

DIPOLAR ADDITION VERSUS OXYGEN TRANSFER IN THE REACTION OF TETRACYANOETHYLENE OXIDE WITH UNSATURATED HYDROCARBONS*

P. BROWN† and R. C. COOKSON

Chemistry Department, Southampton University

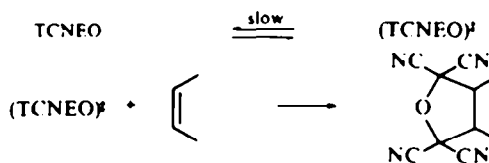
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Abstract With the single exception of anthracene, which yields the unsymmetrical adduct (VA), olefins, polyenes and aromatic compounds react with tetracyanoethylene oxide to give symmetrical 2,2,5,5-tetracyanotetrahydrofurans. With the more nucleophilic olefins, including anthracene, oxygen transfer also occurs, forming ketones and tetracyanoethylene or its adducts with the olefin.

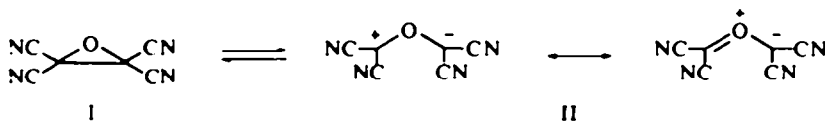
The adduct (VA) of 9-deuterioanthracene and tetracyanoethylene oxide has 19% excess of deuterium on the carbon linked to the oxygen atom (i.e. VA, $R_1 = D$, $R_2 = H$ is formed faster than VA; $R_1 = H$, $R_2 = D$). This large isotope effect agrees with a reaction mechanism in which the first stage is attack on the electrophilic oxygen atom of tetracyanoethylene oxide followed by rapid cyclization of the dipolar intermediate.

INTRODUCTION

TETRACYANOETHYLENE oxide^{1,2} (TCNEO) has been made recently from tetracyanoethylene (TCNE), and attention drawn^{1,3} to its ability to add to multiple C—C bonds, even those in benzene, to form 2,2,5,5-tetracyanotetrahydrofurans.⁵



Kinetic evidence has been presented⁴ for initial promotion of TCNEO to some activated form TCNEO^\ddagger as the slow step. Addition to *cis/trans* isomeric pairs of olefins is stereospecific, *trans* adding faster than *cis*, the polarity of the solvent hardly affects the rate, and with substituted stilbenes the reaction has a very small negative Hammett ρ -value.⁴



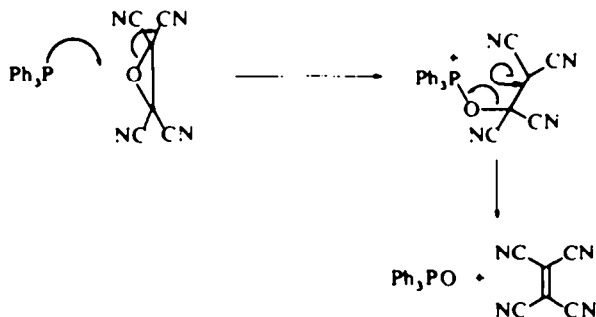
* A preliminary account of this work has appeared. P. Brown and R. C. Cookson, *Proc. Chem. Soc.* 185 (1964); P. Brown and R. C. Cookson, *Abs. Papers, 148th A.C.S. Meeting* p. 7U. Chicago, Sept. (1964). Taken from the Ph.D. Thesis of P. Brown, Southampton (1964).

† Present address: Chemistry Department, Arizona State University, Tempe, Arizona, U.S.A.

All these features are characteristic of 1,3-dipolar cycloadditions,⁵ with TCNEO⁸ pictured as a symmetrical carbonyl ylide dipole II (planar, and isoelectronic with the tetracyanopropene anion). Factors favouring opening of the ring, compared with normal epoxides, must include (1) relief of repulsion between adjacent nitrile groups,⁶ (2) proximity of induced partial positive charges on the C atoms in the ring, and (3) delocalization of the dipole electrons over the whole molecule in the open form.

However, TCNEO is also an oxidizing agent. Epoxides are weak bases compared with acyclic ethers,⁷ the unshared electron pairs on the O atoms being restrained in orbitals of higher *s* hybridization than simple *sp*³. The already relatively electro-positive character of the O atom in cyclic TCNEO (I) will be further enhanced by the inductive pull of the four cyano-groups. Because the dicyanomethyl anion forms such a good leaving group, and the electrophilic oxygen is much more exposed than the C atoms of the ring, nucleophilic attack on oxygen rather than (as usual) on carbon seemed a real possibility in TCNEO.

In fact, the oxide (I) was rapidly reduced by triphenylphosphine at room temperature to TCNE, which could be isolated in high yield as its cyclopentadiene adduct, presumably formed via:



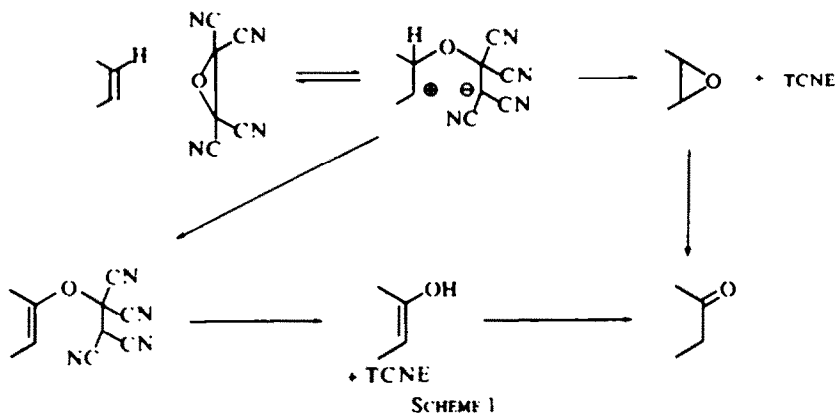
It is not surprising, then, that especially with dienes and aromatics of low ionization potential the TCNEO adducts were often accompanied by oxidation products, and TCNE or (in the presence of cisoid dienes) its adducts. Table 1 summarizes the reactions observed. Amongst the aromatic compounds for example (nucleophilicity at a particular C atom roughly following ionization potential), anthracene (ionization potential = 7.74 eV)⁸ and durene (8.02 eV)⁹ are oxidized, but phenanthrene (8.27 eV),⁸ naphthalene (8.30 eV),⁸ furan (8.89 eV)¹⁰ and benzene (9.24 eV)^{10,11} are not. In the non-aromatics, cycloheptatriene (7.89 eV),¹⁰ cyclopentadiene (8.58 eV)¹⁰ and indene (8.63 eV)¹⁰ are oxidized, but not cyclopentene (9.01 eV)¹² or 1-butene (9.58 eV).¹¹ Again, bicyclo[2.2.1]heptadiene (8.58 eV)¹³ is oxidized, whereas the less strained bicyclo[2.2.2]octadiene is not.

On top of the sufficient reasons cited in the first paragraph, the exclusive formation of symmetrical *cis*-1,2- rather than 1,4- adducts with 1,3- dienes (especially cyclopentadiene, furan, cycloheptatriene, cyclooctatetraene and indene) also tends to favour a concerted addition of the dipolar open form (II) of TCNEO to the double bond in one step. Carbonium-enolate dipoles (open cyclopropanones) on the other hand, containing two rather than four π electrons, add only 1,4 to cisoid 1,3-dienes¹⁴ (cyclopentadiene and furan) as required for concerted *cis*-addition by Hoffmann and Woodward's rules.¹⁵

The oxidation reaction

All reactions were carried out in dry benzene with freshly sublimed TCNEO. With susceptible olefins the colourless solution fast turned yellow on boiling; the UV spectrum of a cooled and filtered sample was identical with that of TCNE in benzene; addition of anthracene to a further sample discharged the yellow colour, and the anthracene-TCNE adduct (VB)¹⁶ precipitated. In some cases (VII, XV, Table 1) free TCNE was isolated at the end of the experiment, and in others (V, X, XIII, XIV, XVI, XVIII) its adduct with the reactant.*

After extended heating the oxidation solutions darkened to opaque brown, and often deposited black tar or powder. Reactions in which oxidation did not occur were in general much cleaner, although the solutions turned a dull yellow after some time. Scheme 1 below summarizes some of the reactions that may follow nucleophilic attack of the olefin on the O atom of TCNEO, leading to the ketone. Whether the epoxide was an intermediate* in any case was not determined, but our early hope

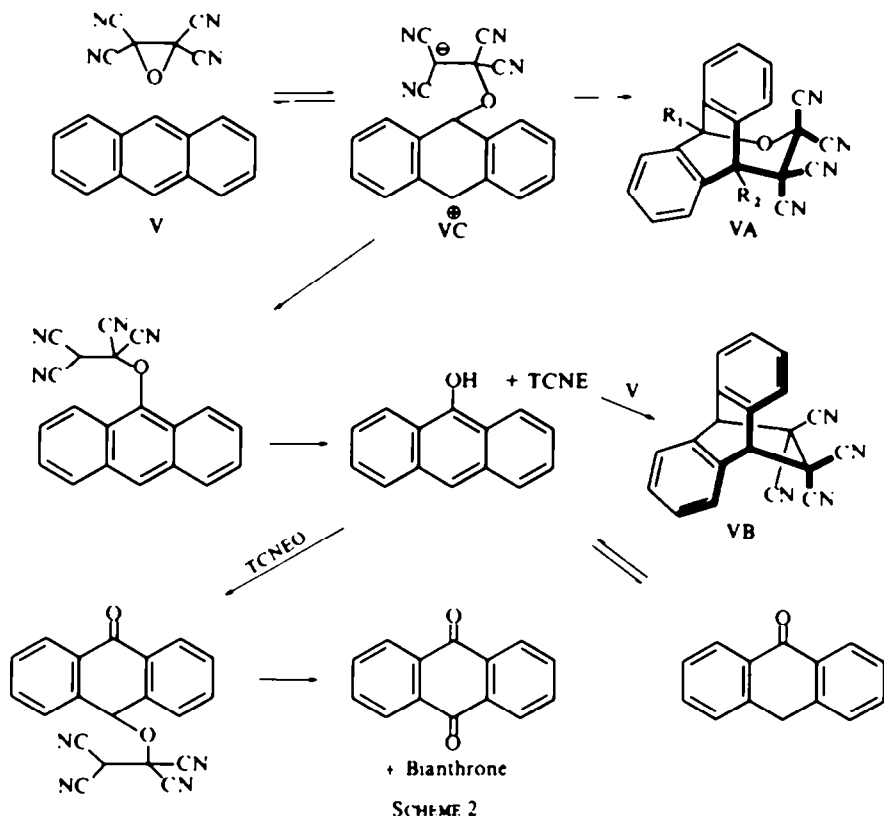


of developing TCNEO or another electrophilic epoxide into a useful epoxidizing agent for nucleophilic olefins has not been realized. The reactions which explain the products produced from anthracene are outlined in Scheme 2 (p. 2554).

Anthracene is obviously the most favourable case for formation of an unsymmetrical adduct (VA), and indeed none of the alternative 1,2-cycloaddition product was isolated. As the most nucleophilic hydrocarbon, it opens TCNEO to the dipolar intermediate (VC) with the carbonium ion well delocalized in the two benzene rings. In the conformation where the dicyanomethide anion is over the carbonium ion centre (C₁₀ of anthracene), the array is stabilized by electrostatic attraction and charge transfer, rapidly passing over into the stable adduct (VA).

It was anticipated that evidence for the unsymmetrical intermediate VC (Scheme 2) might be obtained from measurement of the secondary deuterium isotope effect on the reaction between 9-d₁-anthracene and TCNEO. In previous work,¹⁷ we had found isotope effects of between 1.02 and 1.07 for the Diels-Alder reaction of a series

* The oxidation reaction of TCNEO has also been observed by the DuPont group,³ who report in a footnote the isolation of TCNE from TCNEO/2,3-dimethyl-2-butene, and the TCNE adduct of 2,3-dihydropyran from TCNEO/2,3-dihydropyran. 2,3-Dimethyl-2-butene epoxide was also a product of the first reaction, where formation of any enolic intermediate (Scheme 1) is clearly prohibited.



of unsymmetrical cyano-substituted ethylenes with 9-d₁-anthracene, and it was concluded that the mechanism was concerted, although the transition states were somewhat lopsided. Our system was compared with that of Seltzer¹⁸ (2-methylfuran/d₁-maleic anhydride; isotope effect = 1.00) and of Katz¹⁹ (diphenylketene/1-d₁-cyclohexene; isotope effect = 1.13), the former result being interpreted in terms of a symmetrical transition state, and the latter as unsymmetrical but still concerted. In the 9-d₁-anthracene (Scheme 2, V, R₁ = D, R₂ = H)/TCNEO reaction, a secondary isotope effect of 1.19 was found, using PMR techniques previously described,¹⁷ in favour of adduct VA (R₁ = D, R₂ = H) (Scheme 2). This large effect (19% for one deuterium atom) is good evidence for the preferential formation of dipolar intermediate VC (R₁ = D, R₂ = H), and furthermore indicates that steric effects²⁰ are more important than inductive effects²¹ in determining secondary deuterium isotope effects in this system. The structure of VA follows from the similarity of its UV spectrum (Table 2) to that of 9,10-ethanoanthracene and the anthracene/TCNE adduct (VB), and its having two magnetically different bridgehead protons in its PMR spectrum (Table 3). A separate experiment, using equimolar anthrone and TCNEO under the same reaction conditions, gave the same oxidation products (Table 1), but of course no anthracene/TCNE adduct VB.

The reaction of anthracene with TCNEO strongly resembles its reaction with ozone. In non-polar solvents, an ozonide is produced by concerted 1,3-dipolar addition to

the anthracene 1,2-bond, whereas in polar solvents, a 9,10-bridged ozonide (analogous to VA) is formed by a two-step process.²²

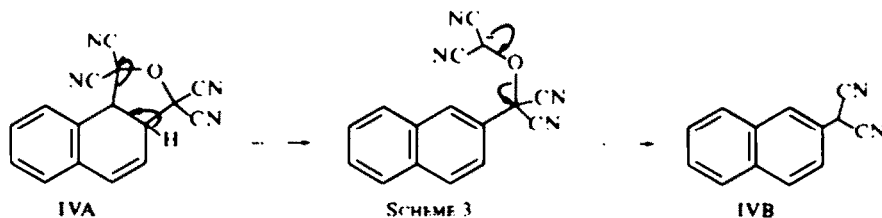
Durene (VII) is presumably oxidized to duroquinone by a very similar series of reactions, but here the keto-tautomer (cf. anthrone) of the phenol that may be an intermediate is not stable. In a separate experiment, 2,3,5,6-tetramethylphenol reduced TCNEO to TCNE in 92% yield.

Reactions of the adducts

The structures of most of the TCNEO adducts were based mainly on spectral evidence (particularly UV [Table 2] and PMR spectra [Table 3]), but they also had the expected chemical properties. For example, the cyclohexa-1,3-dienes (IIIA, VIIA) could be converted into Diels-Alder adducts. Thus, as well as undergoing 1,2-addition of a second molecule of TCNEO to give the bis-adduct (IIIB) in 61% yield (steric hindrance preventing further reaction), the benzene-adduct (IIIA) also afforded 18% of a Diels-Alder adduct (XXI) by 1,4-addition of maleic anhydride. In spite of its much greater electronic reactivity, TCNE did not react under the same conditions, evidently because of congestion of the second pair of nitrile groups.* Similarly, the durene derivative VIIA added maleic anhydride in refluxing benzene, giving 44% of XXII, but did not react with TCNE.

On the other hand, the cyclooctatetraene adduct (XIXA), which presents less hindrance on the side of the diene opposite to the cyclobutane ring than in the adducts with the tetracyanotetrahydrofuran ring fused directly to the cyclohexadiene (IIIA and VIIA), added TCNE readily, affording an almost quantitative yield of XXA. The same adduct (XXA) was obtained in 66% yield by treatment of the cyclooctatetraene/TCNE adduct (XX) with TCNEO in refluxing benzene, the more strained and less hindered double bond only reacting.

A dilute solution of the naphthalene derivative (IVA) in ethanol gradually developed the characteristic naphthalene UV spectrum in place of the styrene type. Treatment of IVA with a trace of acid or base catalysed elimination of carbonyl cyanide (Scheme 3) with production of β -naphthylmalonodinitrile† (IVB) the structure of which was confirmed by oxidation to β -naphthoic acid.



Hydrogenation of the bicycloheptadiene adduct (XVIA) proceeded smoothly at room temperature with platinum oxide catalyst, yielding material identical in all respects to the bicycloheptene/TCNEO adduct (XVA). However, all attempts to

* Linn and Benson³ were unable to add either TCNE or maleic anhydride to the benzene/TCNEO adduct (IIIA).

† Dr. L. S. Beaford has shown that the same change is induced by UV irradiation of IVA in benzene through Pyrex glass.

reduce adducts IVA, XA and XIIA were unsuccessful, in keeping with a previous report³ that the benzene adduct IIIA could not be reduced catalytically.

The IR spectra of the various products showed the expected features, and were always consistent with the structures assigned. In the ultraviolet region the only compounds that absorbed intensely were the 1,3-dienes listed in Table 2, whose spectra resembled the parent hydrocarbons'. (IIIA cf. cyclohexa-1,3-diene,²³ λ_{\max} 256 nm; XIXA cf. bicyclo[4,2,0]-octa-2,4-diene,²⁴ 274 nm, rather than cycloocta-1,3,5-triene,²⁴ 265 nm; XVIIIA cf. cyclohepta-1,3-diene²⁵ 243 nm; VIA cf. 9,10-dihydrophenanthrene,²⁶ 265 and 297 nm.)

Proton magnetic resonance spectra

The PMR spectra of the various adducts are presented in Table 3. Addition of a second molecule of TCNEO to the 1:1 benzene adduct (IIIA) could in principle afford IIIB (1,2-addition *trans* to the functionality already present) or IIIC (1,4-addition, also from the less hindered side).

Sufficient chemical evidence has been collected which clearly demonstrates that TCNEO adds characteristically 1,2 as a 1,3-dipole to unexceptionally nucleophilic C—C multiple bonds. In addition, the PMR spectrum of the 2:1 adduct (IIIB, Table 3) is completely incompatible with structure IIIC.³ Two olefinic protons ($H_{a,b}$) appear as a singlet, while the remaining four protons resonate as an A/B quartet. In systems such as IIIC, the multiplicity of each absorption is invariably greater, and the olefinic protons are represented by a quartet. The simplicity of the spectrum is well accounted for by structure IIIB on the other hand, where Dreiding models indicate an angle of about 70° between protons H_a-H_b , consistent with a very small coupling constant.

Addition of TCNEO to durene gave the unsymmetrical adduct VIIA, rather than 1,2-addition to a more hindered disubstituted double bond, as indicated by the PMR spectrum (Table 3). Further addition of maleic anhydride to the *cis*-diene system of VIIA produced XXII, in which the single low-field proton (H_d) is coupled to the allylic protons of Me_2 ($J = 2.0$ c/s). A two proton signal at 5.98 τ must be $H_{m,m'}$, and H_e is then at 6.15 τ . Comparison of the spectrum of XXII with that of XXI (IIIA + maleic anhydride) confirms that the two adducts have the same general structure.

Coupling constant J_{ui} could not be reliably extracted from the PMR spectrum of cyclooctatetraene adduct XIXA, but the assigned stereochemistry was arrived at by chemical analogy (e.g. 1,2-photo-addition of maleic anhydride to benzene²⁷), and by further addition of TCNE to XIXA to furnish XXA, which had an identical PMR spectrum to the adduct obtained between TCNE/cyclooctatetraene adduct XX and TCNEO.

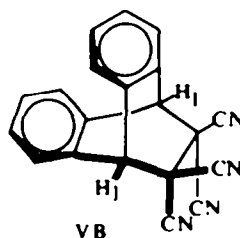
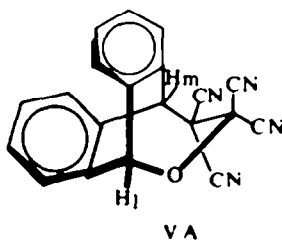
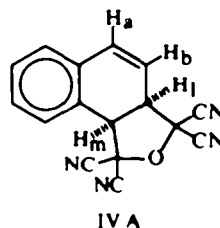
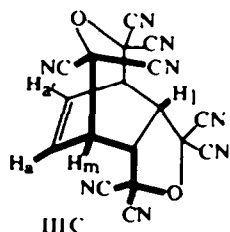
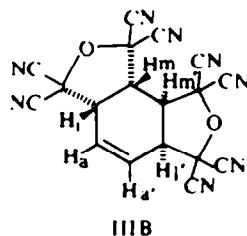
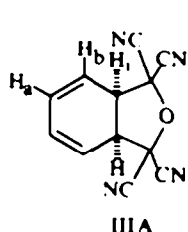
In all cases where TCNE adducts could be obtained (cyclooctatetraene,²⁸ cycloheptatriene,²⁹ cyclopentadiene,^{16,30} indene, bicycloheptadiene³¹ and bicyclooctadiene), the PMR spectra of the 1,4-Diels Alder adducts (XX, XVIIIIB, XIIIB, XVIB, XVIIB) were compared with those of the corresponding 1,2-TCNEO adducts (XIXA, XVIIIIA, XA, XIIIA, XVIA and XVIIA respectively).

In the bicycloheptadiene adduct XVIIA, chemical precedent and the magnitude of J_{ui} (<1 c/s) allow assignment of stereochemistry resulting from *exo*-addition³⁰ of the TCNEO dipole. Essentially the same J value was observed in the identical materials (XVA) obtained from hydrogenation of XVIIA and addition of TCNEO to

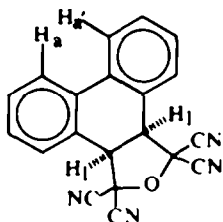
bicycloheptene. Although a similarly small J_{ul} was obtained for bicyclooctadiene adduct XVIIIA, no good model system for the *endo*-isomer of XVIIIA is available,³² and the stereochemistry is therefore tentative.

In all the bicyclo[2.2.1]heptene (XVIA) and bicyclo[2.2.2]octene (XXI, XX, XXA, XVIII B, XVIIIA) type adducts, only the sums of coupling constants between olefinic and adjacent bridgehead protons are listed in Table 3, since the apparent values are averaged by virtual coupling.³⁰

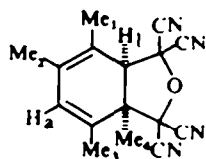
In the spectrum of the indene TCNEO adduct (XIIIA) the outer wings of the absorption from the methylene group were difficult to observe, and the apparent value of J_{uv} of about $(-13$ c/s must surely be numerically too small: indanes with rings fused 1,2 normally show J_{gem} of about -18 c/s.^{33,*}



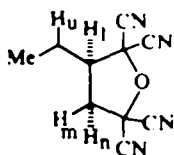
* Examples have been described with J_{gem} as positive as -15 c/s.³⁴



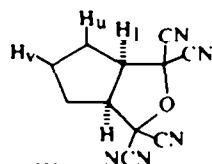
VIA



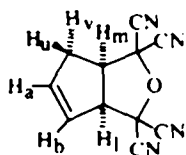
VIIA



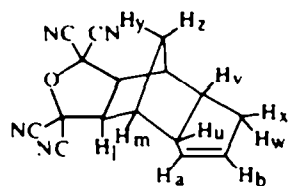
VIII A



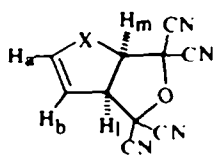
IX A



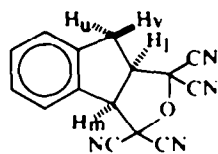
X A



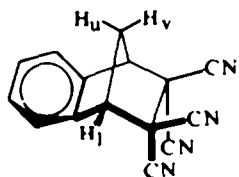
X B



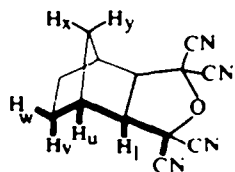
XI A X = O
XII A X = S



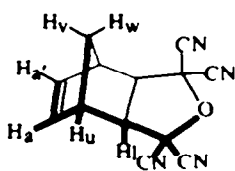
XIII A



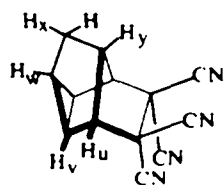
XIII B



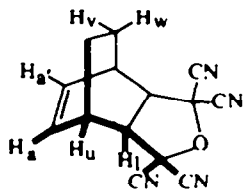
XV A



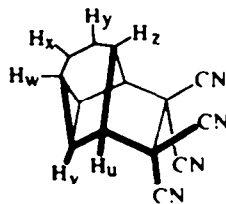
XVIA



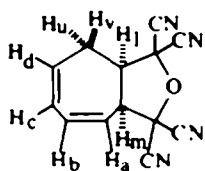
XVIB



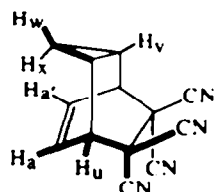
XVIII A



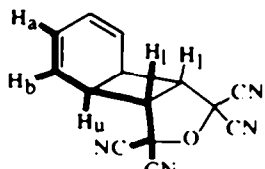
XVIII B



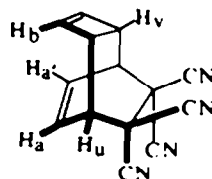
XVIII A



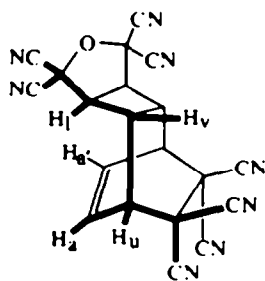
XVIII B



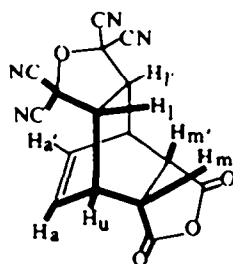
XIX A



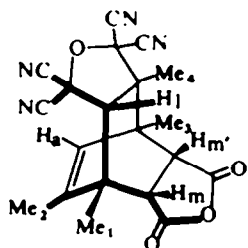
XX



XX A



XXI



XXII

TABLE I. REACTIONS OF TETRACYANOETHYLENE OXIDE

| Hydrocarbon | Conditions (in benzene) | Adduct ^a | Oxygen transfer products | |
|---------------------------------------|----------------------------|------------------------|--|--------------------------|
| | | | Oxidized ^a | Reduced ^a |
| Benzene (III) | 150° 36 hr | IIIA (38) IIIB (36) | — | — |
| Naphthalene (IV) | 155° 16 hr | IVA (92) ^b | — | — |
| Anthracene (V) | 80° 20 hr | VA (13) | Anthrone (4) Anthraquinone (1) Bianthrone (18) | TCNE adduct (VB) (47) |
| Phenanthrene (VI) | 80° 32 hr | VIA (63) ^c | — | — |
| Durene (VII) | 150° 40 hr ^d | VIIA (17) | Duroquinone (17) | TCNE (15) |
| Butene-1 (VIII) | 155° 48 hr | VIIIA (79) | — | — |
| Cyclopentene (IX) | 175° 28 hr | IXA (55) | — | — |
| Cyclopentadiene (X) | 80° 5-6 hr | XA (16) XB (10) | — | XC (5) |
| Furan (XI) | 150° 24 hr | XIA (71) | — | — |
| Thiophen (XII) | 150° 28 hr | XIIA (70) | — | — |
| Indene (XIII) | 80° 9 hr | XIIIA (21) | 2-Indanone (5) | XIIIB (6) |
| Dicyclopentadiene (XIV) | 80° 27 hr | XB (21) | — | XC (13) |
| Bicyclobeptene (XV) | 80° 48 hr | XVA (29) | Norcamphor | TCNE |
| Bicyclobeptadiene (XVI) | 65° 28 hr | XVIA (8) | — | XVIB (42) |
| Bicyclooctadiene (XVII) | 80° 42 hr | XVIIA (40) | — | — |
| Cycloheptatriene (XVIII) | 80° 16 hr | XVIIIA (12) | — | XVIIIB (12) |
| Cyclooctatetraene (XIX) | 80° 50 hr | XIXA (28) | — | — |
| Cyclooctatetraene TCNE adduct (XX) | 110° 24 hr ^e | XXA (66) | — | — |

^a Percentage yields of purified products in brackets ().

^b After allowing for recovery of 17% of naphthalene.

^c After allowing for recovery of 70% of phenanthrene.

^d No benzene solvent.

^e In toluene.

TABLE 2. UV SPECTRA OF TETRACYANOETHYLENE OXIDE ADDUCTS IN ETHANOL.

| Compound | λ_{\max} (nm) | log ϵ |
|----------|-----------------------|----------------|
| IIIA* | 260 | 3.59 |
| VIIA | 269 | 3.78 |
| XIXA | 273 | 3.52 |
| XVIII A | 243 | 4.11 |
| VA | 253 | 4.22 |
| | 275 | 4.28 |
| | 286 (sh) | 4.12 |
| IVA | 265 (sb) | 4.10 |
| | 274 | 4.14 |
| | 325 | 3.92 |
| | 385 | 3.11 |
| VIA | 253 | 4.22 |
| | 275 | 4.28 |
| | 286 (sh) | 4.12 |

* In acetonitrile.

EXPERIMENTAL

IR spectra were measured from Nujol mulls, on a Unicam SP 200 spectrophotometer. UV spectra were obtained from solutions in 95% EtOH, using a Unicam SP 700 recording spectrophotometer. PMR spectra were run on a Varian A-60 instrument, using TMS as internal standard. M.p.s are uncorrected.

Preparation of TCNEO. 100 vol H₂O₂ (30 ml), water (90 ml) and 4N NaOH (8-10 drops) were mixed in a 500 ml 3-neck flask, which was cooled in ice. A soln of TCNE (15 g) in acetonitrile (75 ml) was added dropwise with stirring over 15 min. The reaction mixture rapidly went turbid, and formed an emulsion which, after a further 15 min stirring, was extracted with five 250 ml portions CHCl₃. The combined extracts were filtered rapidly, and the solvent removed under reduced press on a hot water bath. The crude solid resulting was immediately vacuum sublimed at 120-130°/10 mm, giving pure crystalline TCNEO, m.p. 177-178° (reported¹ 177-178°), in a yield of 74% (12.5 g); IR 900, 955, 1160, 1305, 2280 cm⁻¹. (Found: C, 50.08; N, 38.54. Calc. for C₄ON₄: C, 50.00; N, 38.89%.)

Reaction of TCNEO with olefins. Two general methods were adopted. The reactants were heated together in dry benzene (which itself does not react significantly with TCNEO at 80°) either at reflux temp, or sealed in a Carius tube under N₂. The best method for each olefin is indicated in Table 1, together with yields of the respective products obtained. Most of the reaction mixtures turned dark, and often deposited solid black or brown material, despite routine purification of the reactants. Workup always involved removal of excess solvent under reduced press, and chromatography of the residue on silica. Recrystallization solvents, melting points and combustion analysis data are collected in Table 4.

Hydrogenation of XVIA. The adduct (0.057 g) was hydrogenated in EtOAc (5 ml) at room temp, using pre-reduced PtO₂. H₂ uptake was 4.60 ml, corresponding to 0.85 double bond. The reduced product was recrystallized twice from petrol, to a constant m.p. 202-203°. This material was identical in m.p., mixed m.p. and IR spectrum with the bicycloheptene/TCNEO adduct XVA.

Attempted hydrogenation of the naphthalene (IVA), cyclopentadiene (XA) and thiophen adducts. Using EtOAc, dioxan, benzene and di-isopropyl ether as solvents, and PtO₂ or PdCl₂ catalysts, no dihydro derivatives of the above adducts could be isolated. In nonpolar solvents, starting materials were recovered, while polar solvents resulted in general decomposition of the adducts.

TABLE 3. PMR SPECTRA OF ADDUCTS

| Compound | Solvent | Chemical shifts (in τ units) | Coupling constants (in c/sec^{-1}) |
|--|-------------------------|--|---|
| IIIA | acetone | a 3.48 (m), b 3.88 (m), l 5.44 (3) | ab = ca. 9.5 |
| IIIB | acetone benzonitrile | a 3.24 (1), l 4.66 (2), m 5.16 (2) a 3.24 (1); l, m quartet centred 4.99 | lm = 7.6 lm = 8.0 |
| XXI | benzonitrile | a 3.32 (3); m, u 5.75 (broad 1), l 6.15 (broad 2) | (au + a'u) = ca. 7.5 |
| VIIA | pyridine | a 4.22 (broad 1), l 5.93 (broad 1), Me ₂ 7.99 (broad 1), Me ₁ 8.10 (2), Me ₃ 8.26 (2), Me ₄ 8.50 (1) | Me ₃ a = 2.0 |
| XXII | pyridine | a 3.68 (4), m 5.98 (broad 1), l 6.15 (1), Me ₂ 7.99 (2), Me ₁ , Me ₃ 8.05, 8.07; Me ₄ 8.14 (1) | Me ₃ a = 2.0 |
| XIXA | pyridine | a 4.15 (m), b 4.44 (m), u 6.48 (5), l 5.53 (m) | ab = ca. 9.5 |
| XX | pyridine | a 3.59 (4), b 4.16 (1), u 6.00 (m), v 6.57 (m) | (au + a'u) = ca. 8.0 |
| XXA | acetone | a 2.94 (4), u 5.61 (m), l 5.86 (m), v 6.40 (m) | (au + a'u) = ca. 8.0 |
| XVIII A | pyridine | a-d ca. 3.86 (m), l 5.17 (m), m 6.11 (8), xy ca. 7.14 (m) | |
| XVIII B | pyridine | a 3.77 (4), u 5.72 (m), v 8.36 (m), w, x 9.3-10.0 (m) | (au + a'u) = ca. 8.0 |
| IVA | acetone | Ar 2.51 (m), a 3.05 (2 \times 2), b 3.88 (2 \times 2 \times 2), l 5.22 (2 \times 3), m 4.92 (2 \times 2) | ab = 10.0 al = 2.6 bl = 2.5 bm = 1.3 lm = 8.0 |
| VIA | acetone | Ar 2.33 (m), a, l 7.3 (m), l 4.54 (1) | — |
| 9,10- dihydro- phenan- threne | CDCl ₃ | Ar 2.93 (m), a 2.42 (m), CH ₂ 7.29 (1) | — |
| IXA | pyridine | l ca. 6.12 (m); u, v ca. 8.04 (m) | — |
| VIIIA | pyridine | l-n ca. 6.4-7.0; u 8.22 (5), Me 8.98 (3) | Meu = 6.5 |
| XA | pyridine | a, b 4.03 (m), l 5.15 (m), m 5.65 (m); u, v 7.05 (m) | — |

TABLE 3—continued

| Compound | Solvent | Chemical shifts (in τ units) | Coupling constants (in c/sec^{-1}) |
|----------|--------------|--|---|
| XB | pyridine | a, b 4.57 (4), 1 6.50 (2), m 7.06 (broad 1); u, v 7.26 (broad 1); w, x 7.93 (m); y, z 8.40 (m) | |
| XIA | acetone | a 3.12 (3), b 4.52 (3), 1 4.87 (2 \times 3), m 3.78 (2) | lm = 8.5 ab = al = bl = 2.0 |
| XIIA | acetone | a 3.21 (2 \times 2), b 4.11 (2 \times 2), 1 4.72 (2 \times 3), m 4.39 (2) | lm = 9.0 ab = 5.9 al = bl = 2.4 |
| XIIIA | pyridine | m 4.45 (2), 1 5.21 (2 \times 2), u 6.26 (2), v 6.56 (2 \times 2) | lm = 7.7 lv = 3.0 |
| XIIIB | pyridine | Ar ? (m), 1 5.26 (3), u, v each (2 \times 3) 7.36, 7.63 | uv = 12.0 ul = vl = ca. 1.5 |
| VB | acetone | Ar 2.40 (m), 1 4.22 (s) | — |
| VA | acetone | Ar 2.35 (m), 1 3.55 (s), m 4.42 (s) | — |
| XVA | pyridine | 1 6.52 (2), u 7.29 (broad 3); v, w, x, y 8.67 (broad m) | ul = ca. 1.0 |
| XVIA | pyridine | a 3.76 (3), 1 6.40 (1), u 6.68 (5), v, w 8.43 (broad 2) | (au + a'u) = ca. 1.5 ul = <1.0 |
| XVIB | benzonitrile | u 6.77 (2), y 7.38 (m), x 8.16 (broad 1); v, w 8.38 (broad 1) | uy = ca. 1.8 |
| XVIIA | pyridine | a 3.59 (4), 1 6.09 (3), u 6.78 (m), v, w 8.2–9.0 (m) | (au + a'u) = 7.5 ul = ca. 1.0 |
| XVIIIB | pyridine | u 6.58 (1), z 7.66 (m), x, y, v ca. 8.5 (m), w ca. 9.0 (m) | — |

TABLE 4. CHARACTERIZATION OF ADDUCTS

| Adduct | M.p. | Recrystallization solvent | Analyses | | | | | |
|---------|--------------|-------------------------------------|----------|------|-------|-------|------|-------|
| | | | Calc. | | | Found | | |
| | | | C | H | N | C | H | N |
| IIIA | 167-168 dec. | benzene/petrol | 64.85 | 2.73 | 25.22 | 64.90 | 2.90 | 25.34 |
| IIIB* | 226-227 dec. | benzene/ethyl acetate | 59.01 | 1.65 | 30.13 | 60.47 | 1.94 | 30.46 |
| VIIA | 108-109 | petrol | 69.04 | 5.08 | 20.13 | 69.20 | 5.23 | 20.32 |
| XXII | 276-278 dec. | acetone/CCl ₄ | 63.81 | 4.29 | 14.90 | 64.02 | 4.42 | 14.79 |
| XIXA | 191-192 dec. | CHCl ₃ /petrol | 67.72 | 3.25 | 22.57 | 67.40 | 3.24 | 22.17 |
| XX | 250-251 dec. | ethyl acetate/petrol | 72.39 | 3.48 | 24.13 | 72.21 | 3.72 | 24.21 |
| XXA | > 300 dec. | ethyl acetate/petrol | 63.82 | 2.15 | 29.78 | 63.52 | 2.22 | 29.66 |
| XVIII A | 157-158 | CHCl ₃ /petrol | 66.09 | 3.42 | 23.72 | 66.19 | 3.66 | 23.66 |
| XVIII B | 159-160 dec. | CHCl ₃ /petrol | 70.89 | 3.67 | 25.44 | 71.24 | 3.61 | 25.24 |
| IVA | 168-170 dec. | CCl ₄ | 70.57 | 2.97 | 20.58 | 70.13 | 3.12 | 20.74 |
| VIA | 250-255 dec. | CHCl ₃ /CCl ₄ | 74.52 | 3.13 | 17.38 | 74.14 | 2.94 | 17.40 |
| IXA | 114-115 | CCl ₄ | 62.25 | 3.81 | 26.40 | 62.20 | 3.88 | 26.60 |
| VIII A | 67-68 | benzene/petrol | 59.98 | 4.04 | 27.99 | 60.28 | 3.85 | 27.78 |
| XA | 151-152 | CHCl ₃ /CCl ₄ | 62.85 | 2.88 | 26.66 | 62.91 | 2.88 | 26.67 |
| XB | 210-211 dec. | CHCl ₃ /CCl ₄ | 69.54 | 4.39 | 20.28 | 69.29 | 4.34 | 20.94 |
| XC | 222-224 dec. | acetone/petrol | 68.03 | 3.11 | 28.85 | 68.16 | 3.22 | 28.64 |
| XIA | 161-162 | CHCl ₃ /CCl ₄ | 56.60 | 1.90 | 26.41 | 56.72 | 1.85 | 26.35 |
| XII A* | 158-159 | CHCl ₃ /CCl ₄ | 52.62 | 1.77 | 24.55 | 52.81 | 1.68 | 24.67 |
| XIII A | 186-188 dec. | CHCl ₃ /CCl ₄ | 69.22 | 3.10 | 21.53 | 69.01 | 3.11 | 21.56 |
| XIII B | 250-255 dec. | acetone/CCl ₄ | 73.75 | 3.31 | 21.94 | 73.86 | 3.50 | 21.10 |
| VA | dec. | CHCl ₃ /CCl ₄ | 74.52 | 3.13 | 17.38 | 74.65 | 3.12 | 17.56 |
| VB | 268-270 dec. | acetone/petrol | 78.45 | 3.26 | 18.29 | 78.59 | 3.43 | 18.14 |
| XVA | 202-203 dec. | CHCl ₃ /petrol | 65.53 | 4.24 | 23.52 | 65.31 | 4.02 | 23.40 |
| XVIA | 211-213 dec. | CHCl ₃ /petrol | 66.10 | 3.39 | 23.71 | 66.01 | 3.54 | 23.61 |
| XVIB | 197-198 dec. | benzene | 70.89 | 3.66 | 25.44 | 70.90 | 3.58 | 25.35 |
| XVII A | 225-230 dec. | acetone/petrol | 67.18 | 4.03 | 22.39 | 67.45 | 3.86 | 22.78 |

* Mol. wt. (calc.) 366, found (Kofler) 350. † S calc. 14.05, found 13.89

Attempted desulphurization of thiophen/TCNE adduct (XIIA). Using a 10- to 20-fold excess of freshly prepared Raney Ni, or BDH stabilized catalyst, in benzene, dioxan or EtOH solvents, in cold or under reflux, the expected reduced product, identical with the butene-1/TCNEO adduct (VIIIa) was not obtained. Either starting material or intractable gums were recovered.

Acid or base treatment of the naphthalene/TCNEO adduct (IVA). The adduct (0.68 g) was dissolved in 10% aq EtOH (25 ml), and pyridine (5 drops) added. The reaction mixture was refluxed for 4-5 hr, when excess solvent was removed under reduced press. Chromatography of the residue on silica with benzene eluant afforded crude IVB as a pale pink powder. Recrystallization from petrol, and then CCl_4 , gave 67% (0.32 g) of off-white needles, m.p. 123-124°; IR 760, 820, 1505, 1590, 2250 cm^{-1} . (Found: C, 80.94; H, 4.22; N, 14.55. Calc. for $\text{C}_{13}\text{H}_8\text{N}_2$: C, 81.22; H, 4.20; N, 14.58%.)

Repetition using glacial AcOH instead of pyridine afforded 55% of IVB.

Oxidation of β -naphthylmalonodinitrile (IVB). β -Naphthylmalonodinitrile (0.10 g) was dissolved in 0.25N HNO_3 , and refluxed for 60 hr. The resulting yellow soln was filtered hot, and allowed to cool, whereupon a pale brown solid precipitated. Recrystallization from water gave 67% (60 mg) of off-white crystals, m.p. 185-186°, identical in all respects with authentic β -naphthoic acid.

Reaction of TCNEO with triphenylphosphine. TCNEO (100 mg, 0.7 mmole) was dissolved in hot dry benzene (6 ml), cooled to room temp, and mixed with freshly cracked cyclopentadiene (3 ml). A saturated soln of triphenylphosphine (150 mg, 0.6 mmole) in benzene was then added dropwise with stirring, the reaction mixture immediately turning brown and depositing solid material. After standing for 2 hr, the mixture was filtered, and the solid fractionally crystallized from CHCl_3 /benzene. TCNEO (28 mg) was recovered, and 63% (61 mg) of the TCNE/cyclopentadiene adduct (XC) isolated.

Preparation of TCNE adducts. Adducts XVIB,¹¹ VB,¹⁰ XC,¹⁶ XVIIIIB,¹⁹ XX²⁸ and XVIIIB were prepared by published procedures. The indene adduct (XIIIA) was made by refluxing TCNE in an excess of indene, and chromatographing the crude insoluble adduct on silica with benzene eluant. This method yielded 33% of fine buff needles, which were recrystallized to a constant m.p. of 255° from CCl_4 /acetone. IR 770, 1010, 1190, 2260 cm^{-1} .

TCNE adduct of cyclooctatetraene/TCNEO adduct (XIXA). The adduct XIXA (0.30 g, 1.2 mmole) and TCNE (0.50 g, 3.9 mmole) were heated together in refluxing benzene for 20 hr. The reaction mixture was cooled, and a quantitative yield of crude XXA filtered off. This was recrystallized from CCl_4 /acetone, giving small colourless prisms which did not melt, but decomposed above 280-300°; IR 760, 990-1080, 1620, 2300 cm^{-1} .

TCNEO adduct of cyclooctatetraene/TCNE adduct (XX). The adduct XX (0.40 g, 1.7 mmole) and TCNEO (0.30 g, 2.1 mmoles) were heated together in refluxing dry toluene for 24 hr. After cooling the reaction mixture, the crude XXA was filtered off and recrystallized from EtOAc/petrol, affording 66% (0.43 g) of white prisms, identical in all respects (m.p., mixed m.p., IR, PMR spectra) with XXA from the previous reaction.

Attempted formation of TCNE adduct of 1:1 TCNEO/benzene adduct (IIIA). Equimolar TCNE and IIA were heated together in refluxing benzene for 16 hr, and in a sealed tube for 24 hr at 150°, but only starting materials could be recovered.

Preparation of maleic anhydride adducts. TCNEO/benzene adduct (IIIA) and 3 moles of freshly sublimed maleic anhydride were heated together in refluxing dry benzene for 48 hr. The solvent was removed under reduced press, and the crude solid chromatographed on silica, giving 18% of XXI. Recrystallization from CHCl_3 /petrol afforded fine white needles, m.p. 296-300° dec. IR 770, 930, 1070, 1100, 1220, 1770, 1855, 2270 cm^{-1} .

The same procedure utilizing the durene/TCNEO adduct VIIA yielded 44% of the new adduct XXII, as colourless prisms from CCl_4 /acetone, m.p. 276-278° dec. IR 940, 1020-1090, 1210, 1230, 1460, 1765, 1840, 2270 cm^{-1} .

Attempted formation of a 2:1 TCNEO/naphthalene adduct. Equimolar 1:1 TCNEO/naphthalene adduct (IVA) and TCNEO were heated together in refluxing dry toluene for 7 days. The brown reaction mixture was chromatographed in the usual manner, resulting in complete recovery of IVA.

Reaction of TCNEO with 2,3,5,6-tetramethylphenol. TCNEO (0.50 g, 3.5 mmole) and the phenol (0.52 g, 3.5 mmole) were heated together in refluxing dry toluene for 20 hr. The initially colourless solution rapidly turned yellow, and then brown. Chromatography on silica afforded TCNE (0.41 g, 92%), which was characterized as the anthracene adduct VB.

Reaction of TCNEO with anthrone. TCNEO (0.80 g, 5.6 mmoles) and anthrone (0.60 g, 3.1 mmoles) were heated together in refluxing benzene (30 ml) for 27 hr. The dark reaction mixture was allowed to

cool, and 0.26 g TCNEO recovered by filtration. The filtrate was concentrated under reduced press, and the residue chromatographed on silica, with benzene eluant, giving anthraquinone (m.p. 265°), anthrone (m.p. 140-150°) and bianthrone (230-240°)³⁵ in order of elution. The products were crystallized and compared critically with authentic samples.

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REFERENCES

- ¹ W. J. Linn, O. W. Webster and R. E. Benson, *J. Am. Chem. Soc.* **85**, 2032 (1963).
- ² R. Criegee and P. Günthe, *Chem. Ber.* **96**, 1564 (1963); A. Rieche and P. Dietrich, *Ibid.* **96**, 3044 (1963).
- ³ W. J. Linn and R. E. Benson, *J. Am. Chem. Soc.* **87**, 3657 (1965).
- ⁴ W. J. Linn, *Ibid.* **87**, 3665 (1965).
- ⁵ R. Huisgen, *Proc. Chem. Soc.* 357 (1961); R. Huisgen, *Angew. Chem. (Intern. Ed.)* **2**, 565, 633 (1963).
- ⁶ R. H. Boyd, *J. Chem. Phys.* **38**, 2529 (1963).
- ⁷ S. Searles and M. Tamres, *J. Am. Chem. Soc.* **73**, 3704 (1951), S. Searles, M. Tamres and E. R. Lippincott, *Ibid.* **75**, 2775 (1953).
- ⁸ M. Chowdhury, *Trans. Faraday Soc.* **57**, 1482 (1961).
- ⁹ W. E. Wentworth and E. Chen, *J. Phys. Chem.* **67**, 2201 (1963).
- ¹⁰ A. Streitwieser, *J. Am. Chem. Soc.* **82**, 4123 (1960).
- ¹¹ K. Watanabe, *J. Chem. Phys.* **26**, 542 (1957).
- ¹² R. W. Kiser, *Introduction to Mass Spectrometry and Its Applications* p. 310. Prentice-Hall (1965).
- ¹³ S. Meyerson, J. D. McCollum and P. N. Rylander, *J. Am. Chem. Soc.* **83**, 1401 (1961).
- ¹⁴ A. W. Fort, *Ibid.* **84**, 4979 (1962); R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.* 129 (1963); R. C. Cookson, M. J. Nye and G. Subrahmanyam, *Ibid.* 144 (1964); *J. Chem. Soc. C*, 473 (1967); H. G. Richey, J. M. Richey and D. C. Claggett, *J. Am. Chem. Soc.* **86**, 3906 (1964); W. B. Hammond and N. J. Turro, *Ibid.* **88**, 2880 (1966).
- ¹⁵ R. Hoffmann and R. B. Woodward, *Ibid.* **87**, 2046 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *Ibid.* p. 2045, K. Fukui, *Tetrahedron Letters* 2009 (1965); M. J. S. Dewar, *Tetrahedron Suppl.* **8**, 75 (1966).
- ¹⁶ W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Am. Chem. Soc.* **80**, 2783 (1958).
- ¹⁷ P. Brown and R. C. Cookson, *Tetrahedron* **21**, 1993 (1965).
- ¹⁸ S. Seltzer, *J. Am. Chem. Soc.* **85**, 1360 (1963).
- ¹⁹ T. J. Katz and R. Dessau, *Ibid.* **85**, 2172 (1963).
- ²⁰ L. S. Bartell, *Tetrahedron* **6**, 13 (1960); *Ibid.* **83**, 3567 (1961); H. C. Brown and G. J. McDonald, *Ibid.* **88**, 2514 (1966).
- ²¹ E. A. Halevi, M. Nussim and A. Ron, *J. Chem. Soc.* 866 (1963), A. Streitwieser and H. S. Klein, *J. Am. Chem. Soc.* **83**, 2759 (1963).
- ²² R. E. Erickson, P. S. Bailey and J. C. Davies, *Tetrahedron* **18**, 388 (1962); F. Dobinson and P. S. Bailey, *Tetrahedron Letters* 14 (1960).
- ²³ V. Henri and L. W. Pickett, *J. Chem. Phys.* **7**, 439 (1939).
- ²⁴ A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, *J. Am. Chem. Soc.* **74**, 4867 (1952).
- ²⁵ E. Pesch and S. L. Friess, *Ibid.* **72**, 5756 (1950).
- ²⁶ R. N. Jones, *Ibid.* **63**, 1658 (1941).
- ²⁷ D. Bryce-Smith, B. Vickery and G. I. Fray, *J. Chem. Soc. C*, 390 (1967).
- ²⁸ P. Scheiner and W. R. Vaughan, *J. Org. Chem.* **26**, 1923 (1961).
- ²⁹ N. W. Jordan and I. W. Elliott, *Ibid.* **27**, 1445 (1962).
- ³⁰ P. Laszlo and P. R. Schleyer, *J. Am. Chem. Soc.* **86**, 117 (1964) report the PMR spectrum of TCNE: cyclopentadiene adduct XC.
- ³¹ A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.* **81**, 667 (1959).
- ³² K. Tori, Y. Takano and K. Kitahonoki, *Chem. Ber.* **97**, 2798 (1964).
- ³³ R. C. Cookson, T. A. Crabb, J. J. Frankel and J. Hudec, *Tetrahedron Suppl.* **7**, 355 (1966) and unpublished measurements.
- ³⁴ R. T. Parfitt, M. Takeda and H. Kugita, *J. Org. Chem.* **32**, 419 (1967).
- ³⁵ O. Dimroth, *Chem. Ber.* **34**, 219 (1901).