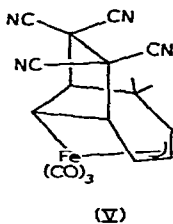


reactions of (VI) with other electron-deficient alkenes. These findings appear to reopen the question of the structure of the (I)-TCNE adduct.

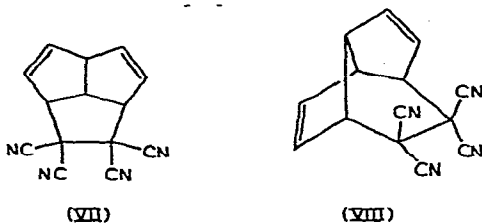


Oxidative degradations have been carried out successfully on a number of iron tricarbonyl complexes, including cyclobutadieneiron tricarbonyl⁷, trimethylenemethaneiron tricarbonyl⁸, and formylcyclooctatetraeneiron tricarbonyl⁹. In the first two cases, the resulting unstable hydrocarbons could be trapped, and in the last case, the stable formylcyclooctatetraene was obtained in good yield.

We felt that examination of the organic fragment liberated by oxidative degradation of the (I)-TCNE adduct, as compared to that liberated from the (VI)-TCNE adduct, now known to possess structure (V), might provide evidence as to the nature of the complexed adducts, and might yield otherwise unobtainable adducts of novel structure.

RESULTS

The cycloadduct of (I) and TCNE was prepared in high yield by mixing benzene solutions of the two reactants⁴; the adduct rapidly precipitated as a yellow powder. When it was stirred with ceric ammonium nitrate in 95% ethanol, the complex slowly decomposed, and white crystals were obtained in 84% yield. This product had an IR absorption at 2237 cm^{-1} , indicative of cyano groups, and a relatively simple PMR spectrum: resonances corresponding to two protons at τ 3.77 (d, $J = 5.8\text{ Hz}$), two protons at 4.26 (d, $J = 5.8\text{ Hz}$), and a sharp four-proton multiplet centered at 5.84. Proton resonances for only four vinyl protons rule out any bicyclic structures such as those for the organic species in (II) or (IV); the PMR data require instead a tricyclic structure having two double bonds. The UV spectrum did not display any maxima above 235 nm, thus eliminating conjugated dienes from consideration. Moreover, the *cis*-geminal coupling constant across the double bonds, 5.8 Hz, requires that they be part of five-membered rings (*cf.* cyclopentene, 5.4 Hz; norbornene, 5.8 Hz; cyclohexene, 9.6 Hz)¹⁰. The only structures which fit these data are 8,8,9,9-tetracyanotricyclo[5.2.1.0^{4,10}]deca-2,5-diene, (VII), a dihydrotriquinacene derivative, and 2,2,3,3-tetracyanotricyclo[5.3.0.0^{4,8}]deca-5,9-diene (VIII). The PMR data appear to be in better agreement with structure (VII) than with (VIII). In particu-



lar, the near-equivalence of the methine protons and the lack of observable couplings between methine and vinyl protons have also been found in both triquinacene*¹¹ and dihydrotriquinacene¹². (The resonances of vinyl and methine hydrogens in the latter were found at τ 4.5 and 6.7, respectively, in reasonable agreement with the PMR data from our product.) In contrast, the relevant vinyl and methine hydrogens of tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene and its 5,6-benzo derivative¹³ fall in the ranges τ 3.4–4.4 and 6.4–7.6. Chemical shift equivalences in the methine protons are not observed, and coupling constants of 3 and 6 Hz are observed between methine and vinyl protons, both unlike our product.

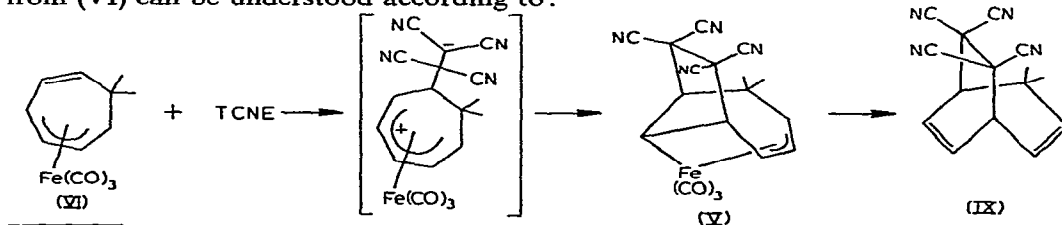
Confirmation that the product is (VII) was obtained by means of ¹³C magnetic resonance spectroscopy. The methine carbons of (VIII) occur in pairs and should give rise to two lines of equal intensity in a proton noise decoupled spectrum. (VII), on the other hand, has three types of nonequivalent methine carbons, and could give as many as three lines, in a 2/1/1 intensity ratio. In the event, two methine ¹³C resonances are observed, in a 3/1 ratio. This result excludes structure (VIII), and fits (VII), assuming an accidental overlap of the pair of equivalent methine carbon resonances with one of the other methines.

The adduct (V) was prepared by the same method as described above, and this complex was chemically degraded with ferric chloride. The resulting white crystals had an IR absorption at 2247 cm⁻¹, attributable to the cyano-groups, and an NMR spectrum which indicated that two double bonds were present in the system: τ 3.23 (triplet of doublets, 2H, $J = 7, 2$ Hz), 4.02 (m, 2H), 6.02 (m, 2H), 7.12 (m, 2H). No absorptions were observed in the UV spectrum above 235 nm, ruling out a conjugated diene. The only structure which can fit the observed NMR spectrum is (IX), the product which would arise from the unobserved [$\pi 2s + \pi 4s$] cycloaddition reaction of TCNE and a diene unit of free cycloheptatriene.

DISCUSSION

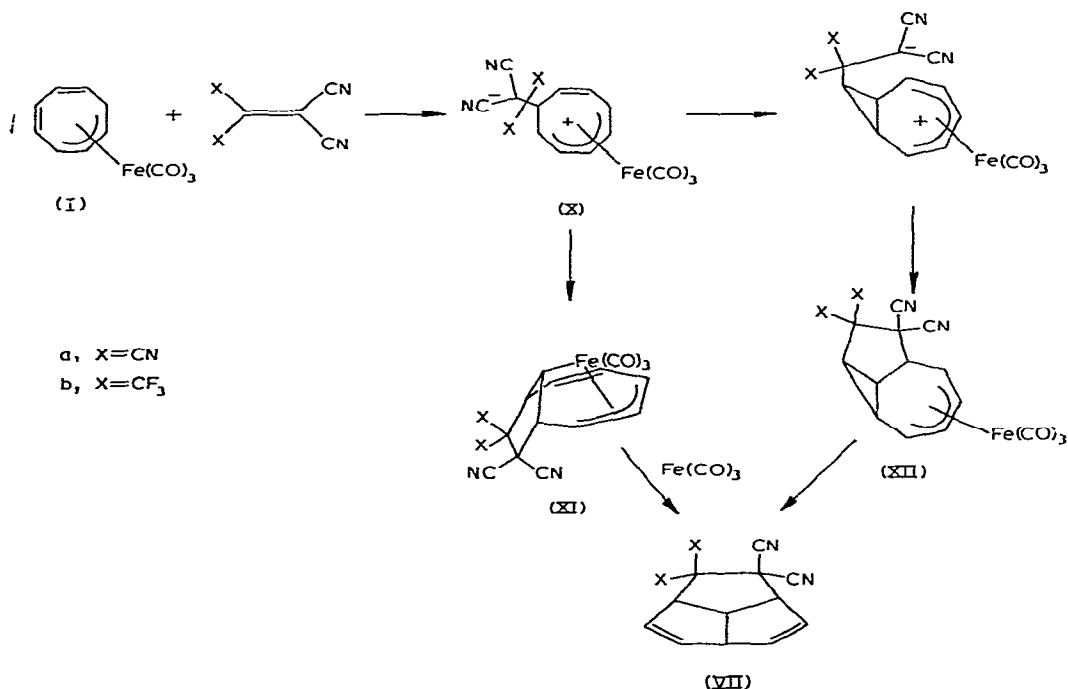
The unanticipated structure (VII) for the organic moiety from oxidative degradation of the (I)-TCNE adduct makes untenable the structures (II) and (III) proposed for that adduct. The nature of (VII) alone does not, however, provide an unequivocal structure for the adduct.

The recent reports of Green⁶, Wojcicki¹⁴, and Giering and Rosenblum¹⁵ make clear that many "cycloadditions" of TCNE with transition metal-complexed organic ligands occur by electrophilic mechanisms, with the transition metal stabilizing a positive charge in a zwitterionic intermediate. It seems very probable that such processes are responsible for the results reported herein. Thus, the products from (VI) can be understood according to:



* Hydrolysis of (VI), followed by lead tetraacetate oxidation of the diacid, may provide a better synthesis of triquinacene. See ref. 11.

Analogously, (I) should react with TCNE to give a zwitterion (X), which may close to (XIa) directly, or isomerize in the manner of protonated (I)¹⁶ before closing to give (XIIa). Either (XIa) or (XIIa) could easily rearrange to the observed (VII) on oxidation.



The structure (XIb) appears to fit the reported PMR data for the (I)-dicyano-bis(trifluoromethyl)ethylene adduct better than the previously suggested structure (IIIb)⁵; we therefore favor structure (XI) for both adducts. Clearly, however, further investigation, preferably by X-ray crystallography, will be needed to definitely resolve these structural questions.

Of possibly greater importance is the synthetic potential of these reactions. In both of the cases dealt with here, reaction of the complexed polyene with TCNE, followed by oxidative degradation, gives an adduct different from that obtained by reaction of the uncomplexed polyene with TCNE*. Moreover, the results of Green^{5,16} show that the use of different metals (Ru instead of Fe) can result in formation of still different adducts. There seems therefore to be substantial synthetic promise to this indirect route for the production of otherwise unobtainable adducts.

EXPERIMENTAL

IR spectra were measured on a Perkin-Elmer Model 137B spectrophotometer, UV spectra on a Beckman DK-2A or Cary Model 14, and proton magnetic resonance spectra on a Varian A-60. The ¹³C magnetic resonance spectrum was obtained through

* See ref. 17a (cyclooctatetraene) and ref. 17b (cycloheptatriene).

the courtesy of Mr. LeRoy Johnson of Varian, on an XL-100 instrument with Fourier transform operation. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

All m.p.'s are uncorrected. Solvents used in reactions and spectra were spectro grade or were redistilled from appropriate drying agents before use.

*Cyclooctatetraeneiron tricarbonyl-tetracyanoethylene adduct*⁴

Cyclooctatetraeneiron tricarbonyl was prepared by a published method¹⁸ and used after purification by sublimation (75° at 0.2 mm).

Cyclooctatetraeneiron tricarbonyl (3.81 g, 15.6 mmoles) was dissolved in 50 ml benzene and TCNE (2.00 g, 15.6 mmoles) was added with vigorous stirring. There was rapid darkening, then lightening of color, and a light yellow precipitate formed. The solution was filtered after 15 h to give 5.55 g of the adduct (96% yield): the yellow crystals darken over 160°, do not melt under 350°; IR (KBr): 2899 w, 2237 m (C≡N), 2066 s (CO), 2016 vs (CO), 1966 vs (CO), 1658 w, 1497 w, 1437 vw, 1401 w, 1340 w, 1318 m, 1305 w, 1284 w, 1264 w, 1238 w, 1218 w, 1182 w, 1142 w, 1116 m, 1082 w, 1065 w, 1026 w, 988 w, 962 m, 931 m, 903 s, 859 m, 843 m, 779 m, 755 m, 678 m cm⁻¹.

Degradation of the cyclooctatetraeneiron tricarbonyl-tetracyanoethylene adduct

The adduct (1.0 g, 2.7 mmoles) was stirred in 200 ml of 95% ethanol at room temperature with ca. 25 g ceric ammonium nitrate for two days. The solution was then poured into 400 ml of water and extracted first with four 50 ml portions of CH₂Cl₂ and then with two 50 ml portions of ethyl ether. These combined layers were washed with two 25 ml portions of water, dried, and the solvent was evaporated at reduced pressure to yield 0.52 g (84%) of white crystals. These were recrystallized from methanol: m.p. 132–133°; IR (KBr): 3012 w, 2899 w, 2882 m, 2237 m (C≡N), 1704 w, 1689 w, 1675 w, 1613 w, 1597 m, 1555 s, 1333 m, 1294 m, 1276 m, 1255 m, 1221 m, 1205 w, 1130 m, 1120 w, 1086 m, 1067 m, 1054 m, 1011 m, 974 s, 964 m, 946 m, 897 m, 873 m, 862 s, 822 s, 801 s, 757 s, 741 s, 677 w cm⁻¹; PMR (acetone): see text. ¹³C magnetic resonance (dimethyl sulfoxide): (ppm downfield from TMS at 25.2 MHz, rel. intensity, interpretation): 141.6, 100, C² or C³; 126.1, 103, C² or C³; 112.3, 26, CN; 110.4, 24, CN; 58.8, 168, C¹, C⁷, and C⁴ or C¹⁰; 51.0, 38, C⁸; 49.7, 50, C⁴ or C¹⁰. With off-resonance single frequency proton decoupling, the peaks assigned to the methine and vinyl carbons were split into doublets; the C⁸ and CN peaks were unchanged. Only end absorption was observed in the UV region, below 235 nm (CH₂Cl₂ or CH₃OH). (Found: C, 72.40; H, 3.55; N, 23.97. C₁₄H₈N₄ calcd.: C, 72.41; H, 3.45; N, 24.14%.)

Preparation of cycloheptatrieneiron tricarbonyl

Cycloheptatrieneiron tricarbonyl was prepared as described in the literature¹⁹, but using a reaction time of only 3 days (20% yield).

The cycloheptatrieneiron tricarbonyl-tetracyanoethylene adduct

Cycloheptatrieneiron tricarbonyl, (III), (19.0 g, 82 mmoles) was dissolved in 50 ml of benzene and freshly sublimed TCNE (10.0 g, 78 mmoles) dissolved in 250 ml of benzene was added quickly with vigorous stirring. The solution turned from yellow

to brown, and, within two minutes, a yellow solid precipitated, leaving a yellow supernatant liquid. The solid was filtered and washed with two 10 ml portions of benzene to give 26 g (92%) of a yellow solid: crystals darken over 160°, do not melt under 350°; IR (KBr): 2976 w, 2899 w, 2849 w, 2257 m (C≡N), 2083 s (CO), 2028 vs (CO), 2004 vs (CO), 1504 w, 1453 m, 1381 w, 1342 m, 1323 w, 1285 w, 1239 m, 1209 m, 1145 w, 111 m, 1086 w, 1033 m, 995 s, 929 m, 911 w, 886 s, 845 m, 834 s, 779 w, 681 s cm⁻¹; the compound was not soluble enough in organic solvents to obtain an NMR spectrum. (Found: C, 53.55; H, 2.23; N, 15.78. C₁₆H₈FeN₄O₃ calcd.: C, 53.33; H, 2.22; N, 15.56%.)

The chemical degradation of the cycloheptatrieneiron tricarbonyl-tetracyanoethylene adduct

The adduct (5.0 g, 13.8 mmoles) was swirled in 200 ml of methanol and 5 ml of water on a steam bath, and FeCl₃ was added until no additional vigorous evolution of gas was observed. The solution was poured into 500 ml of water, and this was extracted with five 75 ml portions of ether. These were combined, washed with 100 ml of water, dried, and the ether was removed on a rotary evaporator. The red-orange residue was dissolved in a minimum amount of hot methanol and cooled to give 1.42 g (47%) of white crystals: m.p. 235–237°; IR (KBr): 3049 w, 2933 w, 2890 w, 2247 w (C≡N), 1658 w, 1653 vw, 1429 m, 1393 w, 1376 m, 1348 w, 1321 w, 1305 w, 1295 w, 1225 m, 1174 w, 1093 w, 1016 w, 987 w, 971 w, 913 w, 896 w, 868 m, 796 m, 736 s, 705 s cm⁻¹; NMR (acetone-*d*₆): τ 3.23 (triplet of doublets, 2H, *J* = 7, 2 Hz), 4.02 (m, 2H), 6.02 (m, 2H), 7.12 (m, 2H); no absorptions were observed in the UV spectrum above 235 nm (CH₂Cl₂). (Found: C, 70.98; H, 3.69; N, 25.68. C₁₃H₈N₄ calcd.: C, 70.90; H, 3.64; N, 25.45%.)

Cycloheptatriene-tetracyanoethylene adduct

This compound was prepared in the same manner as described above for the cycloheptatrieneiron tricarbonyl: TCNE adduct (58% yield). The NMR spectrum of the compound was identical to that reported: (acetone-*d*₆) τ 3.62 (t, 2H, *J* = 5 Hz), 5.70 (m, 2H), 8.30 (m, 2H), 9.24 (m, 1H), 9.60 (m, 1H); m.p. 160° (decompn.), lit.²⁰ m.p. 160–161° (decompn.).

Attempted rearrangement of the cycloheptatriene-tetracyanoethylene adduct with ferric chloride

The normal adduct (0.156 g, 0.71 mmole) was heated in 10 ml of methanol and one ml of water with FeCl₃ (ca. 2 g) on a steam bath for 10 min, then poured into 30 ml of water. This solution was extracted with two 50 ml portions of ether and two 50 ml portions of CH₂Cl₂; these were combined and washed with 50 ml of water, dried, and solvent was removed on a rotary evaporator to give 0.128 g (82% recovery) of white crystals. An NMR spectrum (acetone-*d*₆) showed only unchanged starting material.

Attempted reaction of cyclohexadieneiron tricarbonyl with tetracyanoethylene

1,3-Cyclohexadieneiron tricarbonyl (0.5 ml) was added to freshly sublimed TCNE (0.1 g) in 30 ml of benzene and stirred at room temperature for 1 h. At the end of this period, there was no visible change in the reaction mixture, and the NMR spectrum of the starting complex was unchanged.

Attempted reaction of 1,3-cyclooctadiene with tetracyanoethylene

1,3-Cyclooctadiene (0.50 g, 4.6 mmoles) was added to freshly sublimed TCNE (0.38 g, 3.0 mmoles) dissolved in 100 ml of benzene with stirring. There was no apparent reaction after 30 min, so the solution was heated at gentle reflux for 18 h, then allowed to cool to room temperature. Benzene was removed from the orange solution, leaving a red solid. An NMR spectrum (acetone) showed only unchanged cyclooctadiene.

ACKNOWLEDGEMENTS

Daniel J. Ehntholt gratefully acknowledges receipt of an American Chemical Society-Petroleum Research Fund Graduate Fellowship (1969-1970). We are very grateful to Mr. LeRoy Johnson of the NMR Applications Laboratories, Varian, for the ^{13}C magnetic resonance measurements on (VII).

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