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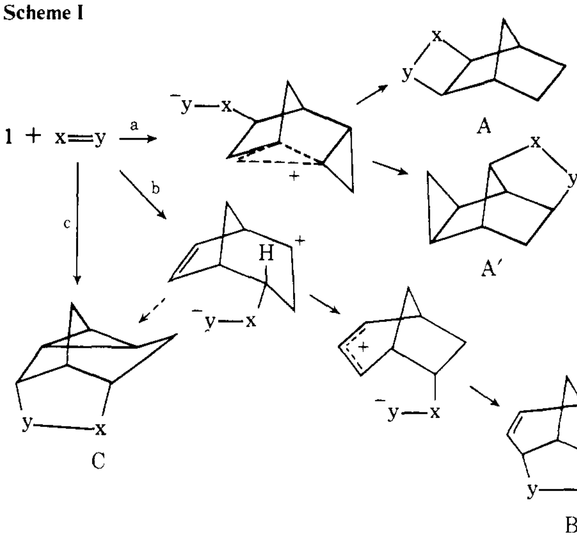
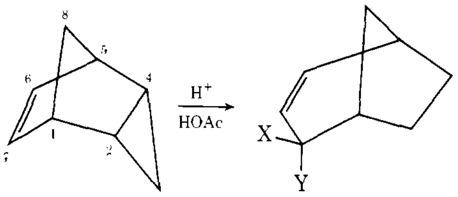
Nonconcerted Polar Cycloadditions to *endo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene. Structure of a Novel Tetracyanoethylene Adduct

Sir:

The acid-catalyzed addition of acetic acid to *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**1**) has been shown to occur with regiospecific cyclopropane ring opening and subsequent 1,2-shift of the bridge carbon (C8) to yield predominantly the allylic acetates **2a** and **2b**.[1] The reaction is remarkable for its specificity as revealed by more recent studies in methanol.[2] Noteworthy features are (i) reaction initiation is exclusively at a cyclopropyl carbon (C2,4), (ii) cyclopropane ring opening occurs with inversion of configuration (corner protonation), and (iii) carbonium ion products appear to be totally in the Goering[3] rather than LeBel[4] series indicating little if any leakage during the addition-rearrangement sequence.[2,5]

Scheme I





1

2a, X = OAc; Y = H
2b, X = H; Y = OAc

The facility of electrophilically promoted ring opening reactions of **1** prompted an investigation of the addition of multiple-bond electrophiles[6] to this strained hydrocarbon. As part of this study we now report a unique example of a polar, nonconcerted cycloaddition by tetracyanoethylene (TCNE).

At the outset three modes of addition of a π-electrophile (x═y) to **1** were envisioned, i.e., attack at the double bond or cyclopropane ring or both as indicated by pathways a, b, and c of Scheme I.[7] Concerted pathway c is considered un-

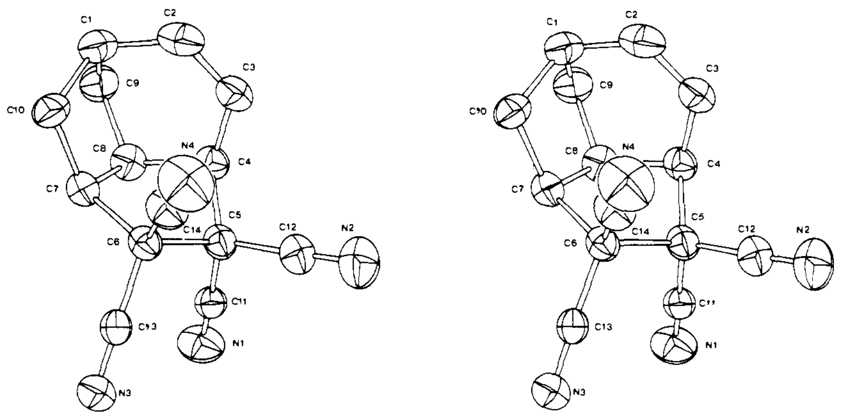
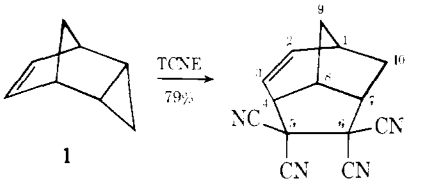


Figure 1. A stereoview of 5,5,6,6-tetracyanotricyclo[5.2.1.0^{4,8}]dec-2-ene (**3**). The hydrogen atoms have not been included for clarity. The double bond is between C2 and C3.

likely on the basis of inappropriate orbital topology in **1**. Nevertheless C would still be a feasible product if π-capture of the initial ionic intermediate in path b is competitive with σ-capture that leads to product B.[8] Of the generalized products A, A′, B, and C, only B retains the vinyl grouping. The π-electrophiles examined include TCNE, chlorosulfonyl isocyanate (CSI), benzyne, dimethyl acetylenedicarboxylate, maleic anhydride, and *N*-phenyltriazolinedione.

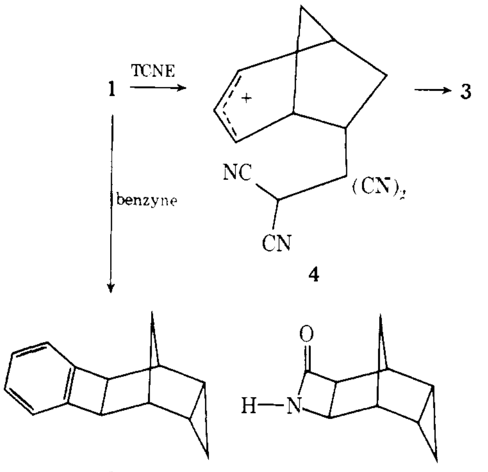
Reaction of an equimolar methylene chloride solution of TCNE and **1** at room temperature for 1 week afforded a 79% yield of a crystalline (white needles) 1:1 adduct, mp 186–187°: $\nu_{max}{}^{CN}$ 2252 cm^{-1}; MS (70 eV) *m/e* (rel intensity) 234 (12; M$^+$], 106 (90; M$^+$ − 128), 79 (100; M$^+$ − 128 − 27); ^{1}H NMR (CDCl$_3$; 100 MHz)[9] τ 3.54 (ddt, 1 H, $J_{2,3} = 9.4$, $J_{1,2} = 6.8$, $J_{2,9a} \cong J_{2,4} \cong 1$ Hz; H^2), 4.43 (ddd, 1 H, $J_{3,4} = 3.2$, $J_{3,8} = 1.5$ Hz; H^3), 6.31 (m, 1 H; H^4), 6.57 (m, 2 H; H^{7,8}) 7.29 (m, 1 H; H^1), 7.44 (d, 1 H, $J_{10n,10x} \cong 19$ Hz; H^{10n}), 7.74 (ddd, 1 H, $J_{7,10x} = 9$, $J_{1,10x} = 5$ Hz; H^{10x}), 8.08 (dt, 1 H, $J_{9a,9s} = 12$, $J_{2,9a} \cong 1$ Hz; H^{9a}), 8.20 (dt, 1 H, $J_{1,9s} = J_{8,9s} = 3$ Hz; H^{9s}). The observation of two olefinic protons in the NMR, and the similarity of their coupling pattern to that of other *endo*-2-bicyclo[3.2.1]oct-3-enyl derivatives, strongly suggested the 5,5,6,6-tetracyanotricyclo[5.2.1.0^{4,8}]dec-2-ene structure **3** for this adduct. While this assignment is in full accord with all of the spectral data, further confirmation of the structure was obtained by single-crystal X-ray analysis.



The colorless crystals of **3** grown from methylene chloride are monoclinic, space group $P2_1/c$, with $a = 7.941$ (3) Å, $b = 11.503$ (3) Å, $c = 13.718$ (8) Å, and $\beta = 110.45$ (4)°. With four molecules of $C_{14}H_{10}N_4$ per unit cell, no molecular symmetry is required. The intensity data were measured on a Syntex P$\bar{1}$ diffractometer using graphite monochromatized Mo Kα radiation and a θ–2θ scan technique. The structure was solved using the symbolic addition procedure with the computer programs FAME-MAGIC-LINK-SYMPL written by Fleischer, Dewar, and Stone. The refinement was by full-matrix least-squares methods. The final *R* (the usual residual) was 0.038 for the 1667 reflections with $I \geq \sigma(I)$ used in the analysis.[10]

The atomic numbering and moleular geometry of **3** are illustrated in Figure 1. The C2–C3 distance of 1.325 (2) Å clearly establishes the position of the double bond. The C5–C6 bond length of 1.596 (2) Å is somewhat long and may indicate steric strain or elongation due to the cyano groups. The cyano groups are slightly bent (the average C—C≡N angle is 178.0 (6)°) but the dimensions (average C—C of 1.474 (4) Å and C≡N of 1.134 (2) Å) are not unusual.

Formation of TCNE cycloadduct **3** to the exclusion of adducts of structural type A, A′, or C (Scheme I) is entirely consistent with the previously summarized results for acid-catalyzed additions to **1**. Thus approach of the electrophile (TCNE) from the underside of the envelope flap of the cyclopropane ring of **1** (corner attack) leads to cleavage of the C2, C4 bond with concomitant σ-participation by the C1, C8 (C5, C8) bridge bond. This mode of ring opening generates allylic zwitterion **4** as the product determining intermediate thereby excluding leakage to LeBel type product C. The absence of ene-type products and the observed 1,2-alkyl shift strongly support the polar nature of this cycloaddition. In view of the ready accessibility of olefin **1**[11] this reaction provides a convenient synthetic entry into the homobrendane ring system, a system structurally related to protoadamantane[12] by a single 1,2-carbon shift.



In sharp contrast with the TCNE reaction, but in accord with anticipated behavior of norbornene derivatives,[13] **1** afforded the (2 + 2) cycloadduct **5**,[14] mp 53–54°, in low yield on treatment with benzyne generated from benzenediazonium 2-carboxylate in methylene chloride. Similarly, preliminary results with CSI indicate formation of the analogous cycloadduct **6** (after hydrolysis). Dimethyl acetylenedicarboxylate, maleic anhydride, and *N*-phenyltriazolinedione failed to react with **1** at room temperature and at elevated temperatures afforded complex product mixtures.

The contrasting reactivity of benzyne and TCNE with **1** is readily accommodated on the basis of their relative electrophilicities and again points to the strongly polar character of the TCNE cycloaddition. For the highly polar heterocumulene CSI the well-known facility to add to unactivated olefins[15] apparently promotes double bond rather than cyclopropane attack. Since TCNE is by comparison unreactive toward simple olefins, it functions as the more discriminating electrophile. Further studies of the synthetic and mechanistic aspects of this unique cycloaddition are in progress.

Acknowledgments. Financial support of this research by the National Science Foundation and a grant of computer time from the Northeast Regional Data Center at the University of Florida is gratefully acknowledged. J.M.C. wishes to thank the Fulbright-Hays Program for the award of a travel grant.

Supplementary Material Available. A listing of the final positional and thermal parameters and the observed and calculated structure amplitudes for 5,5,6,6-tetracyanotricyclo[5.2.1.0^{4,8}]dec-2-ene will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-945.

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(6) Such electrophiles have been previously termed "uniparticulate electrophiles" by L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst (*J. Am. Chem. Soc.*, **93**, 4503 (1971)). In that attack on a strained ring bond is contemplated the term "tanycyclophile," as introduced by P. G. Gassman (*Acc. Chem. Res.*, **4**, 128 (1971)), would also apply.

(7) That only dipolar intermediates are represented in this scheme is purely a consequence of our focus on the electrophilically available pathways for reaction of **1**. Depending on the nature of the π-electrophile and the preponderance of evidence concerning its mode of nonconcerted, e.g. (2 + 2), cycloaddition, diradical intermediates may be preferable.

(8) The implication that the first ionic intermediate of path b has a classical secondary structure is for the purposes of discussion only and should not be construed as having any supportive basis. In fact the evidence from the acid-catalyzed ring opening of **1** in methanol,[2] as well as the TCNE results presented here, strongly argue against a classical intermediate at this stage of the reaction.

(9) The complex proton spectrum was partially unraveled with the help of decoupling experiments and inspection of molecular models. The assigned long-range coupling constants are of the W-type. The subscripts a (anti), s (syn), x (exo), and n (endo) stereolabel the respective methylene bridge protons at C9 and C10 in accordance with accepted practice for bicyclo[3.2.1]oct-2-ene derivatives.

(10) See paragraph at end of paper regarding supplementary material.

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Transition Metal Carbonyl Substitution via a Radical Chain Pathway[1]

Sir:

Recognized pathways for substitution at a transition metal carbonyl center include rate-determining CO dissociation, displacement of CO in an associative step, and ligand migration.[2,3] We report here the first evidence for a heretofore unrecognized radical chain pathway for substitution, which may prove to be of considerable generality and importance.

Although substitution of $HRe(CO)_5$ by triphenylphosphine (PPh_3) and other similar ligands has been reported,[4] no kinetics studies have been reported. We found that it was exceedingly difficult to obtain reproducible kinetics results. Under the most rigorous attainable conditions of solvent and reagent purity, with exclusion of light, the thermal reaction in hexane, under N_2, of 10^{-3} *M* $HRe(CO)_5$ with $\sim 10^{-2}$ *M* tributylphosphine, $P(n\text{-}C_4H_9)_3$, exhibited no reaction after 60 days at 25°. Thus $HRe(CO)_5$ is extraordinarily inert toward substitution via CO dissociation or hydride migration pathways, in comparison with $HMn(CO)_5$.[5] Exposure to light, failure to exhaustively purify the reagents, and various other circumstances caused the reaction to go to completion at widely varying rates to yield $HRe(CO)_4L$ and $HRe(CO)_3L_2$. With PPh_3, $HRe(CO)_4L$ was formed at similarly erratic rates. Similar results were obtained in THF as solvent, except that the reactions were generally much faster. Exposure to air or hydroquinone in low concentration retards reaction. Contrary to an earlier report,[6] $HRe(CO)_5$ alone in either solvent does not react with dissolved oxygen at room temperature.

These observations suggest a radical pathway involving adventitious radicals as initiators. The following mechanism accounts for the observations.

$$R + HRe(CO)_5 \longrightarrow RH + Re(CO)_5 \qquad (1)$$

$$Re(CO)_5 + L \longrightarrow Re(CO)_4L + CO \qquad (2)$$

$$Re(CO)_4L + L \longrightarrow Re(CO)_3L_2 + CO \qquad (3)$$

$$Re(CO)_4L + HRe(CO)_5 \longrightarrow Re(CO)_5 + HRe(CO)_4L \qquad (4)$$

$$Re(CO)_3L_2 + HRe(CO)_5 \longrightarrow Re(CO)_5 + HRe(CO)_3L_2 \qquad (5)$$

$$Re(CO)_{5-n}L_n + Re(CO)_{5-m}L_m \longrightarrow Re_2(CO)_{10-n-m}L_{n+m} \qquad (6)$$

Chain termination steps involving formation of $RRe(CO)_5$, $Re_2(CO)_9L$, and $Re_2(CO)_8L_2$ (but probably not $Re_2(CO)_6L_4$[7]) are all possible.

The following results support the proposed mechanism. A solution containing 10^{-3} *M* $HRe(CO)_5$ with 10^{-2} *M* $P(n\text{-}C_4H_9)_3$ in hexane was irradiated with a 1000-W mercury-xenon lamp filtered through an interference filter centered at 311 nm. There resulted a slow substitution to form initially $HRe(CO)_4L$. After 2 hr the reaction was only about 10% complete. Continued irradiation yielded $HRe(CO)_3L_2$ in addition to $HRe(CO)_4L$. After 12 hr of irradiation the reaction was only about 66% complete. Substitution in this system is presumably due to CO photodissociation from $HRe(CO)_5$ and later from $HRe(CO)_4L$.

Our proposed mechanism requires that $Re(CO)_5$ be labile toward substitution, since it probably has a rather short lifetime in solution. The absorption of $Re_2(CO)_{10}$ at 310 nm is ascribed to the σ–σ^* transition of the Re–Re bond.[8,9] Photochemical studies suggest that irradiation of $Re_2(CO)_{10}$ at this wavelength produces $Re(CO)_5$ radicals.[10] A 5×10^{-4} *M* solution of $Re_2(CO)_{10}$ with excess $P(n\text{-}C_4H_9)_3$ in hexane does not undergo substitution at room temperature over a period of several hours. Irradiation at 311 nm for a period of 150 min results in about 15% loss of $Re_2(CO)_{10}$, with $Re_2(CO)_9P(n\text{-}C_4H_9)_3$ and $Re_2(CO)_8[P(n\text{-}C_4H_9)_3]_2$ as products along with several other as yet unidentified substitution products. These results are suggestive of a rapid substitution of (probably) diffusively separated $Re(CO)_5$ radicals, followed by recombination of substituted radicals.[11,12]

A hexane solution containing 10^{-3} *M* $HRe(CO)_5$, $\sim 10^{-2}$ *M* $P(n\text{-}C_4H_9)_3$, and 10^{-4} *M* $Re_2(CO)_{10}$ shows no evidence of reaction in the dark over a period of several hours. The reaction solution was irradiated at 311 nm. Typically, the parent hydride disappeared very slowly during the first 6–10 min, during which time only $HRe(CO)_4L$ was formed as product. After this initial induction period,[13] the reaction proceeds very rapidly under irradiation; reaction is essentially complete after about 5–6 min. Both $HRe(CO)_4L$ and $HRe(CO)_3L_2$ are formed concurrently, in roughly 3:1 ratio.[14,15]

In all the above experiments the flux of 311 nm photons is constant. The results thus indicate that, whatever the quantum yield for photosubstitution of $Re_2(CO)_{10}$, the quantum yield for substitution of $HRe(CO)_5$ with photocatalysis by $Re_2(CO)_{10}$ or $Mn_2(CO)_{10}$ is enormously higher, consistent with the proposed mechanism.