

Nucleophilic Attacks on Carbon–Carbon Double Bonds. Part XX.¹ Reaction of Active Methylene Compounds with Electrophilic Olefins. Formation of Substituted 2-Amino-4-cyano-4H-pyrans

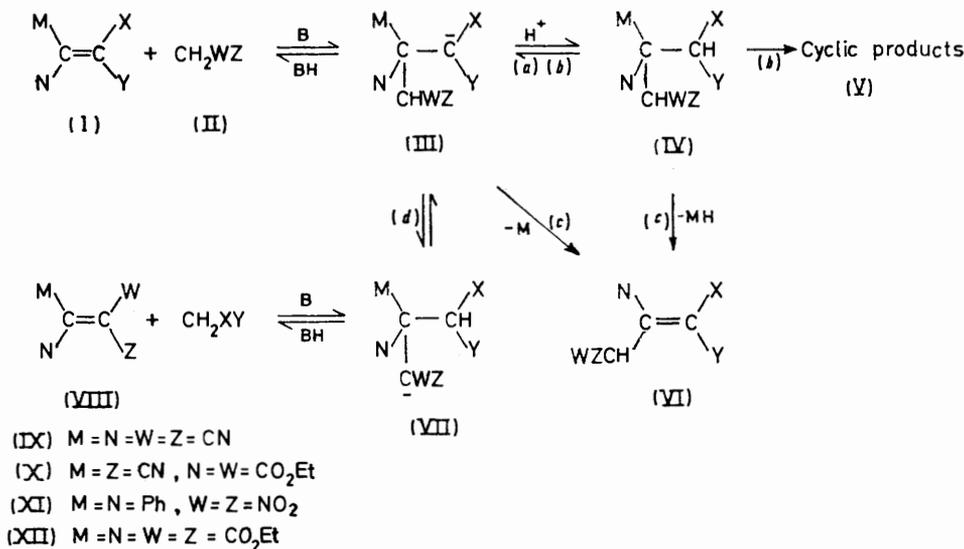
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Reactions of active methylene compounds with several electrophilic olefins are initiated by a nucleophilic attack on the double bond and the following reaction types have been observed. (a) Base-catalysed reaction of malononitrile with 1,1-dinitro-2,2-diphenylethylene gives 'diphenylmethylene transfer' forming 1,1-dicyano-2,2-diphenylethylene. (b) Addition of acetylacetone to tetracyanoethylene (IX) and to diethyl 2,3-dicyanofumarate (X) or of dimedone to (X) gives the non-cyclic Michael adducts 3-(1,1,2,2-tetracyanoethyl)pentane-2,4-dione (XIII), diethyl 2,3-dicyano-2-diacetylmethylsuccinate (XX), and diethyl 2,3-dicyano-2-(4,4-dimethyl-2,6-dioxocyclohexyl)succinate (XXII), respectively. (c) Non-catalysed addition of several active methylene compounds to (IX) or to (X) gives substituted 2-amino-4-cyano-4H-pyrans. These are probably formed by cyclisation of the open adducts, since a non-catalysed cyclisation of (XIII) and of (XXII) gives the 4H-pyran derivatives. (d) Reaction of anthrone with (IX) and (X) gives the 10-substituted anthrone Michael adducts. Addition of bases to the adduct from (IX) gives bianthrone and products derived from (IX), apparently *via* decomposition of the adduct to anthrone and (IX).

REACTIONS of electrophilic olefins (I) with active methylene compounds (II) usually take place in basic media^{2,3} and can lead to a variety of products.^{2,3} Scheme 1, where W–Z are electron-attracting groups (*e.g.* CN, CO₂Et, NO₂, *etc.*), M and N are substituents, and B is a base, indicates four routes, from the carbanion (III)

elimination from (III), or elimination of MH from (IV) can lead to the vinylic substitution product (VI). (d) Internal proton transfer in (III) gives the carbanion (VII), which can expel [−]CHXY, thus converting one electrophilic olefin (I) into another (VIII).

Tetracyanoethylene (TCNE) is an electrophilic olefin



SCHEME 1

which is formed by nucleophilic attack of the carbanion [−]CHWZ (from CH₂WZ + B) on (I).³ (a) Protonation of (III) gives the normal Michael adduct (IV). (b) Intramolecular reactions of (III) and (IV), especially in basic media, involving unsaturated groups (X, Y, *etc.*) can lead to secondary products, including cyclic products (V). (c) If M or N is a potential leaving group (*e.g.*, CN), its

for which products from routes (a)–(d) have been observed previously.^{4–8} The reaction of several active methylene compounds with TCNE and related electrophilic olefins has now been investigated in an attempt to understand some of the factors governing these possible reaction courses.

¹ Part XIX, Z. Rappoport and D. Ladkani, *Chemica Scripta*, 1974, **5**, 124.

² E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, 1959, **10**, 179.

³ S. Patai and Z. Rappoport, in 'The Chemistry of Alkenes,' ed. S. Patai, John Wiley, New York, 1964, ch. 8.

⁴ W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1958, **80**, 2783.

⁵ H. Junek and H. Aigner, *Z. Naturforsch.*, 1970, **25b**, 1423.

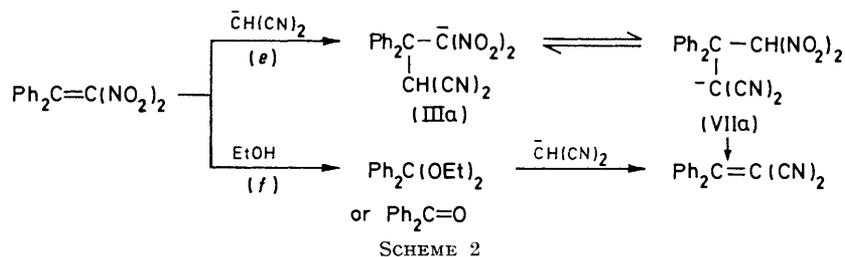
⁶ (a) E. Ciganek, W. J. Linn, and O. W. Webster, in 'The Chemistry of the Cyano Group,' ed. Z. Rappoport, John Wiley, New York, 1970, ch. 9; (b) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Amer. Chem. Soc.*, 1958, **80**, 2806; Z. Rappoport, *J. Chem. Soc.*, 1963, 4498.

⁷ H. Junek and H. Sterk, *Tetrahedron Letters*, 1968, 4309.

⁸ (a) J. W. Van Dyke, jun., and H. R. Snyder, *J. Org. Chem.*, 1962, **27**, 3888; (b) M. Acar, A. Cornélis, and P. Laszlo, *Tetrahedron Letters*, 1972, 3625; (c) A. Cornélis, P. Laszlo, and C. Pasquet, *ibid.*, 1973, 4335.

RESULTS AND DISCUSSION

The active methylene compounds were treated with the substituted ethylenes (IX)—(XII). Most of the reactions were conducted in the absence of base in order to reduce the possibility of secondary reactions. Most of the methylene compounds are sufficiently acidic, and their conjugate bases are formed to an appreciable extent



in neutral solution. Compound (XII) is apparently not activated enough, as no reaction took place with indane-1,3-dione or with malononitrile in neutral solution.

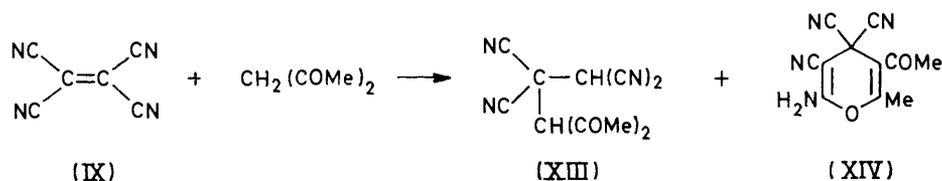
Route (d) was observed only in the reaction between malononitrile and compound (XI) in ethanol in the presence of triethylamine, where high yields of 1,1-dicyano-2,2-diphenylethylene were obtained. No reaction took place in neutral solution. The 'diphenylmethylene transfer' can take place *via* either route (e) (Scheme 2) (*i.e.*, *via* Scheme 1) or route (f) (Scheme 2) where hydrolysis of (XI) to benzophenone³ or its diethyl acetal is followed by condensation with malononitrile. Since under our conditions, benzophenone is not formed in ethanolic triethylamine, and neither benzophenone nor its diethyl acetal condense with malononitrile to form the

reaction of (XI) with the stronger carbon acids, acetylacetone and indane-1,3-dione, does not take place under similar conditions. The formation of a highly crowded transition state may be responsible for the apparent unreactivity of these highly reactive substrates.

Routes (a) and (b) were followed for reactions of (IX) and (X). Reaction of TCNE with acetylacetone in the

absence of base gave two products with analyses corresponding to 1:1 adducts: compound (XIII) was obtained in ethanol while (XIV) was obtained in acetonitrile. When (XIII) was left for 2 days in acetonitrile, its long wavelength λ_{max} at 253 nm changed rapidly to those of (XIV) at 243 and 385 nm, and the appearance of two isosbestic points at 252 and 270 nm suggests that the transformation (XIII) \rightarrow (XIV) is the only process occurring. Corresponding changes occur in the n.m.r. spectrum (see Experimental section). The first order reaction was followed by u.v. at room temperature (*ca.* 20 °C) and had a half-life of 90 min ($k_1 = 1.3 \times 10^{-4} \text{ s}^{-1}$).

Compound (XIII) was identified as the normal Michael adduct on the basis of spectral evidence. (i) The single λ_{max} (MeCN) 253 nm ($\log \epsilon 4.03$) is reminiscent of that of



product, route (e) seems more plausible. While the acidities of malononitrile and dinitromethane⁹ suggest that the proton transfer equilibrium (IIIa) \rightleftharpoons (VIIa) highly favours (IIIa), there is evidence¹⁰ that the acidity of H-1 in 2-substituted 1,1-dinitro-2,2-diphenylethanes is markedly reduced owing to steric factors. This, coupled with the high stability of the dinitromethanide carbanion provides the driving force for expulsion of the dinitromethyl group and for the 'diphenylmethylene transfer.' We note that usually the entering CH_2WZ is more acidic than the leaving CH_2XY in route (d).³ Excluding reactions of TCNE,^{7,8} the only other example of reversal of this principle is in the reaction of α -nitrostilbene with benzyl methyl ketone where phenylnitromethane is the leaving group.¹¹ Unfortunately, generalisations regarding route (d) are not yet possible since

⁹ R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

¹⁰ S. Hoz, Ph.D. Thesis, Bar-Ilan University, Israel, 1973.

¹¹ A. Dornow and F. Boberg, *Annalen*, 1952, **578**, 101.

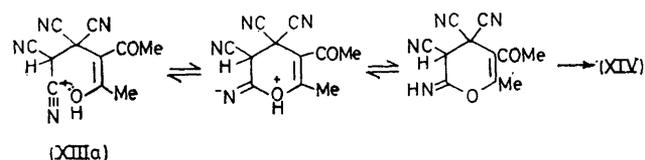
acetylacetone [λ_{max} (CHCl_3) 274 nm ($\log \epsilon 4.03$)].¹² The hypsochromic shift caused by replacement of the central proton of the pentanedione by the tetracyanoethyl group and the intensity of the absorption suggests that the species in solution is the enol (XIIIa), where the bulky substituents distort the planarity of the absorbing enol system. This is substantiated by a (presumably) O-H absorption at 3270 cm^{-1} . (ii) The absence of a cyano-group absorption in the i.r. spectrum in Nujol at 2200—2250 cm^{-1} is characteristic of tetracyanoethanes substituted with electron-attracting substituents.¹³ (iii) The mass spectrum contains low intensity peaks at m/e 128 and 100 corresponding to ionised TCNE and acetylacetone; if TCNE and acetylacetone had reacted further,

¹² R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, 1958, **80**, 5658.

¹³ (a) Z. Rappoport and E. Shohamy, *J. Chem. Soc. (B)*, 1969, 77; (b) P. G. Farrell, J. Newton, and R. F. M. White, *ibid.*, 1967, 637; P. G. Farrell and R. K. Wojtowski, *J. Chem. Soc. (C)*, 1970, 1390.

their discrete ions would not be expected in the spectrum. Moreover, the loss of $\text{CH}_2(\text{CN})_2$ and $\text{CH}(\text{CN})_2$ fragments, as observed with other tetracyanoethanes,^{13a} and the metastable $m^* 112$ for the $m/e 228 \rightarrow 163$ transformation, suggest the presence of the $\text{CH}(\text{CN})_2$ group. The n.m.r. spectrum is complicated by the rapid formation of signals for the cyclic product (XIV). However, singlets at $\delta 2.50$ and 2.65 for the MeCO and the $=\text{CMe}$ groups, and a broad signal at $\delta 9.46$, probably due to the exchanging acidic protons, were observed.

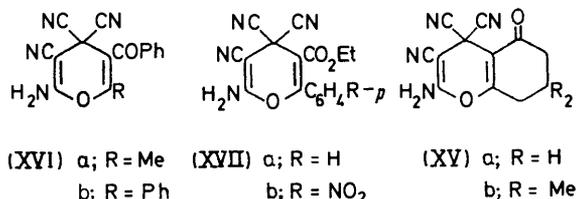
The isomer (XIV), which was formed either directly from the reactants in acetonitrile or from (XIII) is formed by cyclisation of the enol (XIIIa) (Scheme 3). The strongest evidence comes from the i.r. spectrum which shows two N-H absorptions for a primary amine which are replaced by an N-D absorption at 2350 cm^{-1} on shaking the compound with



SCHEME 3

D_2O . The vinylic cyano-group absorbs at 2210 cm^{-1} and the bis-allylic cyano-groups at 2225 cm^{-1} . The n.m.r. spectrum in CD_3OD shows signals for the vinylic Me and Ac groups at $\delta 1.76$ and 2.65 , and a broad absorption for the exchanging $\text{CD}_3\text{OD}-\text{NH}_2$ protons at $\delta 4.66$. The

were not observed. Formation of substituted enamino-4H-pyrans in neutral media can be an important synthetic method since these compounds (see Experimental section) are very sensitive to base. The generality of our method is shown by the analogous reactions of TCNE with benzoylacetone, dibenzoylmethane, ethyl benzoylacetate, ethyl *p*-nitrobenzoylacetate, and dimedone in acetonitrile which give the substituted 4H-pyrans (XVIa), (XVIb), (XVIIa), (XVIIb), and (XVb), respectively (Table 1). The spectral properties of these



compounds (Table 2) closely resemble those of (XIV), suggesting the cyclic structures. Two possible isomers can be formed in the reaction with benzoylacetone, but only one was obtained. Its structural assignment as (XVIa) rather than the 5-acetyl-6-phenyl analogue is based on its C=O absorption at 1670 which is comparable to that of (XVIIb) at 1675 , while that of (XIV) is at 1690 cm^{-1} , on the identical chemical shift of the methyl group of (XIV) and (XVIa) at $\delta (\text{CD}_3\text{OD}) 1.76$, and on the appearance of $m/e 105 (\text{PhCO}^+)$ as the base peak in the mass spectrum. No evidence for the

TABLE I

Analytical data for the 4H-pyrans obtained from the reaction of active methylene compounds with electrophilic olefins

Compound	Yield (%)	M.p. ($^{\circ}\text{C}$)	Analysis						
			Found (%)			Formula	Requires (%)		
			C	H	N		C	H	N
(XIV)	80	>300	57.55	3.3	24.2	$\text{C}_{11}\text{H}_8\text{N}_4\text{O}_2$	57.9	3.55	24.55
(XVb)	90	200 ^a	62.8	4.4	20.7	$\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2$	62.7	4.5	20.9
(XVIa)	90	>300	65.95	3.5	19.55	$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$	66.2	3.45	19.3
(XVIb)	51	195 ^b	74.4	3.4	15.65	$\text{C}_{21}\text{H}_{12}\text{N}_4\text{O}_2$	71.6	3.4	15.9
(XVIIa)	80	163–165	63.85	3.75	17.6	$\text{C}_{17}\text{H}_{12}\text{N}_4\text{O}_3$	63.75	3.8	17.5
(XVIIb)	82	184–185	55.75	3.4	18.1	$\text{C}_{17}\text{H}_{11}\text{N}_5\text{O}_5$	55.9	3.05	19.15
(XVIII)	70	211–212	61.85	4.15	7.45	$\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_5$	61.95	4.4	7.6
(XIX)	90	112	59.4	5.85	7.65	$\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_6$	59.65	6.1	7.75

^a Lit.,⁵ m.p. 195° . ^b Decomp.

mass spectrum differs markedly from that of (XIII). The molecular ion peak is more pronounced and cleavage α to the pyrano-oxygen by either or both of the 2- NH_2 and 6-Me groups give high intensity fragments. The cross-conjugated system shows absorption in the u.v., which has much higher intensity than observed for less conjugated enamino-nitriles.¹⁴

While many cyclic compounds, including enamino-nitriles, were prepared *via* the Michael addition,^{2,14} the only analogy known to us for the formation of (XIV) are the reactions of TCNE with cyclohexane-1,3-dione or dimedone, where structures (XV) were suggested for the products⁵ and non-cyclic adducts [similar to (XIII)]

¹⁴ E. C. Taylor and A. McKillop, 'The Chemistry of Enamino-nitriles and *o*-Aminonitriles,' Interscience, New York, 1970.

normal adducts was observed in any of these cases, although the reactions were not conducted in ethanol, and no attempt was made to stop the reaction in acetonitrile at a very early stage.

Reaction of TCNE with fluorene, xanthen, *p*-nitrobenzyl cyanide, Meldrum's acid (*OO'*-isopropylidene malonate),¹⁵ and ω -nitroacetophenone gave back the starting material. While the first three compounds may not be sufficiently acidic to react under neutral conditions, the others are more acidic, but presumably give highly stable, and therefore relatively unreactive, derived carbanions.

The cyclisation is not restricted to TCNE derivatives,

¹⁵ D. Davidson and S. A. Bernhard, *J. Amer. Chem. Soc.*, **1948**, **70**, 3426.

as shown by the formation of the substituted 4*H*-pyrans (XVIII) and (XIX) from (X) with indane-1,3-dione and dimedone (Table 1). The structural assignments are again based on spectral evidence (Table 2), mainly the i.r. spectra which showed absorptions for NH₂, vinylic CO₂Et, and saturated CN and CO₂Et groups. The λ_{max.} (MeCN) values were lower than those for the enamino-nitriles in Table 2, possibly due to steric distortion of the unsaturated ethoxycarbonyl chromophore compared with the unsaturated cyano-group. The n.m.r. spectra

Indane-1,3-dione gives 2-dicyanomethyleneindane-1,3-dione with tetracyanoethylene,⁷ *via* route (d) of Scheme 1, but only the cyclic product (XVIII) with (X). The open-chain adduct (XX) was isolated from (X) and acetylacetone, but we could not cyclise it to the 4*H*-pyran (XXI), while the open-chain adduct (XXII) which was obtained from (X) and dimedone and identified in a similar way to that discussed for (XIII) (see Experimental section), gave the cyclic adduct (XIX). The reasons for these differences are not yet clear.

TABLE 2
Spectral data of the substituted 4*H*-pyrans

Compound	λ _{max.} (MeCN)/ nm (log ε)	ν _{max.} (KBr)/cm ⁻¹ ^a	δ (CD ₃ OD) ^b	<i>m/e</i> (% relative intensity)
(XIV)	243 (4.20), 272s (3.89), 385 (3.82)	3345, 3240(N-H), 2225, 2210(C≡N), 1690(C=O), 1605, 1580(C=C)	1.76 (s, Me), 2.65 (s, COMe), 4.66br (s, NH ₂) ^{d,e}	228 (M ⁺ , 22), 213 (M - Me, 100), 212 (M - NH ₂ , 33), 211 (M - OH, 15), 197 (M - Me - NH ₂ , 83), 195 (M - Me - H ₂ O, 53), 186 (M - Me - HCN, 57), 185 (M - Ac, 14), 170 (M - Me - Ac, 60) ^f
(XVb) ^g	228 (4.25), 287 (3.30)	3400, 3150(N-H), 2230, 2200(C≡N), 1675(C=O), 1650, 1590(C=C)	1.13br (s, 2Me), 2.50br (s, CH ₂ CO), 2.66br (s, CH ₂), 4.66br (s, NH ₂) ^d	268 (M, 14), 241 (M - HCN, 41), 226 (M - Me - HCN, 100), 213 (M - CO - HCN, 24), 185 (76), 129 (TCNE, H ⁺ , 21)
(XVIa)	242 (4.20), 265s (4.10), 360 (3.85)	3440, 3320(N-H), 2225, 2210s(C≡N), 1670(C=O), 1640, 1595(C=C)	1.76 (s, Me), 7.86 (m, ArCO), 4.66br (s, NH ₂) ^d	290 (M ⁺ , 5), 275 (M - Me, 11), 274 (M - NH ₂ , 13), 273 (M - OH, 18), 246 (M - Me - HCO, 10), 197 (M - Ph - NH ₂ , 33), 170 [PhCOCH(CN) ₂ , 16], 105 (PhCO ⁺ , 100), 43 (MeCO ⁺ , 39) ^h
(XVIb)	245 (4.28), 360 (3.92)	3430, 3330(N-H), 2230, (C≡N), 1675 (C=O), 1610, 1600(C=C)	4.67br (s, N-H), ^d 7.30, 7.52 (2m, 2 Ar)	352 (M ⁺ , 2), 336 (M - NH ₂ , 12), 334 (M - H ₂ O, 100), 325 (M - HCN, 44), 297 (M - CO - HCN, 12), 246 (M - PhCO - H, 11), 221 (M - PhCO - CN, 12), 105 (PhCO ⁺ , 81)
(XVIIa)	241 (4.28), 393 (3.84)	3400, 3250(N-H), 2230(C≡N), 1735(C=O), 1620(C=C)	1.16 (t, Me), 4.26 (q, CH ₂), 4.66br (s, NH ₂), ^d 7.30 (m, Ar) ⁱ	320 (M ⁺ , 0.8), 304 (M - NH ₂ , 14), 302 (M - H ₂ O, 7), 293 (M - HCN, 100), 265 (M - CO - HCN, 41), 247 (M - CO ₂ Et, 85), 220 (M - CO ₂ Et - HCN, 30), 105 (PhCO ⁺ , 8)
(XVIIb)	243 (4.25), 268 (4.24), 395 (3.88)	3430, 3340(N-H), 2220(C≡N), 1710(C=O), 1625, 1600(C=C)	1.20 (t, Me), 4.26 (q, CH ₂), 4.66br (s, NH ₂), 8.00 (centre of AA'BB'q, Ar)	338 (M - HCN, 54), 310 (M - CO - HCN, 100), 293 (M - CO ₂ C ₂ H ₅ , 80), 266 (M - CO ₂ Et - CN, 95), 240 (M - CO ₂ Et - 2CN, 35), 239 (M - CO ₂ Et - HCN - CN, 49)
(XVIII)	242 (4.71), 320 (3.36)	3410, 3400(N-H), 2245(C≡N), 1745(CO ₂ Et), 1700(C=O), 1665(C=O), 1620(C=C)	1.30 (t, 2Me), 4.32 (q, CH ₂), 4.35 (q, CH ₂), 7.50 (s, Ar), 8.08br (s, NH ₂)	368 (M ⁺ , 1), 295 (M - CO ₂ Et, 100), 267 (M - CO ₂ Et - CO, 9), 250 (M - CO ₂ Et - OEt, 7), 249 (M - CO ₂ Et - EtOH, 25), 222 [C(CN)CO ₂ Et ⁺ , 3.6]
(XIX)	242 (4.22), 293 (3.40)	3400, 3300(N-H), 2220(C≡N), 1740(CO ₂ Et), 1690(C=O), 1670(C=O), 1610(C=C)	1.07, 1.09 (2s, 2 Me), 1.30, 1.33 (2t, 2Me), 2.30, 2.35 (2s, 2CH ₂), 4.26 (q, 2CH ₂), 6.83br (s, NH ₂) ^j	362 (M ⁺ , 0.5), 289 (M - CO ₂ Et, 66), 205 (34), 121 (19), 119 (100), 117 (77)

^a Only strong or strong to medium peaks were reported. The N-H peaks are broad. ^b Integration corresponds to the assignments. ^c A similar spectrum is obtained in Nujol except for the NH₂ peaks which appear at 3350 and 3230 cm⁻¹. ^d A signal at average position for the exchanging NH₂-CD₃OD system. ^e δ [(CD₃)₂CO] 1.90 (s, Me) and 2.65 (s, COMe). ^f *m** 136 (213 → 170) and 178.5 (213 → 195). ^g Lit., ⁵ ν_{max.} (KBr) 3450—2860 (NH₂, NH, CH), 2200 (C≡N), and 1680 (C=O); δ [(CD₃)₂CO] 1.0 (2Me), 2.3, 2.5 (2CH₂), 2.9 (CH), and 7.4 (NH₂). ^h *m** 146.7 (197 → 170). ⁱ A similar spectrum was observed in (CD₃)₂SO except for the appearance of the NH₂ protons at δ 11.3. ^j Spectrum in CDCl₃.

were consistent with the assigned structures, and loss of the ethoxycarbonyl group alone or in combination with other groups gave important fragments in the mass spectra.

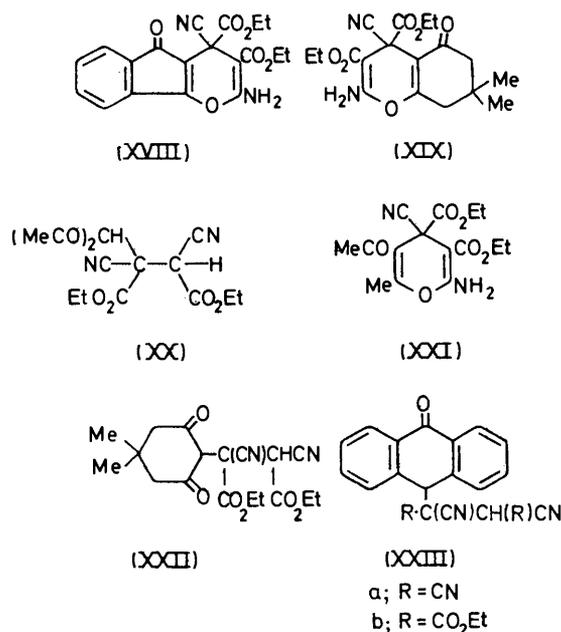
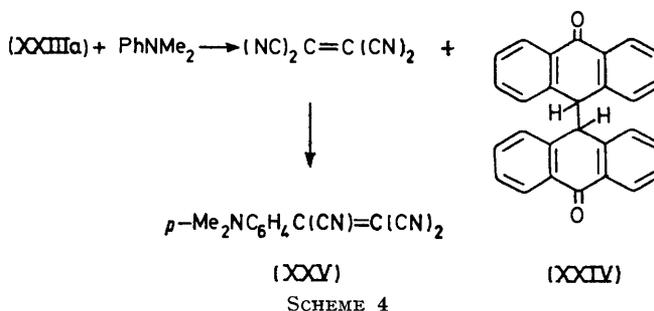
We note, however, that the details of the reaction of the two electrophilic olefins (IX) and (X) with the active methylene compounds differ. The cyclic products from (IX) were obtained in acetonitrile, while the open-chain compound (XIII) was obtained in ethanol, whereas with (X), all the cyclic products were formed in ethanol.

In an attempt to avoid the cyclisation reaction and to direct the reaction into one of the other routes, the reaction of anthrone with (IX) or with (X) was studied in acetonitrile in the absence of a base. The products obtained were the non-cyclic Michael adducts (XXIIIa) and (XXIIIb), which were characterised by a very weak [for (XXIIIa)] or no [for (XXIIIb)] C≡N absorption in the i.r. spectrum.

The adducts (XXIII) are unstable in basic or neutral solution. Spectral changes occur on dissolution in

acetonitrile, and the spectrum of (XXIIIa) after a long time resembles that of anthraquinone. While we hoped that the addition of base to (XXIIIa) would result in the formation of 10-dicyanomethyleneanthrone,¹⁶ addition of triethylamine or pyridine in several solvents gave 10,10'-bianthrone (XXIV), and the spectra of the final reaction mixtures were identical with a superposition of the spectra of (XXIV) and the spectrum of tetracyanoethylene in the presence of base. This latter spectrum is probably that of the 1,1,2,3,3-pentacyanopropenide ion,¹⁷ which is known to be formed from TCNE and bases such as pyridine. Apparently, (XXIV) is formed by decomposition of (XXIIIa) to anthrone and TCNE which then reacts further. This was shown by the reaction of (XXIIIa) with *NN*-dimethylaniline which gave both (XXIV) and *NN*-dimethyl-4-tricyanovinylaniline

[(XXIIIa), (XXIV), anthraquinone, pentacyanopropenide ion] on the solvent and the base probably reflects the sensitivity of TCNE to protic solvents and to bases, which



(XXV), the product of capture of TCNE by *NN*-dimethylaniline (Scheme 4).^{6b}

When TCNE and anthrone reacted in neutral ethanol-chloroform, (XXIIIa) was not observed, but 10,10'-bianthrone was isolated. Formation of (XXIV) amounts to oxidative-dimerisation of anthrone by TCNE. This is plausible since anthrone derivatives can be oxidised to substituted bianthrone by FeCl₃,^{18a} or by benzoquinone,^{18b} while TCNE oxidises 1,4-dihydrobenzenoid compounds to the corresponding aromatic derivatives.¹⁹

The dependence of the nature of the products

¹⁶ (a) J. Silverman and N. F. Yannoni, *J. Chem. Soc. (B)*, 1967, 194; (b) H. Takimoto and L. Krbeček, *J. Org. Chem.*, 1962, **27**, 4688.

¹⁷ (a) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1958, **80**, 2795; (b) C. E. Looney and J. R. Downing, *ibid.*, p. 2840.

¹⁸ (a) E. D. Bergmann and E. Loewenthal, *Bull. Soc. chim. France*, 1952, 66; (b) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 1944, 67.

¹⁹ D. T. Longone and G. L. Smith, *Tetrahedron Letters*, 1962, 205.

by substitution and cleavage reactions lead to various products, some of which may react further. The possibility of aerial oxidation of anthrone to anthraquinone in basic solution cannot be discounted, since base-catalysed oxidation is known for fluorene derivatives.²⁰

In summary, we have observed in the present work routes (a), (b), and (d) of Scheme 1: 'diarylmethylene transfer' with (XII), uncatalysed Michael addition [with (IX) and (X)] and its reversal [with (XXIIIa)] and cyclisation to substituted 4*H*-pyrans [with (IX) and (X)] which may be used as a general synthetic route. However, generalisations regarding the specific route which the reaction will take are not yet possible, except that cyclisation, when possible, will be a favoured route.

EXPERIMENTAL

Materials.—1,1-Dinitro-2,2-diphenylethylene, m.p. 149° (lit.,²¹ 149–150°), was prepared by reaction of 1,1-diphenylethylene with fuming nitric acid in acetic acid according to Bergmann *et al.*,²¹ λ_{max} (MeCN) 285sh (log ϵ 3.85) and 320 nm (3.87), ν_{max} (Nujol) 1570 and 1550 cm⁻¹, δ (CDCl₃) 7.35 (m, Ph). Diethyl 2,3-dicyanofumarate, white crystals, m.p. 114–115° (from EtOH), was prepared by either Naik's²² or Ireland's²³ procedure, λ_{max} (MeCN) 242 nm (log ϵ 4.12) [lit.,²⁴ 242 nm (4.03)], ν_{max} 1760 (CO₂Et) and 1260 cm⁻¹, δ (CDCl₃) 1.38 (6H, t, *J* 7 Hz, Me) and 4.40 (4H, q, *J* 7 Hz, CH₂). Tetrakisethoxycarbonylethylene, m.p. 54° (lit.,²⁵ 52.5–53.0°), λ_{max} (MeOH or Et₂O) <210 nm, ν_{max} (Nujol) 1740, 1715 (CO₂Et), 1560 (C=C), and 1250 cm⁻¹, δ (CDCl₃) 1.25 (6H, t, *J* 7 Hz, Me) and 4.19 (4H, q, *J* 7 Hz, CH₂), and benzophenone diethyl acetal,²⁶ m.p. 51°, δ (CDCl₃) 1.16 (Me), 3.33 (CH₂), and 7.40 (Ph), were prepared according to the literature.^{25,26} Tetracyanoethylene (TCNE) (Aldrich) was crystallised twice from chlorobenzene. The active methylene compounds were pure commercial products (Fluka, purum).

Reaction of 1,1-Dinitro-2,2-diphenylethylene with Malononitrile.—(a) On keeping a mixture of the ethylene (XI) (54)

²⁰ Y. Sprinzak, *J. Amer. Chem. Soc.*, 1958, **80**, 5449.

²¹ E. Bergmann, L. Engel, and H. Meyer, *Ber.*, 1932, **65**, 446.

²² H. G. Naik, *J. Chem. Soc.*, 1921, **118**, 1239.

²³ (a) C. J. Ireland and J. S. Pizey, *J.C.S. Chem. Comm.*, 1972, 4; (b) C. J. Ireland, personal communication.

²⁴ K. Kudo, *Bull. Chem. Soc. Japan*, 1962, **35**, 1490.

²⁵ B. B. Corson and W. L. Benson, *Org. Synth.*, Coll. Vol. II, 1943, p. 273.

²⁶ J. E. Mackenzie, *J. Chem. Soc.*, 1896, **69**, 985.

mg, 2 mmol) and malononitrile (190 mg, 3 mmol) in absolute ethanol (25 ml) at room temperature for 3 weeks, work-up gave the starting olefin.

(b) A mixture of (XI) (540 mg, 2 mmol), malononitrile (190 mg, 3 mmol), and triethylamine (0.3 ml, 3 mmol) in absolute ethanol (15 ml) was refluxed for 6 h, and kept for an additional 15 h at room temperature. Half the solvent was evaporated off, giving crystals (370 mg, 80%), m.p. 135°, ν_{\max} 2215 cm^{-1} (C≡N). Recrystallisation from ethanol gave white needles of 1,1-dicyano-2,2-diphenylethylene, m.p. 138° (lit.,²⁷ 140–141°; lit.,²⁸ 136°) (Found: C, 83.2; H, 4.35; N, 12.15. Calc. for $\text{C}_{16}\text{H}_{10}\text{N}_2$: C, 83.45; H, 4.4; N, 12.15%), ν_{\max} (Nujol) 2220 (C≡N), 1580, and 1560 cm^{-1} , λ_{\max} (MeCN) 227 (log ϵ 3.98) and 317 nm (4.16) [lit.,²⁷ λ_{\max} (EtOH) 227 (4.16) and 320 (3.28); lit.,²⁹ λ_{\max} (EtOH) 320 nm (4.16)].

(c) Reaction as in (b) gave, after 24 h at 20°, (XII) (75%), identical (m.p., mixed m.p., u.v., i.r.) with the sample obtained in (b).

Reaction of TCNE with Acetylacetone in Ethanol.—TCNE (0.64 g, 5 mmol) was added to a solution of acetylacetone (0.5 g, 5 mmol) in absolute ethanol (20 ml). The solution turned red with evolution of heat, and within a few minutes white crystals separated. The solid was filtered off after 15 min, giving 3-(1,1,2,2-tetracyanoethyl)pentane-2,4-dione (XIII) (1.0 g, 88%), m.p. 114–115°. Recrystallisation [light petroleum (b.p. 40–60°) or CCl_4 -MeCN] gave pale yellow crystals, decomp. at 156–160° (Found: C, 58.1; H, 3.6; N, 24.8. $\text{C}_{11}\text{H}_8\text{N}_4\text{O}_2$ requires C, 57.9; H, 3.55; N, 24.55%), ν_{\max} (KBr) 3270s (enol O-H), 2220m (C≡N), 1730s (C=O), 1650, and 1635m (C=C) cm^{-1} , ν_{\max} (Nujol) as for KBr, but no peak at 2220 cm^{-1} , m/e 228 (M^+ , 6%), 213 (M - Me, 5), 201 (M - HCN, 4), 186 (M - Me - HCN, 5), 163 [M - $\text{CH}(\text{CN})_2$, 100], 162 [M - $\text{CH}_2(\text{CN})_2$, 34], 148 [M - Me - $\text{CH}(\text{CN})_2$, 8], 128 (TCNE⁺, 6), and 100 (M - TCNE, 3), m^* 112 (228 → 163), m/e (after shaking with D_2O) 229 (M^+ , 20%), 163 (30), 162 (30), and 139 (100), λ_{\max} (MeCN) (immediately after dissolution) 253 nm (log ϵ 4.03), λ_{\max} (on standing) 243, 280sh, and 385 nm; the spectrum of the final product is identical with that of (XIV) and the kinetics of the transformation (XIII) → (XIV) were followed by u.v. (see Discussion section); δ [(CD_3)₂CO] (immediately after dissolution) 1.90 (ca. 1H), 2.50 (ca. 3H), 2.65 (ca. 4H), and 9.46br (ca. 1H); on standing, the signal at δ 1.90 increases in intensity, and those at 2.50 and 9.46 decrease and disappear; in the final spectrum the ratio of the integrals of the δ 1.90–2.65 signals is 1:1 and the spectrum is similar to that of (XIV) which was obtained directly in acetonitrile.

Reaction of TCNE with Acetylacetone in Acetonitrile.—A mixture of TCNE (1.28 g, 10 mmol) and acetylacetone (1 g, 10 mmol) in acetonitrile (20 ml) was kept for 4 days at 20°. Half the solvent was evaporated off, and addition of carbon tetrachloride (10 ml) to the remainder gave pale yellow crystals (1.7 g, 75%), m.p. >300° of 5-acetyl-2-amino-3,4,4-tricyano-6-methyl-4H-pyran (XIV), whose analytical and spectral properties are given in Tables 1 and 2. When (XIV) was shaken with D_2O in acetonitrile and dried, the NH_2 absorption at 3345 cm^{-1} was much weaker than in the undeuteriated (XIV) and an N-D absorption appeared at 2350 cm^{-1} .

When triethylamine was added to (XIV) the absorption at ca. 400 nm increased in intensity, and a new peak ap-

peared at 310 nm. This change was not investigated further.

Reaction of the Adduct (XIII) in Acetonitrile.—The adduct (XIII) (228 mg, 1 mmol) was kept in acetonitrile (10 ml) at room temperature for 48 h. The solution was concentrated and carbon tetrachloride (30 ml) was added, giving pale yellow crystals of (XIV) (180 mg, 80%), m.p. >300°, which had identical u.v., i.r., and mass spectra with those of the sample obtained directly from TCNE and acetylacetone in acetonitrile (Table 2).

Reaction of Diethyl 2,3-Dicyanofumarate with Acetylacetone.—A mixture of the diester (X) (244 mg, 1.1 mmol) and acetylacetone (150 mg, 1.5 mmol) in absolute ethanol (10 ml) was kept for 24 h at 25°. Addition of carbon tetrachloride (15 ml) after evaporation of half the solvent gave diethyl 2,3-dicyano-2-diacetylmethylsuccinate (XX) (230 mg, 65%), m.p. 92–93° (Found: C, 55.8; H, 5.6; N, 8.75. $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_6$ requires C, 55.9; H, 5.65; N, 8.7%), λ_{\max} (MeCN) 259 nm (log ϵ 4.04), ν_{\max} (KBr) 3250 (enolic O-H), 1750 (CO_2Et), and 1650 (MeCO) cm^{-1} , δ (CDCl_3) 1.26 and 1.36 (6H, 2t, $\text{CO}_2\text{CH}_2\text{CH}_3$ in keto and enol forms), 2.36, 2.43, 2.46, and 2.53 (6H, 4s, CH_3CO in keto and enol forms), 4.26 and 4.30 (4H, 2q, $\text{CO}_2\text{CH}_2\text{CH}_3$ in keto and enol forms), and 4.83, 5.00, and 8.26br (2H, 3s, CH and OH), signals at δ 5.00 and 8.26 disappear on shaking for 3 min with D_2O , m/e 322 (M^+ , 8%), 277 (M - OEt, 11), 249 (M - CO_2Et , 26), 232 (M - CO_2Et - OH, 14), 208 (M - CO_2Et - Me - CN, 25), 207 (M - CO_2Et - MeCO, 26), 205 (41), 204 (M - CO_2Et - EtO, 100), 178 (M - CO_2Et - OEt - CN, 21), 177 (M - $2\text{CO}_2\text{Et}$, 90), 160 (M - CO_2Et - EtOH - MeCO, 51), 135 (55), and 100 [(MeCO)₂CH₂, 34].

Reaction of Diethyl 2,3-Dicyanofumarate with Dimedone.—A mixture of the diester (X) (1.1 g, 5 mmol) and dimedone (700 mg, 5 mmol) in absolute ethanol (50 ml) was kept for 24 h at 25°. Half the solvent was evaporated off, and addition of carbon tetrachloride (50 ml) precipitated diethyl 2,3-dicyano-2-(4,4-dimethyl-2,6-dioxocyclohexyl)succinate (XXII) as pale yellow crystals, m.p. 190° (1.0 g, 55%) (Found: C, 59.85; H, 6.4; N, 6.95. $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_6$ requires C, 59.65; H, 6.1; N, 7.75%), λ_{\max} (MeCN) 251 nm (log ϵ 4.04), ν_{\max} (Nujol) 3200, 3100 (enolic O-H), 1750, 1735 (CO_2Et), 1660, 1650 (C=O), and 1620 (C=C) cm^{-1} , ν_{\max} (KBr) 2250w (C≡N) cm^{-1} , δ (CDCl_3) 1.15 and 1.16 (6H, 2s, 2Me), 1.20 and 1.23 (6H, 2t, 2Me), 2.26 (s), 2.36, 2.50 (m), and 2.56 (4H, s, enolic and ketonic CH_2), 3.38br [1H, $\text{CH}(\text{CN})\text{CO}_2\text{Et}$], 3.93 (2H, q, CH_2), 4.26 (2H, q, CH_2), and 9.43br (1H, s, enolic O-H), signals at δ 3.38 and 9.43 disappear on shaking with D_2O , m/e 362 (M^+ , 2.7%), 317 (M - OEt, 3), 289 (M - CO_2Et , 7), 262 (M - CO_2Et - HCN, 7), 261 (M - CO_2Et - CO, 20), 140 (dimedone⁺, 10), 112 (27), 84 (31), and 83 ($\text{Me}_2\text{C}=\text{CH}-\text{CO}^+$, 100).

Formation of Substituted 4H-Pyrans.—(a) *From TCNE.* A mixture of TCNE (10 mmol) and the active methylene compound (10 mmol) in acetonitrile (20 ml) was kept for 42 h at 25°. In each case the mixture turned red, and the product either crystallised directly from the mixture or was precipitated after concentration of the solution and addition of carbon tetrachloride. The products were crystallised from MeCN- CCl_4 .

(b) *From diethyl 2,3-dicyanofumarate (X).* A mixture of the diester (X) (1 mmol) with indane-1,3-dione (1 mmol) in absolute ethanol (10 ml) was kept at 25° for 24 h, and the

²⁸ R. Schenck and H. Finken, *Annalen*, 1928, **462**, 267.

²⁷ E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and D. R. Maulding, *J. Org. Chem.*, 1962, **27**, 4428.

²⁹ H. Weiler-Feilchenfeld, I. Agranat, and E. D. Bergmann, *Trans. Faraday Soc.*, 1966, **62**, 2084.

crystals which separated were recrystallised from chloroform. A mixture of (X) (1 mmol) and dimedone (1 mmol) in absolute ethanol was refluxed for 8 h, half the solvent was evaporated off, and addition of carbon tetrachloride gave the 4*H*-pyran. Analytical and spectral data for the 4*H*-pyrans are given in Tables 1 and 2.

Reaction of TCNE with Anthrone in Chloroform, Benzene, or Acetonitrile.—To a solution of anthrone (1.94 g, 10 mmol) in chloroform (40 ml), TCNE (1.28 g, 10 mmol) was added. The mixture turned yellow-green and crystals began to separate within 2 h. The mixture was kept overnight, filtered, and the solid was crystallised from chloroform, giving 10-(1,1,2,2-tetracyanoethyl)anthrone (XXIIIa) (2.66 g, 80%), m.p. 184–185° (with subl., blue melt) (Found: C, 74.5; H, 3.2; N, 17.6. $C_{20}H_{10}N_4O$ requires C, 74.55; H, 3.2; N, 17.4%), λ_{\max} (MeCN) (immediately after dissolution) 273 (log ϵ 4.07) and 257 nm (4.15), ν_{\max} (Nujol) 1660s (C=O), 1625sh,m, 1595s, and 1575sh,m cm^{-1} , ν_{\max} (KBr) as for Nujol and 2250w (C≡N) cm^{-1} , *m/e* no M^+ , 296 ($M - CN$, 1%), 194 (anthrone, 100), 193 (anthrone - H, 13), 166 (fluorene⁺, 16), 165 (anthrone - HCO, 75), 139 (7), and 128 (TCNE⁺, 58), m^* 141.5 (194 → 166).

Similar reaction in acetonitrile gave the adduct in 80% yield after few minutes, while reaction in benzene required 1 h reflux for completion, giving 60% yield.

Reaction of TCNE with Anthrone in Ethanol-Chloroform.—Anthrone (400 mg, 2 mmol) and TCNE (260 mg, 2 mmol) were dissolved in a mixture of ethanol (10 ml) and chloroform (5 ml). After 3 h at 25°, crystals began to separate from the blue mixture, and were identified as 10,10'-bianthrone (XXIV), m.p. 252° (subl. at 230°) [ν_{\max} (Nujol) 1670s, 1650sh, and 1600 cm^{-1}] by m.p. and mixed m.p. with the sample of (XXIV) isolated from the reaction of (XXIIIa) with pyridine in acetonitrile (see below).

When TCNE was dissolved in ethanol-chloroform and anthrone was added after 20 h, the mixture turned blue within 15 min, and white needles, m.p. 279–280°, of anthraquinone (identified by i.r. and mixed m.p.) were obtained.

Reaction of TCNE with Anthrone in the Presence of Pyridine.—(a) From reaction between anthrone (10 mmol) and TCNE (10 mmol) in acetonitrile (20 ml) in the presence of pyridine (2.5 mmol) at 25°, only anthrone was recovered.

(b) A mixture of anthrone (10 mmol) and TCNE (10 mmol) in benzene (50 ml) was refluxed for 5 min, pyridine (3 mmol) was added, and reflux was continued for an additional 15 min. The mixture turned green, and yellow crystals of 10,10'-bianthrone, m.p. 247° (from EtOH), were isolated.

Spectral Behaviour of (XXIIIa).—The u.v. spectrum of (XXIIIa) in acetonitrile changes rapidly. After 30 min there is a sharp increase in the absorption intensity at 257 nm, and a new absorption at 263 nm, and moderate changes in the absorption are observed at 273 and 314 nm. After standing for 1 week, the final spectrum is λ_{\max} 250 (log ϵ 4.57), 260sh (4.16), 270 (4.05), and 320 nm (3.53) (log ϵ calculated on the basis of the molecular weight of anthraquinone). For authentic anthraquinone: λ_{\max} (MeCN) 250 (log ϵ 4.66), 260sh (4.27), 270 (4.17), and 320 nm (3.65), while for anthrone: λ_{\max} (MeCN) 263 nm (log ϵ 4.26) and 306sh nm (3.56).

Reaction of the Adduct (XXIIIa) with Amines.—(a) With

triethylamine. Addition of one drop of triethylamine to a dilute solution of (XXIIIa) in MeCN results in spectral changes, and appearance of maxima at 251sh, 263sh, 273, 305, and 400 nm, after long reaction time. A similar spectrum is obtained on addition of triethylamine to a solution of (XXIIIa) after its uncatalysed decomposition. The spectra of anthraquinone and of anthrone are only slightly affected by the addition of Et₃N, while addition of Et₃N to TCNE [λ_{\max} (MeCN) 256sh, 260, and 270 nm] results in replacement of these maxima by new ones at 305 and 405 nm. The spectrum of (XXIIIa) in the presence of Et₃N is similar to the superimposed spectra of bianthrone and TCNE in the presence of Et₃N.

(b) *With pyridine in acetonitrile.* To (XXIIIa) (200 mg, 0.6 mmol) in acetonitrile (10 ml), pyridine (118 mg, 1.2 mmol) was added. The solution turned red immediately and white crystals of 10,10'-bianthrone (XXIV), m.p. 250–252° before crystallisation (lit.^{18b} 256°), were separated (Found: C, 86.9; H, 4.7. Calc. for $C_{28}H_{18}O_2$: C, 87.05; H, 4.7%), ν_{\max} (Nujol) 1660s (C=O), 1600s (C=C), 1455, 1400, and 1325s cm^{-1} , *m/e* 386 (M^+ , 0.08%), 195 (5), 193 ($M - anthryl$, 100), and 165 (fluorenyl⁺, 39), m^* 141.5 (193 → 165).

(c) *With pyridine in EtOH.* To (XXIIIa) (100 mg, 0.3 mmol) in EtOH (20 ml), pyridine (118 mg, 1.2 mmol) was added. The mixture changed to yellow, pink, and red, and white crystals of 10,10'-bianthrone, m.p. 245–247° (subl.) (50 mg, 83%) were separated and identified by i.r.

(d) *With NN-dimethylaniline in chloroform.* To a suspension of (XXIIIa) (320 mg, 1 mmol) in chloroform (20 ml), *NN*-dimethylaniline (240 mg, 2 mmol) was added, and the mixture was stirred for 48 h, during which it turned red. The solvent was evaporated off, and the solid obtained was crystallised from acetic acid, giving white crystals of bianthrone (0.15 g, 78%), m.p. 250° (crude), identified by m.p., mixed m.p., i.r., and mass spectra. The mother liquor was evaporated, giving blue crystals (15 mg) of *NN*-dimethyl-4-tricyanovinylaniline, m.p. 173° (lit.^{6b} 173°), mixed m.p. 173° and u.v. spectra [λ_{\max} (MeCN) 512 nm] identical with those of an authentic sample.

Reaction of Diethyl 2,3-Dicyanofumarate (X) with Anthrone.—A mixture of (X) (300 mg, 1.4 mmol) and anthrone (310 mg, 1.6 mmol) in absolute ethanol (25 ml) was kept for 24 h at 25°. Evaporation of most of the solvent and addition of carbon tetrachloride gave white crystals of 10-(1,2-dicyano-1,2-bisethoxycarbonylethyl)anthrone (XXIIIb) (400 mg, 70%), m.p. 186° (Found: C, 69.5; H, 4.9; N, 6.55. $C_{24}H_{20}N_2O_8$ requires C, 69.2; H, 4.85; N, 6.75%), λ_{\max} (MeCN) (immediately on dissolution) 234sh (log ϵ 4.04) and 273 nm (4.08), spectrum changes and new maxima are formed at ca. 250 and 330 nm, ν_{\max} (KBr) 2250w (C≡N), 1760 (CO₂Et), 1680 (C=O), and 1605 (C=C) cm^{-1} , ν_{\max} (Nujol) as in KBr but no peak at 2250 cm^{-1} , δ [(CD₃)₂CO] 1.08 and 1.30 (each 3H, t, Me), 4.01 and 4.33 (each 2H, q, CH₂), 4.53 and 5.12 (each 1H, s, CH), and 7.33–8.38 (8H, m, Ar), *m/e* no M^+ , 304 [$M - CH(CN)CO_2Et$, 0.7%), 278 [$M - CH(CN)CO_2Et - CN$, 0.6], 194 (anthrone⁺, 100), 193 (anthrone - H, 99.5), 166 (fluorene⁺, 35), and 165 (fluorenyl⁺, 99).