochemistry of the salts **2**, the mechanism of the rearrangement, and the reactions of the novel phenols **3** are presently under study.

(3) R. A. Abramovitch and G. M. Singer, *J. Amer. Chem. Soc.*, **91**, 5672 (1969).

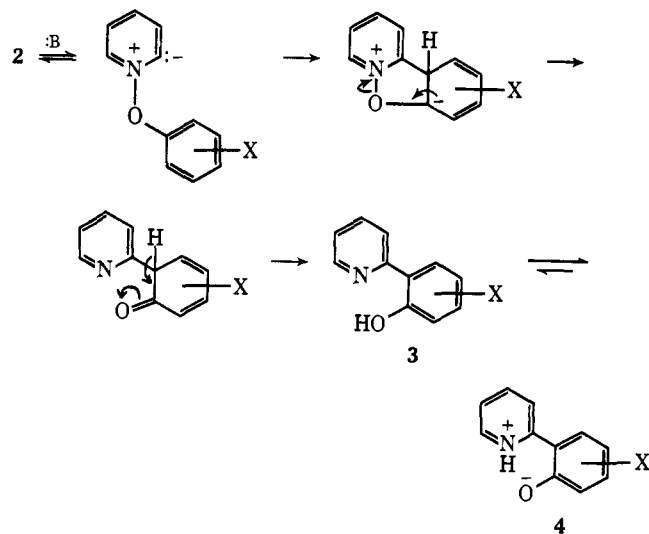
(4) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970).

(5) J. Streith, A. Blind, J.-M. Cassal, and C. Sigwalt, *Bull. Soc. Chim. Fr.*, 948 (1969); T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 427 (1970). A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *ibid.*, **35**, 433 (1970).

(6) J. D. Mee, D. W. Heseltine, and E. C. Taylor, *J. Amer. Chem. Soc.*, **92**, 5814 (1970).

(7) J. W. Haworth, I. M. Heilbron, and D. H. Hey, *J. Chem. Soc.*, 358 (1940).

(8) R. A. Abramovitch, G. M. Singer, and A. R. Vinutha, *Chem. Commun.*, 55 (1967); J. A. Zoltewicz and L. S. Helmick, *J. Amer. Chem. Soc.*, **92**, 7547 (1970).



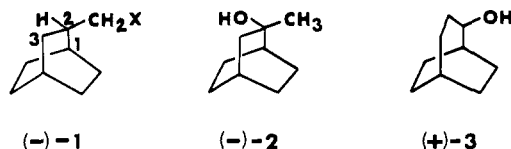
Acknowledgment. We wish to thank the National Institutes of Health for a grant (GM-16626).

R. A. Abramovitch,* S. Kato, G. M. Singer
Department of Chemistry, University of Alabama
University, Alabama 35486
Received March 13, 1971

Carbonium Ion Rearrangements of Bicyclo[2.2.2]oct-2-ylcarbinyloxy Derivatives¹

Sir:

The products of carbonium ion rearrangements of the bicyclo[2.2.2]oct-2-ylcarbinyloxy system (**1**) include those resulting from hydride shift (tertiary alcohol or acetate **2**) and from rearrangement of C₃ (bicyclo[3.2.2]nonan-2-yl derivatives **3**).² The present stereochemical



and tracer experiments on these processes reveal a new type of geometric restriction in multiple carbonium ion rearrangements. They also are relevant to the question whether ion-pairing effects may cause the special stereochemical properties characteristic of the first rearranged intermediates in these reactions and in related processes where "memory effects" are observed.⁴

(1) We are grateful for the support of this work by grants from the National Science Foundation (GP-1608, GP-6212X, and GU-3282), the National Institute of Arthritis and Metabolic Diseases (AM-07505), the National Institute of General Medical Sciences (GM-16962), the Petroleum Research Fund, and the Hoffmann-La Roche Foundation.

(2) (a) Previous studies of these reactions have been reported by K. Alder and R. Reubke, *Chem. Ber.*, **91**, 1525 (1958). (b) The product distribution depends on conditions. Deamination in aqueous dioxane gives 40% of hydrocarbons, 7% of **2**, 27% of **3**, 7% of **1**, and 4% each of bicyclo[3.3.1]- and -[3.2.2]nonan-2-ol. Control experiments in deuterated media³ show that in hydrolysis none of the alcohol products arises by hydration of hydrocarbon intermediates. In deamination, the conclusion is the same, the observed small amount of incorporation of deuterium being virtually identical in all the alcohol products, presumably because of partial exchange *via* the diazoalkane occurring in competition with rearrangement.

(3) R. T. Luibrand, Ph.D. Thesis, University of Wisconsin, 1971.

(4) (a) J. A. Berson, *Angew. Chem., Int. Ed. Engl.*, **7**, 779 (1968); (b) J. A. Berson, J. J. Gajewski, and D. S. Donald, *J. Amer. Chem. Soc.*, **91**, (1969); (c) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *ibid.*, **91**, 5601 (1969).