The product of this reaction contained four moles of $BF_3$ for each mole of $K_2Ni(CN)_4$.

Failure to obtain X-ray diffraction patterns from the foregoing compounds indicates an amorphous structure. Solvents ($H_2O$, acetone, dimethyl sulfoxide, dimethylformamide, nitrobenzene, ethers and ethyl alcohol) either fail to dissolve the adduct or bring about decomposition. Furthermore, even brief contact with atmospheric moisture results in partial decomposition.

Despite the foregoing experimental difficulties, it was possible to obtain fairly conclusive structural evidence. The infrared spectrum of pure potassium tetracyanonickelate(II) displays a single absorption at 2130 cm.$^{-1}$. This band represents the degenerate $C\equiv N$ stretch for the square planar array of terminal cyanides coördinated to nickel. By contrast, the compound $K_2Ni(CN)_4 \cdot 4BF_3$ yields a single absorption (2250 cm.$^{-1}$) which is over 100 wave numbers higher than that of the parent $K_2Ni(CN)_4$. For the intermediate compound, $K_2Ni(CN)_4 \cdot BF_3$, infrared absorption in the $C\equiv N$ stretch region consists of one band at 2127 cm.$^{-1}$ and another at 2235 cm.$^{-1}$. It thus appears logical to assign the 2127 cm.$^{-1}$ absorption primarily to stretching frequencies of terminal cyanides and the 2235 cm.$^{-1}$ band primarily to the stretching frequency of $C\equiv N$ in a bridge environment ($-Ni-C\equiv N-BF_3$). Significantly, the frequency region assigned to the bridge cyanide stretch is well outside the reported range of Raman active non-degenerate modes for $Ni(CN)_4$: 2149 and 2160 cm.$^{-1}$.[3] The shift of $C\equiv N$ stretch to higher frequencies upon bridge formation is in keeping with observations on boron trihalide-nitrile systems[4] and transition metal cyanide bridged compounds.[5]

If the infrared and stoichiometry data were taken without reference to the nitrile–$BF_3$ and cyanide bridged metal complexes, a good case could be made for abstraction of $C\equiv N^-$ from the first coördination sphere of nickel by $BF_3$. However, the possibility of a large change in the first coördination sphere of nickel, which would occur upon $C\equiv N^-$ abstraction, is effectively ruled out by the similarity of color and electronic spectra of $K_2Ni(CN)_4$, $K_2Ni(CN)_4 \cdot BF_3$ and $K_2Ni(CN)_4 \cdot 4BF_3$. A similar conclusion may be derived from the observed diamagnetism of both $K_2Ni(CN)_4 \cdot BF_3$ and its parent $K_2Ni(CN)_4$.

The reflectance spectrum of another $BF_3$ adduct, $K_4Mo(CN)_8 \cdot 7.3BF_3$, displays a broad maximum at 365 mμ (27,400 cm.$^{-1}$) and a shoulder at *ca.* 415 mμ (24,100 cm.$^{-1}$). These bands agree within experimental error with those of $K_4Mo(CN)_8$. Again, it is inferred that addition of $BF_3$ leaves the first coördination sphere of the metal unchanged. This is consistent with simple addition of $BF_3$ to the nitrogen end of cyanide groups. Lower frequency infrared bands for the above compounds also agree with the proposed bridge structures. Upon coördination $BF_3$ assumes a pyramidal configuration which should display symmetric and asymmetric stretching frequencies; also a B–N stretch frequency should appear in the NaCl infrared region. In harmony with these expectations, a broad intense maximum about 1100 cm.$^{-1}$, another around 900 cm.$^{-1}$ and a weak maximum near 700 cm.$^{-1}$ are observed with all of the compounds reported.

Preparation of the bridge adducts, $K_2Ni(CN)_4 \cdot 4BF_3$, $K_4Fe(CN)_6 \cdot 3.7BF_3$ and $K_4Mo(CN)_8 \cdot 7.3BF_3$, demonstrates the generality of Lewis base behavior by metal cyanide complexes. Lack of simple $BF_3$-metal cyanide ratios for some of the above compounds is attributed to the kinetically unfavorable situation of solid–gas reactions involved in their formation. In all of these cases bridge formation is accompanied by the appearance of new $C\equiv N$ stretch absorptions at higher frequencies than found in the original nonbridged complex. Evidence for a $BH_3$ adduct of $K_4Fe(CN)_6$ also has been obtained. The scope of bridge adduct formation found in the present work makes a bridge structure plausible for the compound $AgCN \cdot BBr_3$.[6]

The compounds produced in this study are remarkably stable with respect to evolution of $BF_3$. For example a 0.9 millimole sample of $K_4Mo(CN)_8 \cdot 1.2BF_3$ was subjected to a vacuum of less than $10^{-4}$ mm. for one hour at a temperature of 32°, but less than $2 \times 10^{-3}$ millimole of condensables was collected. This behavior contrasts sharply with observations that benzonitrile–$BF_3$ would exert a boron trifluoride pressure of 3.1 mm. at 32°,[2] while acetonitrile–$BF_3$ would exert a $BF_3$ pressure of 6.2 mm. at this temperature.[7] The origin of this great stability is one aspect of bridge adduct formation currently under investigation.[8]

This research was supported by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.

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[3] J. P. Mathieu and S. Cornevin, *J. Chim. Phys.*, **36**, 271 (1939). If the $C\equiv N—BF_3$ group is approximated as a cylindrically symmetrical "ligand" the square planar $Ni(CN)_4 \cdot BF_3^{--}$ anion would have $C_{2v}$ symmetry and selection rules for the isolated ion would predict three infrared active modes in the terminal $C\equiv N$ stretch region. An effort was made to resolve the single 2127 cm.$^{-1}$ band using a Perkin Elmer 112 equipped with $CaF_2$ optics, but without success.

[4] H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

[5] D. A. Dows, A. Haim and W. K. Wilmarth, *J. Inorg. and Nucl. Chem.*, **21**, 33 (1961).

[6] E. Pohland, *Z. anorg. Chem.*, **201**, 282 (1931).

[7] A. W. Laubengayer and D. S. Sears, *J. Am. Chem. Soc.*, **67**, 164 (1945).

[8] Absorption rate experiments show no definite break at a 1:1 stoichiometry but under the proper conditions this composition is easily attained.

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## AN UNUSUAL INTRAMOLECULAR DIELS-ALDER REACTION IN THE PHOTOÖXIDATION OF A (FURANO) HETEROCYCLOPHANE

*Sir:*

The dye-sensitized photoöxidation of furans in reducing solvents such as methanol yields, among other products, diacyl or diaroylethylenes as in the conversion of tetraphenylfuran to *cis*-dibenzoylstilbene.[1,2] Applied to the heterocyclophane I,[3]

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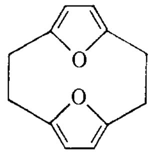
[1] H. H. Wasserman and A. Liberles, *J. Am. Chem. Soc.*, **82**, 2086 (1960).

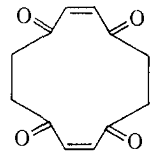
[2] R. E. Lutz, W. J. Welstead, Jr., R. G. Bass and J. I. Dale, *J. Org. Chem.*, **27**, 1111 (1962).

[3] H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theo-

this reaction could lead to the macrocyclic unsaturated tetraketone II, if, as observed in the related reaction with bromine and methanol,[3-5] both furan rings undergo oxidation.

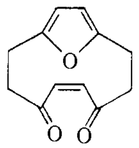


I

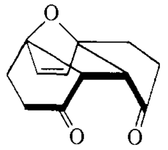


II

We wish to report that on exposure of I to air in an ethanolic solution containing methylene blue, during irradiation with a 150-watt floodlamp, partial oxidation takes place yielding the bicyclic diketone IV (or *exo* isomer) as the main product. The reaction appears to take place through intermediate III, which incorporates diene and dienophile in a particularly favorable geometry for an intramolecular Diels-Alder reaction.[6]



III

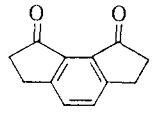


IV

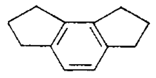
The proof of structure of IV which is outlined below does not discriminate between the *endo* form, shown above, or the *exo* form.

The photoöxidation product IV, formed in 42% yield, m.p. 186–187° (dec.), shows a single carbonyl peak in the infrared at 1740 cm.$^{-1}$ ($CHCl_3$) and no aromatic (furanoid) absorption in the ultraviolet. (*Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; mol. wt., 204. Found: C, 70.73; H, 6.14; mol. wt., 204, 216). Hydrogenation of the double bond in IV with palladium on charcoal in ethanol gave the dihydro derivative V, m.p. 150.5–151°. (*Anal.* Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.91; H, 6.96). The n.m.r. spectrum of V, exhibiting, among other peaks, a singlet at 7.26 $\tau$ corresponding to the two tertiary protons $\alpha$- to the carbonyl group, and a singlet at 8.08 $\tau$ (four protons at the site of the hydrogenated double bond) is completely consistent with the proposed structure.

Treatment of IV with dilute sulfuric acid yielded 1,8-dioxo-2,3,6,7-tetrahydro-*as*-indacene (VI) m.p. 208–209.5° (dec.). (*Anal.* Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.32; H, 5.47; $\lambda^{95\%\ EtOH}_{max}$: 257 m$\mu$ ($\epsilon$ 7750), 264 m$\mu$ ($\epsilon$ 6950), 313 m$\mu$ ($\epsilon$ 4560), 321 m$\mu$ ($\epsilon$ 4220); $\lambda^{CH\ CL_3}_{max}$ 3010, 1715, 1601, 832 cm.$^{-1}$. The n.m.r. spectrum shows a singlet at 2.34 $\tau$ corresponding to the two aromatic hydrogens and a typical $A_2B_2$ spectrum centered at 7.05 $\tau$, corresponding to the eight remaining protons.



VI



VII

The carbon skeleton in IV, V and VI was conclusively established by hydrogenation of IV (palladium on charcoal) to the known hydrocarbon, 1,2,3,6,7,8-hexahydro-*as*-indacene (VII). The hydrogenation product (VII) m.p. 38–40° is identical (superimposable infrared and ultraviolet absorption spectra, mixture melting point) with an authentic sample prepared through an independent route by Rapoport and Smolinsky.[7]

Further studies on the stereochemistry of IV, and on furan photoöxidations are in progress.

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bald, *J. Am. Chem. Soc.*, **82**, 1428 (1960). In this work, compound I was prepared by the procedure outlined by Winberg and co-workers. The initial studies were carried out on a sample kindly provided by Dr. Winberg.

(4) D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961).

(5) N. Clauson-Kaas, *Kgl. Danske Videnskab. Selskab. Mat-fys. Medd.*, **23** (6), 18 (1947).

(6) A related intramolecular process may be involved in the reaction of I with dicarbomethoxyacetylene, ref. 4.

(7) H. Rapoport and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 1171 1960). We wish to thank Prof. Rapoport for providing us with a sample of 1,2,3,6,7,8-hexahydro-*as*-indacene for comparison.

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RECEIVED OCTOBER 17, 1962

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## PHOTOCHEMICAL PREPARATION OF XENON DIFLUORIDE[1]

*Sir:*

When Claassen, Selig and Malm of this laboratory first reported $XeF_4$, they also suggested the existence of a lower fluoride of xenon.[2] Further evidence for this lower fluoride was found by Studier and Sloth,[3] who, in mass spectrometric studies, have observed $XeF_2$ as a minor component of the xenon fluorides prepared by thermal reaction of xenon and fluorine. We have now prepared $XeF_2$ in relatively pure form by the photochemically induced reaction of xenon and fluorine at room temperature. The light source was a 1000-watt General Electric AH-6 high pressure mercury arc. Both the arc and the water-cooled jacket were of fused silica. Fused silica lenses concentrated the light in a narrow intense beam. The ultraviolet absorption spectrum of gaseous fluorine[4] is a continuum with a maximum at 2900 Å. The effective wave lengths in our work are probably about 2500–3500 Å. and presumably produce F atoms.

Early preparations were carried out by irradiating in fused silica vessels, but $SiF_4$ produced by attack on the cell by fluorine made analyses difficult. All of the work reported herein, except for one run, made use of an all-nickel system with synthetic sapphire windows. The cell was of a closed-loop design consisting of a reservoir of about 400 cc., the sapphire windowed reaction chamber of nearly 100 cc., and 8 mm i.d. nickel tubing completing a loop. Circulation was effected by use of a heating tape operated at near 90° on one leg of the loop. The

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) M. H. Studier and E. N. Sloth, *J. Phys. Chem.*, in press; *Science*, **138**, 136 (1962).

(4) H. V. Wartenberg, G. Sprenger and J. Taylor, *Z. physik. Chem.*, Bodenstein-Festband, Akademische Verlagsgesellschaft m.b.H. Leipzig, 1931, p. 61.