

Reactions of Electron Donor–Acceptor Systems : Cycloaddition Reactions of Aryl-substituted Olefins with Tetracyanoethylene

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Cycloaddition reactions of several aryl-substituted olefins with tetracyanoethylene (TCNE) are reported. Acenaphthylene, indene, 1-vinylpyrene, and vinylferrocene underwent $[\pi 2 + \pi 2]$ cycloaddition to give the corresponding cyclobutane derivatives, whereas 1-vinylnaphthalene and 9-vinylanthracene underwent Diels–Alder reactions. With 9-vinylanthracene the addition of TCNE occurred at the 9- and 10-positions, the vinyl group remaining unaffected. The reactions occurred under mild conditions, especially for 1-vinylnaphthalene, 1-vinylpyrene, 9-vinylanthracene, and vinylferrocene. They involved the formation of a charge transfer complex, the electronic spectrum of which was measured to estimate the ionization potential of the olefin. In general, the reactivity of the aryl-substituted olefin increased with decrease in its ionization potential. The 9-vinylanthracene–TCNE adduct dissociated readily in solution.

TETRACYANOETHYLENE (TCNE) is one of the most reactive dienophiles in the Diels–Alder reaction.¹ It also undergoes $[\pi 2 + \pi 2]$ cycloaddition with electron-rich olefins to give cyclobutane derivatives under mild conditions.² The olefins reported to undergo ready cycloaddition with TCNE are mostly those with a

strongly electron-donating substituent, *e.g.*, vinyl ethers, vinyl sulphides, vinylamines, vinyl amides, cyclopropyl-

¹ J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.

² (a) J. K. Williams, D. W. Wiley, and D. C. McKusick, *J. Amer. Chem. Soc.*, 1962, **84**, 2210, 2216; (b) P. D. Bartlett, *Quart. Rev.*, 1970, 473.

substituted olefins, and styrene derivatives with an electron-donating *para*-substituent,^{2,3} or some 1,3-dienes for which Diels-Alder reaction is difficult.⁴ Recent mechanistic studies on the cycloaddition of vinyl ethers with TCNE⁵ have shown the involvement of a zwitterionic intermediate. Reactions of electron-rich olefins

TABLE I

Electronic absorption maxima of TCNE charge-transfer complexes of some aryl-substituted olefins and the corresponding aromatic hydrocarbons, and their ionization potentials (I_p)

(A) Aryl-substituted olefin-TCNE charge-transfer complexes

Olefin	$\lambda_{CT \text{ max.}}/\text{nm}^a$	I_p/eV^b	
		From eq. (ii)	From eq. (i)
Styrene	483 ^c	8.54	8.42
Acenaphthylene	510 ^d		
Indene	537, 422	8.25	8.12
1-Vinylnaphthalene	603, 432	7.95	7.81
1-Vinylpyrene	780, 505	7.41	7.24
9-Vinylanthracene	745	7.49	7.33

(B) Aromatic hydrocarbon-TCNE charge-transfer complexes

Aromatic hydrocarbon	$\lambda_{CT \text{ max.}}/\text{nm}^a$	I_p/eV^b	
		From eq. (ii)	From eq. (i)
Benzene	387 ^c	9.26	9.18
Naphthalene	560, 430 ^e	8.13	7.99
Acenaphthene	655, 440 ^e	7.76	7.60
Pyrene	730, 500 ^e	7.54	7.37
Anthracene	715	7.57	7.41
Ferrocene	1 075, 900 ^f	6.91	6.71

^a Measurement made in CH_2Cl_2 at room temperature except for anthracene-TCNE and 9-vinylanthracene-TCNE which were measured below -50°C (the charge-transfer complex decayed rapidly at higher temperatures). The difference in measurement temperature does not affect the absorption position appreciably; the 1-vinylpyrene-TCNE system shows maxima at the same wavelength at room temperature and below -50°C . ^b Calculated from the empirical equations for the TCNE complex in CH_2Cl_2 described in the text. Lower values are obtained when equation (iii) is used. ^c Ref. 8.

^d The half-width of the charge-transfer band is *ca.* $7.8 \times 10^3 \text{ cm}^{-1}$, which is larger than those for the other systems (*ca.* $5 \times 10^3 \text{ cm}^{-1}$ or smaller), as pointed out by Voigt and Reid.⁸ Hence, in this system the first charge-transfer band which exists at longer wavelength seems to overlap with the intense second charge-transfer band. ^e Ref. 9. ^f M. Rosenblum, R. W. Fish, and C. Bennett, *J. Amer. Chem. Soc.*, 1970, **86**, 5166; measured in cyclohexane.

with electron-deficient trisubstituted olefins have been reported recently.⁶ We have studied the reactions of TCNE with several aryl-substituted olefins (acenaphthylene, indene, 1-vinylnaphthalene, 1-vinylpyrene, 9-vinylanthracene, and vinylferrocene), to see whether $[\pi 2 + \pi 2]$ cycloaddition occurs and to discover the effect on the reactivity of the olefin of its electron-donating character.

* An analogous reaction has been reported with 2-vinylnaphthalene.¹³

† The other band may overlap with the band at 995 cm^{-1} , characteristic of ferrocene derivatives in which at least one ring remains unsubstituted.

³ S. Nishida, I. Moritani, and T. Teraji, *J. Org. Chem.*, 1973, **38**, 1878.

⁴ J. K. Williams, *J. Amer. Chem. Soc.*, 1959, **81**, 4013.

⁵ (a) R. Huisgen and G. Steiner, *J. Amer. Chem. Soc.*, 1973, **95**, 5054, 5056; (b) G. Steiner and R. Huisgen, *ibid.*, p. 5058.

Formation of a charge-transfer complex was observed in most reaction systems, as evidenced from electronic absorption spectra. The spectra were measured, and ionization potentials of the olefins were estimated from empirical equations [(i) and (ii)] relating the energy of the charge-transfer band to the ionization potential (I_p), derived from the spectra of TCNE charge-transfer complexes with substituted benzenes^{7,8} and with polynuclear hydrocarbons⁹ in dichloromethane. Kuroda

$$h\nu_{CT} = 0.83 I_p - 4.42 \quad (\text{i}) \text{ for TCNE-substituted benzenes }^8$$

$$h\nu_{CT} = 0.87 I_p - 4.86 \quad (\text{ii}) \text{ for TCNE-polynuclear hydrocarbons }^9$$

et al. also give equation (iii), which takes into account

$$h\nu_{CT} = 0.92 I_p - 5.12 \quad (\text{iii})$$

other experimental data.⁹ The results (Table I) show that the ionization potential of the olefin is generally lower than that of the corresponding aromatic hydrocarbon. It has been reported that the ionization potential of anthracene is lower than that of pyrene;¹⁰ however, the order of the charge-transfer energies of TCNE complexes was the reverse of that expected in the cases of pyrene and anthracene, and of 1-vinylpyrene and 9-vinylanthracene.

When the aryl-substituted olefins reacted with TCNE in a solution, either $[\pi 2 + \pi 2]$ cycloaddition or Diels-Alder reaction occurred. Cycloaddition occurred with acenaphthylene, indene, 1-vinylpyrene, and vinylferrocene to give the corresponding cyclobutane derivatives (I), (II), (IV), and (VI). The cycloaddition of vinylferrocene with TCNE has recently been reported independently,¹¹ after our communication dealing with this reaction was published.¹² Diels-Alder reaction occurred with 1-vinylnaphthalene and 9-vinylanthracene to give the adducts (III) and (V).^{*} The addition of TCNE to 9-vinylanthracene occurred at the 9- and 10-positions, the vinyl group remaining unaffected. Although vinylnaphthalene exhibits diene character, vinylpyrene does not. The reaction conditions and the product yields are summarized in Table 2.

Each cycloadduct shows a weak nitrile i.r. absorption at $2\ 250 \text{ cm}^{-1}$. The characteristic vinylic C-H out-of-plane deformation bands due to the vinyl group in the olefins [at 910 and 980 cm^{-1} for 1-vinylnaphthalene, at 900 and 980 cm^{-1} for 1-vinylpyrene, and at 900 cm^{-1} in vinylferrocene †] had disappeared in the cycloadducts

⁶ H. K. Hall, jun., and P. Ykman, *J. Amer. Chem. Soc.*, 1975, **97**, 800.

⁷ R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1964, **86**, 3930.

⁸ E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, 1964, **86**, 3930.

⁹ H. Kuroda, M. Kobayashi, M. Kinoshita, and S. Takemoto, *J. Chem. Phys.*, 1962, **36**, 457.

¹⁰ F. A. Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

¹¹ K. R. Berger, E. R. Biehl, and P. C. Reeves, *J. Org. Chem.*, 1974, **39**, 477.

¹² Y. Shiota, T. Yoshida, T. Nogami, and H. Mikawa, *Chem. Letters*, 1973, 1271.

¹³ L. H. Klemm, W. C. Solomon, and A. J. Kohlic, *J. Org. Chem.*, 1962, **27**, 2777.

(III), (IV), and (VI). The strong bands at 725 cm^{-1} for acenaphthylene and at 685 cm^{-1} for indene, ascribable to olefinic C-H out-of-plane deformation had disappeared in the cycloadducts (I) and (II). In the case of the

spectrum of (IV) resembles those of pyrene and 1-vinylpyrene in band shape, with the absorption position at intermediate wavelength. The 9-vinylanthracene-TCNE adduct (V) dissociated readily in solution, giving

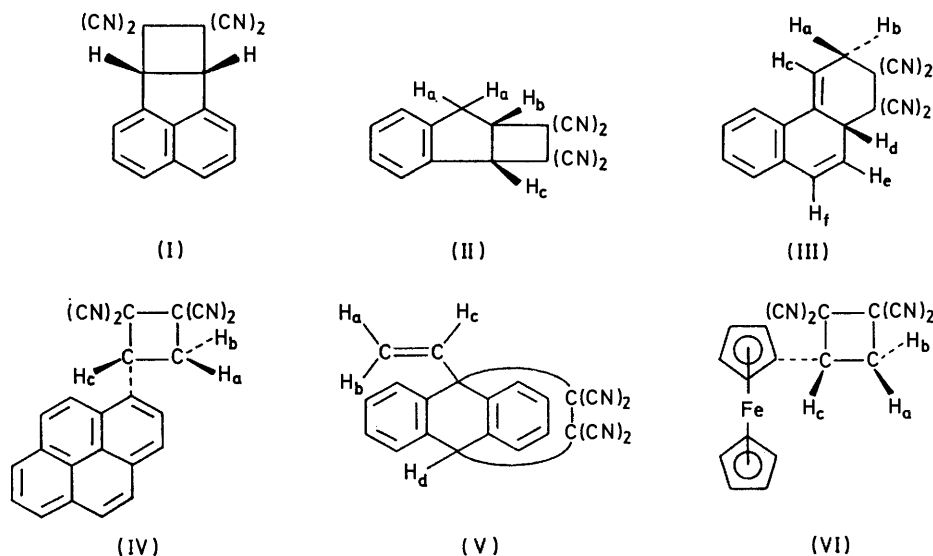
TABLE 2
Cycloaddition reactions of aryl-substituted olefins with TCNE

Olefin	Conditions ^a			Product	Yield (%)	Time for disappearance of initial colour
	Solvent	Temp. (°C)	Time (h)			
Acenaphthylene	DCE	83—84	30	(I)	0	<i>b</i>
	AN	86	20	(I)	9	<i>b</i>
Indene	AN	86	30	(I)	16	<i>b</i>
	DCE	83—84	30	(II)	0.5	<i>b</i>
	AN	86	20	(II)	15	<i>b</i>
1-Vinylnaphthalene	AN	86	30	(II)	29	<i>b</i>
	B	22	24	(III)	46	<i>ca.</i> 5 h
1-Vinylpyrene	DCE	15	5	(III)	39	<i>ca.</i> 2 h
	AN	15	5	(III)	41	<i>ca.</i> 2 h
	B	19	96	(IV)	81	<i>ca.</i> 90 h
9-Vinylanthracene	DCE	15	1	(IV)	68	<i>ca.</i> 20 min
	AN	15	1	(IV)	69	<i>ca.</i> 20 min
	B	19	1	(V)	84	Within 30 s
Vinylferrocene ^d	B	25	2	(VI)	55	<i>c</i>
	B	25	5	(VI)	75	<i>c</i>
	B	25	24	(VI)	94	<i>c</i>

^a Concentration of reactants 0.05 mol l^{-1} ; DCE, 1,2-dichloroethane; AN, acetonitrile; B, benzene. ^b The characteristic colour of the reaction solution persisted during the reaction. ^c No colour change observed. ^d When equimolar amounts of vinylferrocene and TCNE were ground to a fine powder, formation of the cycloadduct (VI) was observed, confirmed by the measurements of m.p. and i.r. spectrum before recrystallization, whereas ferrocene and TCNE form a green solid charge-transfer complex on similar treatment.²¹

9-vinylanthracene-TCNE adduct, the C-H out-of-plane deformation bands due to the vinyl group, observed in 9-vinylanthracene at 925 and 995 cm^{-1} , remained, whereas the characteristic bands at 725 and 875 cm^{-1} due to the

a spectrum consisting of the absorptions of 9-vinylanthracene (λ_{max} 259, 335, 352, 368, and 388 nm in 1,2-dichloroethane) and TCNE (λ_{max} 263 and 278 nm). The 263 nm TCNE absorption and the absorption due to



anthracene ring had disappeared, indicating that the 9-vinylanthracene-TCNE adduct lacks an intact anthracene system. The mass spectra of compounds (I)—(IV) [but not (V)] showed molecular ions, at m/e 280, 244, 282, and 356, respectively. The electronic absorption spectrum of (I) is similar to that of acenaphthylene; however, that of (III) is entirely different from that of naphthalene in both band shape and absorption position, being shifted to longer wavelength. The absorption

the undissociated adduct are hidden by the intense 259 nm absorption of 9-vinylanthracene. Almost 55% of the adduct is dissociated at $0.85 \times 10^{-4}\text{ mol l}^{-1}$ concentration in 1,2-dichloroethane. The dissociation constant was estimated to be *ca.* $7.0 \times 10^{-5}\text{ mol l}^{-1}$ in 1,2-dichloroethane at room temperature on the basis of molar extinction coefficient values of 9-vinylanthracene and TCNE at each peak. The electronic absorption spectrum of the adduct (V) in the solid state (KBr disc)

shows λ_{max} 262.5 and *ca.* 258sh nm. The anthracene-TCNE adduct dissociates only very slightly. The ready dissociation of the 9-vinylanthracene-TCNE adduct may be attributed to a steric effect.* The dissociation of the Diels-Alder adduct into the component molecules has been observed previously with a few substituted anthracene-TCNE adducts, *e.g.* those of 9-phenyl-, 9-chloro-, 9-methoxy-, and 9,10-dimethoxy-anthracene.¹⁴ The proton n.m.r. spectra of all TCNE adducts (Table 3) are in agreement with the assigned structures. We were able to obtain data for the adduct (V) since the concentration of dissociated molecules was negligibly small at the high concentration used for measurement of the spectrum; this may be understood in terms of the value of the dissociation constant.

TABLE 3
N.m.r. spectra of cycloadducts ^a

Compound	τ	J/Hz
(I)	1.75—2.25 (6 H, m, aromatic)	
	4.47 (2 H, s, methine)	
(II)	2.24—2.64 (4 H, m, aromatic)	
	5.06 (1 H, d, methine H _c)	J_{bc} 8.0
	5.54 (1 H, m, methine H _b)	J_{ab} 6.0
(III)	2.40—2.82 (4 H, m, aromatic)	
	3.14 (1 H, dd, olefinic H _e) *†	J_{ef} 9.5
	3.88 (1 H, dd, olefinic H _f) *†	J_{ed} 3.0
	3.68 (1 H, m, olefinic H _c)	J_{fd} 2.0
	5.33 (1 H, m, methine H _d)	$J_{bd} = J_{ad} = 3.0$
	6.13 (1 H, ddd, methylene H _a or H _b) †	$J_{bc} = J_{ac} = 5.0$
	6.42 (1 H, ddd, methylene H _b or H _a , 1 H) †	J_{ab} 20.0
(IV)	1.34—1.86 (9 H, m, aromatic)	
	3.72 (1 H, q, methine H _c)	J_{ac} 9.0
	5.54 (1 H, q, methylene H _b)	J_{bc} 11.0
(V)	2.20—2.56 (8 H, m, aromatic)	J_{ab} 13.0
	3.17 (1 H, q, olefinic H _e)	J_{ac} 12.0
	3.62 (1 H, d, olefinic H _a)	J_{bc} 18.2
	3.95 (1 H, d, olefinic H _b)	J_{ab} 0 §
	4.17 (1 H, s, methine H _d)	
(VI)	5.64 (4 H, s, ferrocene ring)	
	5.80 (5 H, s, ferrocene ring)	
	5.74 (1 H, q, methine H _c) ‡	J_{ac} 3.0
	6.74 (1 H, d, methylene H _a)	J_{bc} 5.5
	6.84 (1 H, d, methylene H _b)	J_{ab} 10.2

^a In deuteriochloroform for (I) and (VI), and in hexa-deuterioacetone for (II)—(V).

* Chemical shifts of H_e and H_f were assigned on the basis of J_{ed} and J_{fd} . † The dd and ddd patterns changed to d and dd patterns on irradiation at τ 5.33 (H_d). ‡ Partially overlapped with signal at τ 5.80. § J_{ab} 2.0 Hz for 9-vinylanthracene.

It has been reported that styrene is unreactive toward TCNE under mild conditions, and that when the reaction is carried out in refluxing xylene, benzylidene-malononitrile and 1:2 TCNE-styrene adduct are obtained.^{2a} The present study shows that aryl-sub-

* The isolated 9-vinylanthracene-TCNE and anthracene-TCNE adducts retain solvent even after drying under vacuum as revealed from n.m.r. spectra; however, this is not responsible for the dissociation since the anthracene-TCNE adduct dissociates only slightly.

† The $[\pi 2 + \pi 2]$ cycloaddition of acenaphthylene with TCNE occurs photochemically in 1,2-dichloroethane.¹⁷

stituted olefins with a lower ionization potential than styrene give a $[\pi 2 + \pi 2]$ cycloadduct or a Diels-Alder adduct with TCNE under mild conditions, especially in the cases of 1-vinylnaphthalene, 1-vinylpyrene, 9-vinylanthracene, and vinylferrocene. Although whether or not a charge-transfer complex is a true intermediate in the reaction is not established kinetically,^{15,16} the time for disappearance of the intense colour due to the charge-transfer complex provides a qualitative measure of the reaction rate. The cycloaddition reaction was accelerated in polar solvents, whereas the Diels-Alder reaction was only slightly affected by solvent polarity. In the cases of acenaphthylene and indene, which have relatively high ionization potentials, the cycloaddition reaction proceeded only in a polar solvent such as acetonitrile.† In the reaction of 1-vinylpyrene with TCNE, the intense colour disappeared in *ca.* 20 min in 1,2-dichloroethane, whereas in benzene it took *ca.* 90 h for the colour to fade at the same concentration. The results support the accepted notion that a mechanism involving charge-separation in the rate-determining step is operative in the $[\pi 2 + \pi 2]$ cycloaddition reactions of TCNE. The increased reactivity of the olefin with decrease in its ionization potential suggests that the zwitterionic intermediate is stabilized by increased electron-donating character of the olefin. In particular, the ease of the cycloaddition of vinylferrocene with TCNE was attributed to the stabilization of the α -ferrocenyl carbocation by the ferrocene ring.¹² This view was supported by Reeves and his collaborators,¹¹ who observed that *cis*- and *trans*-propenylferrocene gave the same cycloaddition product with TCNE, showing the occurrence of rotation in the dipolar intermediate. With regard to the Diels-Alder reaction, the reaction of 9-vinylanthracene was much faster than that of 1-vinylnaphthalene. In general, the reactivity of the aryl-substituted olefin towards TCNE increases with decrease in its ionization potential, as shown in Table 2.

EXPERIMENTAL

I.r. spectra were taken with a JASCO IR-G spectrophotometer. Electronic absorption spectra were taken with a Hitachi 124 spectrophotometer. The measurement at a low temperature was made in a Dewar vessel with an EPS-3T Hitachi spectrometer. Absorption spectra of solids were measured with a Shimadzu multipurpose 50L spectrometer. Mass spectra were recorded with a Hitachi RMU-6E spectrometer by use of a direct inlet. N.m.r. spectra were obtained with a JEOL JNM 4p-100 spectrometer. The molecular weight of the vinylferrocene-TCNE adduct was determined with a Mechrolab vapour pressure osmometer.

Acenaphthylene (extra pure grade, Wako) was decolourized with activated charcoal, recrystallized three times from

¹⁴ J. Sauer, *Angew. Chem.*, 1963, **75**, 1123.

¹⁵ C. C. Thompson and D. D. Holder, *J.C.S. Perkin II*, 1972, 257.

¹⁶ (a) J. Nagata, K. Furushita, T. Nogami, Y. Shiota, and H. Mikawa, 5th Symposium on Charge-Transfer Complexes, Osaka, 1973, preprints p. 25; (b) K. Furushita, T. Nogami, Y. Shiota, and H. Mikawa, 30th Annual Meeting of the Chemical Society of Japan, Osaka, 1974, preprints III, p. 1156.

¹⁷ Y. Shiota, J. Nagata, and H. Mikawa, *Chem. Letters*, 1972, 49.

methanol, and fractionally sublimed twice *in vacuo* to give yellow needles, m.p. 92–93 °C. Indene (extra pure grade, Wako) was distilled twice under reduced pressure in the dark immediately before use; b.p. 90–91 °C at 40 mmHg. 1-Vinylnaphthalene was prepared¹⁸ by reduction of 1-acetylnaphthalene with lithium aluminium hydride in ether, followed by dehydration with potassium hydrogen sulphate and redistilled under reduced pressure; b.p. 135–138 °C at 15 mmHg. 1-Vinylpyrene was synthesized by a method¹⁹ involving a Wittig reaction of pyrene-1-carbaldehyde (prepared by a Vilsmeier reaction), chromatographed over alumina and recrystallized twice from ethanol; m.p. 87–89 °C. 9-Vinylanthracene (Aldrich) was recrystallized thrice from ethanol–n-hexane in the dark; m.p. 62–63 °C. Vinylferrocene was prepared by dehydration of 1-ferrocenylethanol on alumina at 155 °C and 13 mmHg pressure,²⁰ chromatographed over silica gel and sublimed twice *in vacuo*; m.p. 49–50 °C. Tetracyanoethylene (extra pure grade, Wako) was purified by repeated sublimation *in vacuo*. Solvents were purified and dried by the usual methods, and distilled immediately before use.

Reactions.—Solutions of the olefin and TCNE prepared independently were mixed instantaneously to give a solution 0.05M with respect to each. A characteristic colour due to the charge-transfer complex developed immediately (except in the case of vinylferrocene), *viz.* blackish purple for acenaphthylene, deep reddish purple for indene, deep blue or purple for 1-vinylnaphthalene, blackish brown for 1-vinylpyrene, and green for 9-vinylanthracene. In the reactions of acenaphthylene (380 mg) and of indene (290 mg) with TCNE (320 mg), the solution (50 ml) in 1,2-dichloroethane or acetonitrile was refluxed in the dark. The characteristic colour did not disappear in these reactions. After an appropriate time, the solution was cooled to room temperature, the solvent was removed *in vacuo*, and benzene (*ca.* 25 ml) was added to give the cycloadduct (I) (65 and 112 mg after 20 and 30 h reflux in acetonitrile, respectively) or (II) (87 and 179 mg after 20 and 30 h reflux in acetonitrile, respectively) as benzene-insoluble white solids. The benzene fraction was chromatographed over silica gel to give unchanged materials. The reaction solution [in benzene, 1,2-dichloroethane, or acetonitrile (50 ml)] of 1-vinylnaphthalene (385 mg) and TCNE (320 mg) was kept in the dark at 22 or 15 °C. The characteristic colour faded gradually to dark yellow in *ca.* 5 h in benzene. In 1,2-dichloroethane or in acetonitrile, the solution became almost colourless in *ca.* 2 h. The solvent was removed *in vacuo*, and benzene (*ca.* 25 ml) was added to give the Diels–Alder adduct (III) (278 mg in 1,2-dichloroethane; 287 mg in acetonitrile after 5 h) as a benzene-insoluble white solid. The solution in benzene (20 ml) of 1-vinylpyrene (228 mg) and TCNE (128 mg) was kept in the dark at 19 °C for 96 h, the cycloadduct (IV) precipitating as a white solid. After filtration the solution was concentrated to give small further amounts of adduct (IV) (total yield 289 mg). The residual solution was chromatographed over a silica gel column to give small amounts of starting materials. In a reaction in 1,2-dichloro-

¹⁸ 'Beilsteins Handbuch der Organischen Chemie,' 1964 E III, vol 5, p. 1773.

ethane or acetonitrile the initial colour of the solution changed in *ca.* 20 min to a pale greenish yellow, which then almost disappeared, and the cycloadduct (IV) was precipitated as a white solid (243 mg in 1,2-dichloroethane and 247 mg in acetonitrile after 1 h). The benzene solution (10 ml) of 9-vinylanthracene (102 mg) and TCNE (64 mg) was kept in the dark at 19 °C. The initial green colour disappeared within 30 s. After 1 or 2 min the Diels–Alder adduct (V) began to be precipitated as a white solid (140 mg after 1 h). The reaction of vinylferrocene (212 mg) with TCNE (128 mg) was carried out in benzene at 25 °C. The solvent was removed *in vacuo* and the yellow cycloadduct (VI) was obtained (186, 254, and 321 mg after 2, 5, and 24 h, respectively).

Products.—When the adduct was heated, a part of the material sublimed and the colour changed to dark brown before melting, probably with decomposition in some cases.

6b,7,8,8a-Tetrahydrocyclobut[a]acenaphthylene-7,7,8,8-tetracarbonitrile (I) gave white columnar crystals (from 1,2-dichloroethane) which changed colour at *ca.* 192 °C, but did not melt below 285 °C; λ_{\max} (1,2-dichloroethane) 288 (log ϵ 4.86), 269 (3.66), 279 (3.86), 290 (3.96), 300 (3.86), and 317 nm (2.85) (Found: C, 76.85; H, 2.6; N, 20.3. $C_{18}H_8N_4$ requires C, 77.15; H, 2.85; N, 20.0%).

2,2a,7,7a-Tetrahydro-1H-cyclobut[a]indene-1,1,2,2-tetracarbonitrile (II) gave fine white needles (from benzene), which changed colour at 188–189 °C and melted at 196–199 °C; λ_{\max} (in 1,2-dichloroethane) 230 (log ϵ 3.38), 263 (2.84), 269 (3.02), and 276 nm (3.04) (Found: C, 74.05; H, 3.05; N, 23.05. $C_{15}H_8N_4$ requires C, 73.75; H, 3.3; N, 22.95%).

1,2,3,10a-Tetrahydrophenanthrene-1,1,2,2-tetracarbonitrile (III) gave white columnar crystals (from chloroform), which changed colour at *ca.* 160 °C and melted at 178–181 °C; λ_{\max} (1,2-dichloroethane) 294 nm (log ϵ 3.62) (Found: C, 76.6; H, 3.55; N, 19.8. $C_{18}H_{10}N_4$ requires C, 76.75; H, 3.45; N, 19.8%).

4-(Pyren-1-yl)cyclobutane-1,1,2,2-tetracarbonitrile (IV), recrystallized from 1,2-dichloroethane, changed colour at 189–192 °C and melted at 192–195 °C; λ_{\max} (1,2-dichloroethane) 238 (log ϵ 4.60), 245 (4.63), 270 (4.35), 280 (4.54), 336 (4.33), 352 (4.47), and 378 nm (3.38) (Found: C, 80.2; H, 3.6; N, 15.15. $C_{24}H_{12}N_4$ requires C, 80.9; H, 3.35; N, 15.7%).

9,10-Dihydro-9-vinyl-9,10-ethanoanthracene-11,11,12,12-tetracarbonitrile (V) had m.p. 158–159 °C (decomp.) (Found: C, 81.0; H, 3.5; N, 15.3. $C_{22}H_{12}N_4 \cdot 0.5C_8H_8$ requires C, 80.85; H, 4.05; N, 15.1%).

4-Ferrocenylcyclobutane-1,1,2,2-tetracarbonitrile (VI) gave fine yellow needles (from benzene), which changed colour at *ca.* 130 °C and melted at 138–139 °C; λ_{\max} (1,2-dichloroethane) 260 (log ϵ 3.42), 302 (2.88), and 433 nm (2.27) (Found: C, 63.9; H, 3.35; N, 16.65%; *M*, 342. $C_{18}H_{12}FeN_4$ requires C, 63.55; H, 3.55; N, 16.45%; *M*, 340).

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¹⁹ K. Tanikawa, T. Ishizuka, K. Suzuki, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Japan*, 1968, **41**, 2719.

²⁰ M. D. Raush and A. Siegel, *J. Organometallic Chem.*, 1968, **11**, 317.