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 $K_2Ni(CN)_4$. $4BF_3$ yields a single absorption (2250 cm.⁻¹) which is over 100 wave numbers higher than that of the parent K₂Ni(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 $(-Ni-C = N-BF_3)$. 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=N stretch to higher frequencies upon bridge formation is in keeping with observations on boron trihalide-nitrile systems4 and transition metal cyanide bridged compounds.⁵

If the infrared and stoichiometry data were taken without reference to the nitrile-BF₃ and cyanide bridged metal complexes, a good case could be made for abstraction of $C = N^-$ from the first coördination sphere of nickel by BF₃. However, the possibility of a large change in the first coördination sphere of nickel, which would occur upon $C = N^-$ abstraction, is effectively ruled out by the similarity of color and electronic spectra of K₂Ni(CN)₄, K₂Ni(CN)₄·BF₃ and K₂Ni(CN)₄·4BF₃. A similar conclusion may be derived from the observed diamagnetism of both K₂Ni(CN)₄·BF₃ and its parent K₂Ni(CN)₄.

The reflectance spectrum of another BF₃ adduct, $K_4Mo(CN)_8 \cdot 7.3BF_3$, displays a broad maximum at 365 m μ (27,400 cm.⁻¹) and a shoulder at *ca*. 415 m μ (24,100 cm.⁻¹). These bands agree within experimental error with those of K_4Mo -(CN)₈. Again, it is inferred that addition of BF₃ leaves the first coördination sphere of the metal unchanged. This is consistent with simple addition of BF₃ to the nitrogen end of cyanide groups.

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Preparation of the bridge adducts, $K_2Ni(CN)_4$. $4BF_3$, $K_4Fe(CN)_6 \cdot 3.7BF_3$ 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==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 · BBr₃.⁶

The compounds produced in this study are remarkably stable with respect to evolution of BF₃. For example a 0.9 millimole sample of K₄Mo-(CN)₈·1.2BF₃ was subjected to a vacuum of less than 10⁻⁴ mm. for one hour at a temperature of 32°, but less than 2×10^{-3} millimole of condensables was collected. This behavior contrasts sharply with observations that benzonitrile–BF₃ would exert a boron trifluoride pressure of 3.1 mm. at 32°,² while acetonitrile–BF₃ would exert a BF₃ 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

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Sir:

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

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*-dibenzoyl-stilbene.^{1,2} Applied to the heterocyclophane I,³ (1) H. H. Wasserman and A. Liberles, J. Am. Chem. Soc., **82**, 2086 (1960).

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⁽³⁾ J. P. Mathieu and S. Cornevin, J. Chim. Phys., **36**, 271 (1939). If the C=N—BFs group is approximated as a cylindrically symmetrical "ligand" the square planar Ni(CN)₄·BFs⁻⁻ anion would have C_{3v} symmetry and selection rules for the isolated ion would predict three infrared active modes in the terminal C=N stretch region. An effort was made to resolve the single 2127 cm.⁻¹ band using a Perkin Elmer 112 equipped with CaFs optics, but without success.

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.



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



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 (CHCl₃) and no aromatic (furanoid) absorption in the ultraviolet. (*Anal.* Calcd. for C₁₂H₁₂O₃: 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 C₁₂H₁₄O₃: 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 τ corresponding to the two tertiary protons α - to the carbonyl group, and a singlet at 8.08 τ (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; $\lambda^{95\%} \stackrel{\text{EtOH}}{=} 257 \text{ m}\mu \ (\epsilon \ 7750), \ 264 \text{ m}\mu \ (\epsilon \ 6950), \ 313 \text{ m}\mu \ (\epsilon \ 4560), \ 321 \text{ m}\mu \ (\epsilon \ 4220); \ \lambda^{\text{CH}} \stackrel{\text{CL}_3}{=} 3010, \ 1715, \ 1601, \ 832 \text{ cm.}^{-1}$. The n.m.r. spectrum shows a singlet at 2.34 τ corresponding to the two aromatic hydrogens and a typical A_2B_2 spectrum centered at 7.05 τ , corresponding to the eight remaining protons.

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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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PHOTOCHEMICAL PREPARATION OF XENON DIFLUORIDE¹

Sir:

When Claassen, Selig and Malm of this laboratory first reported XeF4, 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 XeF2 as a minor component of the xenon fluorides prepared by thermal reaction of xenon and fluorine. We have now prepared XeF₂ 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 fluorine⁴ 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 SiF₄ 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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