Reaction of Dimethyl Acetylenedicarboxylate with Derivatives of Malonic Acid: Pentamethoxycarbonylcyclopentadienide Anion, Tetramethoxycarbonylcyclopentadienone, Cyanotetramethoxyfulvenolate Anion, and Related Compounds

By **R. C. Cookson, J. B. Henstock, J. Hudec, and B. R. D. Whitear,** Chemistry Department, Southampton University

The revised formulation of the adducts of dimethyl malonate with dimethyl acetylenedicarboxylate in the presence of pyridine and acetic acid as tautomeric octamethyl cycloheptadienoctacarboxylates [(III) and (IV)] is confirmed. Both tautomers, or the analogues from other esters of malonic acid, are converted by potassium acetate into Diels' potassium pentamethoxycarbonylcyclopentadienide (VIa). Diazomethane methylates the free cyclopentadiene, which is a very strong acid, to the *C*-methyl derivative (Vb), easily hydrolysed to the 1,2,3,4-tetramethoxycarbonyl-5-methylcyclopentadienide anion (VIII). The *C*-chloro- and bromo-derivatives (Vd and e), formed by treatment of the salt (VIa) with chlorine or bromine, are strong halogenating agents.

The yellow pyridinium 1-cyano-1-ethoxycarbonyl-2,3,4,5-tetramethoxycarbonylpentadienide (XIIIa) produced by reaction of cyanoacetic ester with dimethyl acetylenedicarboxylate in the presence of pyridine and acetic acid [corresponding to our original formula for (III)] easily loses a mole of methanol to form a blue dye, pyridinium 2-cyano(ethoxycarbonyl)methylene-3,4,5-trimethoxycarbonylcyclopentadienolate (XIVa). The colourless pseudo-acids reversibly formed by treatment of the blue dyes (XIV) with acid are dimers, but the absence of an infrared carbonyl stretching band at high enough frequency makes it unlikely that they are Diels–Alder dimers of the cyclopentadienones (XVIII). The bridging carbonyl group of tetramethoxycarbonylcyclopentadienone dimer (XXIVc), for example, absorbs at 1835 cm.$^{-1}$.

The blue dye (XIVd) from *p*-bromobenzyl cyanoacetate adds ethanol at the cyclopentadienone carbonyl group to give a colourless product (XXVIa) that regenerates the blue dye with elimination of ethanol on reaction with pyridine. The analogous methanol derivative (XXVIb) is the conjugate acid of the intermediate anion (XIIIa) in the usual synthesis of the blue dye.

DURING investigation of the reaction of dimethyl acetylenedicarboxylate with various heterocyclic nitrogen compounds Diels[1] examined the reaction of the ester with dimethyl malonate, ethyl cyanoacetate and malononitrile in the presence of pyridine and acetic acid. From the reaction with dimethyl malonate he isolated two products, melting at 183 and 226°. Largely because of his preconceptions about the likely mechanism of reaction he formulated the compounds as the stereoisomeric hemiacetals (I), even though they were recrystallised from acetic acid. Initially we did not find the lower-melting isomer, and, accepting Diels' molecular weight (for a 2 : 1-adduct), formulated the substance (which showed no hydroxy-absorption in the i.r., and had $\lambda_{max.}$ 286 nm, ε 3300) as the open-chain compound (II) or the other conjugated tautomer.[2] The ^{1}H n.m.r. spectrum, which we were able to measure later, was however inconsistent with such a structure and indicated a 1 : 3-adduct of dimethyl malonate with dimethyl acetylenedicarboxylate. A redetermination of the molecular weight with an osmometer confirmed the higher value.[3,4] Soon afterwards Le Goff and LaCount[5] proposed structures (IIIa) and (IV) for the high- and the spectral properties.

Diels[1] reported a yellow crystalline product (actually colourless when recrystallised) from the reaction of the adduct (IIIa) or (IV) with potassium acetate in water. Treatment of this potassium salt with hydrochloric acid liberated the colourless crystalline acid Diels' pentamethoxycarbonylcyclopentadiene (Va). The empirical formulae $XC_5(CO_2Me)_5$ for the salts and the acid, the i.r.[6] ($\nu_{max.}$ 1755, 1735, 1715, and 1620 cm.$^{-1}$ for the acid; 1735, 1725, 1700, and 1685 cm.$^{-1}$ for the tetra-n-butylammonium salt; 1715, 1700, and 1670 for the potassium salt, all in Nujol) and u.v. spectra[6] ($\lambda_{max.}$ 265 and 295 nm, ε 49,800 and 14,600 for the salts or the acid in methanol), and especially the p.m.r. spectrum, which showed only a singlet at τ 5·8 for either the potassium salt or the free acid in deuterium oxide (with a peak from HOD in the latter case), all agree with Diels' assignment.

The mechanism we suggested at first,[2] based on an erroneous structure (II) for the adduct, is now beside the point. The crystalline adducts from dimethyl malonate (IIIa), methyl ethyl malonate (IIIb), and diethyl malonate (IIIc) all gave the same potassium salt (VIa), so, as pointed out by Le Goff and LaCount, the malonate fragment must be lost during the reaction. The simplest mechanism would be a transannular Michael reaction to form (VII), followed by elimination of trimethyl ethylenetricarboxylate from the anion. The transient absorption bands at 365 and 446 nm that appear when the dimethyl or methyl ethyl malonate adduct (IIIa or b) in ethanol is treated with alkali (quickly replaced by the spectrum of the cyclopentadienide) probably come from the intermediate anion corresponding to (III). When the adduct (IIIa) is treated with potassium acetate in water just below 100° almost no carbon dioxide is formed; however, nearly 1

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[1] O. Diels, *Ber.*, 1942, **75**, 1452; O. Diels and U. Kock, *Annalen*, 1944, **556**, 38.

[2] R. C. Cookson, J. Hudec, and B. R. D. Whitear, *Proc. Chem. Soc.*, 1961, 117.

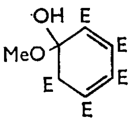
[3] P. Bamfield, R. C. Cookson, A. Crabtree, J. Henstock, J. Hudec, A. W. Johnson, and B. R. D. Whitear, *Chem. and Ind.*, 1964, 1313.

[4] B. R. D. Whitear, Ph.D. Thesis, Southampton, 1962.

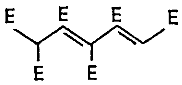
[5] E. Le Goff and R. B. LaCount, *J. Org. Chem.*, 1964, **29**, 423.

[6] Cf. R. C. Cookson and K. Friedrich, *J. Chem. Soc.* (*C*), 1966, 1641.

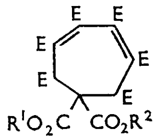
mol. is evolved when the solution is boiled, presumably by hydrolysis of trimethyl ethylenetricarboxylate, as suggested by Le Goff and LaCount.[5] Treatment of 1,2,3,4,5,6,7-heptaphenylcycloheptatriene with potassium to give 1,2,3,4,5-pentaphenylcyclopentadienide and stilbene [7] may well be a related reaction, although there a reduction is also involved.



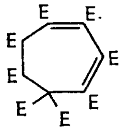
(I)



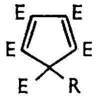
(II)



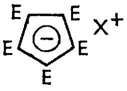
(III) a; $R^1 = R^2 = Me$
b; $R^1 = Me, R^2 = Et$
c; $R^1 = R^2 = Et$



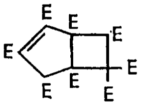
(IV)



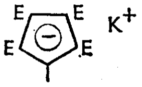
(V) a; R = H
b; R = Me
c; R = Ph
d; R = Cl
e; R = Br



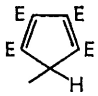
(VI) a; X = K
b; X = Bu_4N
c; X = ½ Fe^{II}



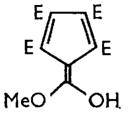
(VII)



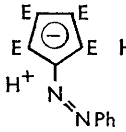
(VIII)



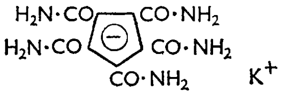
(IX)



(X)



(XI)



(XII)

Throughout, E = CO_2Me

The cyclopentadiene (Va) is one of the strongest acids known. Dilution with water of a solution of the tetra-n-butylammonium salt in concentrated hydrochloric acid gave the salt back unchanged. A 0·01N solution of the acid in water had a pH of 2·0 and titrated as a typical strong acid. With a glass electrode the apparent pH values of aqueous solutions of sulphuric acid (as a dibasic acid), hydrochloric acid, and the cyclopentadiene were respectively (at 0·04N) 1·66, 1·54, and 1·54; (at 0·08N) 1·4, 1·24, and 1·24. At 0·8N, hydrochloric acid gave a reading of 0·2, while the cyclopentadiene gave a small negative value. An aqueous solution of the acid dissolved metallic iron with evolution of hydrogen and formation of the ferrous salt (VIc), which showed the reactions of ferrous iron and the spectra of the cyclopentadienide. As with the tetracyano- and dicyanodiethoxycarbonyl analogues [6] the anion is much too stable to rearrange to the ferrocene.

The cyclopentadiene decomposed diazomethane in benzene solution (but not in methanol where it merely acts as a strong acid catalysing the formation of dimethyl ether) to give the *C*-methyl derivative (Vb), which was hydrolysed by mild bases to salts of the anion (VIII). The ultraviolet spectra of these compounds suggested the likely position of protonation of the acids in different media.[4] The potassium and tetra-n-butylammonium salts (VIa and b) and the free pentamethoxycarbonylcyclopentadiene, as already mentioned, all had the same u.v. spectrum in methanol ($\lambda_{max.}$ 265 and 295 nm, ε 49,800 and 14,600); that of the tetra-n-butylammonium salt was unaltered in benzene (where it presumably exists as ion pairs and larger clusters; $\lambda_{max.}$ 294 nm, ε 15,500). The methyltetramethoxycarbonyl compound, also a strong acid, had the same spectrum in methanol as its potassium salt (VIII). Unlike 1,2,3,4,5-pentamethoxycarbonyl-1-methylcyclopentadiene (Vb), of fixed structure, which had the same spectrum in methanol, benzene, or cyclohexane ($\lambda_{max.}$ 220 and 295 nm, ε 8000 and 5700—the first band obscured in benzene), the spectra of the acids (Va) and (IX) were sensitive to the solvent; this suggests a tautomeric change. The long wavelength band of the tetraester [(IX) or tautomer] in benzene occurred at a longer wavelength ($\lambda_{max.}$ 315 nm, ε 7500) than that in methanol, but the contrast was more marked with the pentaester (Va) ($\lambda_{max.}$ 318sh and 340 nm, ε 10,000 and 15,900 in benzene or cyclohexane, with an additional intense band at 265 nm, in the latter solvent). To which part of the cyclopentadiene molecule is the proton attached in a non-basic solvent? The *C*-protonated cyclopentadiene (Va) would absorb very like the *C*-methylated compound (Vb) (295 nm), so the maximum at 340 nm can come only from the *O*-protonated species (X). Surprisingly, the diffuse reflectance spectrum of the crystalline acid (Va) ($\lambda_{max.}$ 263 and 300 nm) closely resembles that of the anion in solution. The electronic spectrum is a rather unspecific property, and one cannot say whether this spectrum is produced by lattice perturbations of that expected of (Va) or (X), or whether the crystal has a three dimensional H-bonded structure whereas in solution the hydroxyfulvene (X) is monomeric and internally H-bonded. The reflectance spectrum may, however, not be a genuine property of the crystal in bulk; since the spectrum is contributed by the few layers of molecules on the surface, it may be due to the hydroxonium salt (VI; X = H_3O) formed by traces of absorbed water, or to displacement of hydrogen fluoride from the potassium fluoride matrix.

Diels [1] described an unstable 1 : 1-adduct between the cyclopentadiene (Va) and maleic anhydride, m. p. 85°, which he considered to be a normal Diels–Alder adduct; this apparently substantiated his formula for the cyclopentadiene (Va). A similar but more stable adduct, m. p. 127°, was formed with tetracyanoethylene. However, in hydroxylic solvents the adducts immediately dissolved to give solutions with the spectra of the cyclopentadienide (VI); the Diels–Alder adducts would have had only the dimethyl maleate chromophore (dimethyl bicyclo-[2,2,1]hept-2-ene-2,3-dicarboxylate has $\lambda_{max.}$ 247 nm, ε 9000). In benzene the tetracyanoethylene adduct gave a pale yellow solution; that in styrene was a deep

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[7] R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, 1965, **87**, 2200.

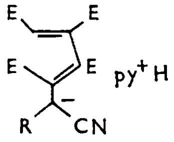
red. In fact in aromatic solvents the visible spectra were those of the tetracyanoethylene charge-transfer complexes. Evidently the adducts immediately broke down in solution into their components. To find out whether they were covalently linked in the solid state the diffuse reflectance spectra of the adducts dispersed in lithium fluoride[8] were measured. The maleic anhydride adduct showed $\lambda_{max.}$ 265, 300, and 340 nm and the tetracyanoethylene adduct $\lambda_{max.}$ 265, 297, 420, and 450 nm (see ref. 4 for curves); the wavelengths and relative intensities of the first two bands in each case indicate the presence of the unchanged cyclopentadienide. The adducts must be merely molecular complexes, which show the long wavelength charge-transfer transitions from the cyclopentadienide to the olefin, but largely dissociate in solution. Replacement of the acidic proton by other cations shifted the charge-transfer band to longer wavelengths; *e.g.*, in ethyl acetate the tetra-n-butylammonium salt (VIb) and tetracyanoethylene produced a blue solution with $\lambda_{max.}$ 425 and 602 nm. Had the acidic proton in the cyclopentadiene complexes been attached to the electron acceptor, which would increase its electron affinity, the charge-transfer maxima might have been expected at longer wavelengths. It must presumably therefore be associated in some way with the electron donor. Both the acidity of the cyclopentadiene [(Va) or (X)] and the change in charge-transfer spectrum when the proton was replaced by a metal could be demonstrated by drawing a nickel spatula across the powdered tetracyanoethylene adduct; a blue-black line was produced on the yellow background. (The radical anion may also be involved here.[9])

The cyclopentadienide (VI) combined with strong electrophiles. The salts, dissolved in water, reacted with chlorine or bromine (but not iodine) to form the *C*-halogeno-derivatives (Vd and e), which, as expected from the stability of the corresponding cyclopentadienide anion, were strong halogenating agents. Iodide was oxidised to iodine with quantitative regeneration of the cyclopentadienide salt (VI), and phenols were halogenated. A solution of the bromo-compound (Ve) in methanol had a u.v. spectrum identical with that of the cyclopentadienide (VI).

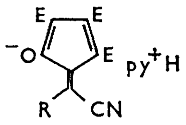
In acid solution diazonium salts slowly (*ca.* 1 month) condensed with the cyclopentadienide salts (VI) to give azo-dyes (XI) with loss of an ester group (phenyl compound: $\lambda_{max.}$ 284 and 408 nm, ε 19,500 and 14,600 in ethanol, unchanged in alkaline solution). A crystalline by-product ($\lambda_{max.}$ *ca.* 208, 230sh, and 280sh nm, ε 17,600, 9600, and 3100 in methanol) had the correct analysis for the *C*-phenyl derivative (Vc) The hydrolysis and decarboxylation in the first case and not the second probably reflects the greater electronegativity of the phenylazo-substituent compared with phenyl

A solution of the potassium salt (VIa) in strong aqueous ammonia slowly deposited crystals that had the correct analysis for the penta-amide (XII).

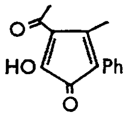
Diels found[1] that ethyl cyanoacetate reacts differently from diethyl malonate with dimethyl acetylenedicarboxylate in the presence of pyridine and acetic acid, to give a yellow compound composed of cyano-ester, acetylene ester, and pyridine (1 : 2 : 1), which very easily eliminates a molecule of methanol, to give a deep blue dye. Analogous products are formed from malononitrile. The original formulations[1] of these compounds are irrelevant; our initial tentative assignments (in 1955) were structure (XIII) for the yellow compound and (XIV) for the blue. Others[5,10] independently reached the same conclusions, which are compatible with the spectroscopic and chemical properties of the compounds. The chromophore of the anion (XIV) is analogous to that of the 2-hydroxycyclopentadienone anion. For example[11] the yellow 2-hydroxy-3,5-diphenylcyclopent-2-ene-1,4-dione gives a yellow mono- but a blue di-anion. The hydroxycyclopentadienone[12] [(XV) or tautomer] and, even more to the point, the triester[13] [(XVI) or tautomer] both form red crystals that yield blue salts even with such weak bases as piperidine or sodium carbonate[14]



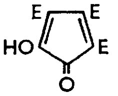
(XIII)



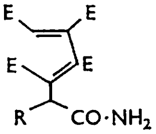
(XIV)



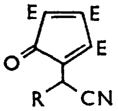
(XV)



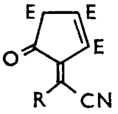
(XVI)



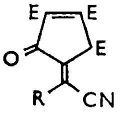
(XVII)



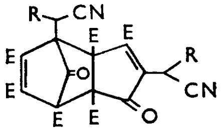
(XVIII)



(XIX)



(XX)



(XXI)

For formulae (XIII) to (XXI) a; R = CO_2Et, b; R = CO_2Me, c; R = CN, d; R = $CO_2{\cdot}CH_2{\cdot}C_6H_4Br$

Treatment of the yellow adduct (for spectra see Experimental section) with formic acid[1] or, much better, with 80% sulphuric acid produced a substance that had lost pyridine and added 1 mole of water. In agreement with

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[8] T. R. Griffiths, K. A. K. Lott, and M. C. R. Symons, *Analyt. Chem.*, 1959, **31**, 1338.

[9] O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, 1960, **25**, 1470; *J. Amer. Chem. Soc.*, 1962, **84**, 3678.

[10] P. Bamfield, A. Crabtree, and A. W. Johnson, *J. Chem. Soc.*, 1965, 4355.

[11] von L. Claisen and Th. Ewan, *Annalen*, 1895, **284**, 245.

[12] S. Ruhemann and R. W. Merriman, *J. Chem. Soc.*, 1905, **87**, 1383; see further C. Grundmann and E. Litten, *Ber.*, 1952, **85**, 261.

[13] S. Ruhemann and A. S. Hemmy, *J. Chem. Soc.*, 1897, **71**, 334.

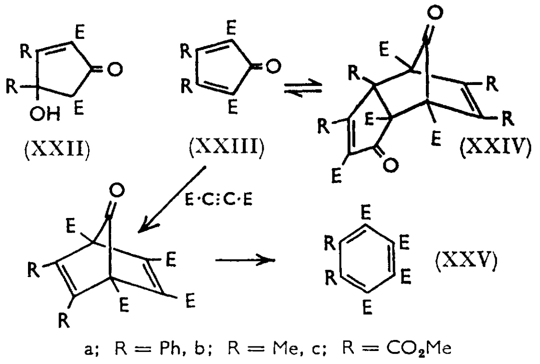
[14] These and other less closely related examples are reviewed by T. A. Geissman and C. F. Koelsch, *J. Org. Chem.*, 1939, **3**, 489.

Johnson *et al.*[10] we formulated[4] this substance as the amide (XVII).

The blue dye (XIVa) also lost pyridine on treatment with formic acid to give a colourless pseudo-acid[1] discussed later. Similar yellow and blue compounds were formed with cyanoacetic and acetylenedicarboxylic ester by β- and γ-picoline (but not α-picoline, 3-bromopyridine or quinoline). The presence of the pyridine only as the protonated cation (XIVa) was confirmed by preparation of salts of the same colour and visible spectrum in which the pyridinium ion was replaced by other cations: the potassium salt was amorphous, but the strontium and silver salts crystallised.

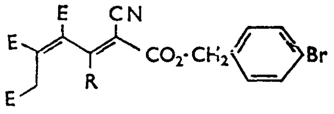
Treatment of the blue dyes (XIVa, b, and c) with formic acid formed colourless, insoluble pseudo-acids,[1] which regenerated the blue salts with bases, or to some extent even when dissolved in water, methanol, or acetonitrile. The insolubility tells against one of the tautomeric structures (XVIII)—(XX), from simple protonation of the anion, and the cyclopentadienone (XVIII) is unlikely because of the lack of colour. The dimeric structure [(XXI) or isomer] from the cyclopentadienone (XVIII), still favoured by Johnson *et al.*,[10] seemed doubtful owing to the lack of a sufficiently high carbonyl stretching frequency. The spectrum showed a broad band with maxima at 1730 and 1755 cm.$^{-1}$.

Some cyclopentadienones were therefore made for comparison by condensing dimethyl acetonedicarboxylate with the appropriate α-diketone in base to give the hydroxycyclopentenones (XXII), followed by dehydration with acid. The orange diphenyl compound (XXIIIa) rapidly dimerised above its melting point. The other two examples, both dimeric (XXIVb and c), decomposed when melted, with loss of carbon monoxide. The presence of some monomer in equilibrium with the dimer at higher temperatures was shown by addition to dimethyl acetylenedicarboxylate in boiling toluene with elimination of carbon monoxide and production of the tetra-esters (XXV). The three authentic dimers all showed the expected high frequency maximum from the bridging carbonyl group [1795 cm.$^{-1}$ in (XXIVa and b) and 1835 cm.$^{-1}$ in (XXIVc)]. The absence of a band in this region above 1755 cm.$^{-1}$ in the pseudo-acids makes structures such as (XXI) most unlikely. Furthermore, none of the pseudo-acids gave any indication of decarbonylation when heated nor of reaction with dimethyl acetylenedicarboxylate under conditions where the authentic dimers (XXIV) reacted.



a; R = Ph, b; R = Me, c; R = CO$_2$Me

p-Bromobenzyl cyanoacetate led to similar yellow (XIIId) and blue compounds (XIVd). When the blue pyridinium salt (XIVd) was recrystallised from ethanol the blue needles were accompanied by a colourless crystalline product, the analytical composition of which showed that a mole of ethanol had been incorporated and one of pyridine lost. Its spectral properties indicated that it arose from addition of ethanol to the cyclopentadienone carbonyl group (XXVIa); absorptions identified included nitrile (2200 cm.$^{-1}$), ester (1735 cm.$^{-1}$) and a conjugated diene system (weak bands at 1640 and 1600 cm.$^{-1}$; $\lambda_{max.}$ 224 and 250 nm, ε 23,000 and 13,000). Peaks in the ^{1}H n.m.r. spectrum included those due to methyl, ethyl, and *p*-bromobenzyl esters and a singlet from two equivalent protons at τ 5·95, the low field suggesting a methylene group flanked by a double bond and an ester group. Treatment with methanol gave a small amount of the methanol adduct (XXVIb) with similar spectral properties, but reaction then occurred mainly with the benzyl ester group to form substantial quantities of *p*-bromobenzyl alcohol. The diene (XXVIb) is a protonated form of the anion in the pyridinium salt (XIIId) (and corresponds with our original formula[2] for the dimethyl malonate adduct). Accordingly, it, and the ethyl ester (XXVIa), dissolved in pyridine to yield an orange solution that slowly turned blue. The yellow solution formed by the colourless ethyl ester (XXVIa) in methanol and pyridine, when boiled (3 hr.), yielded the crystalline blue dye (XIVd). In this case, therefore, the cyclisation to give the blue dye is reversible.



(XXVI) a; R = CO$_2$Et
b; R = CO$_2$Me

Treatment of the blue *p*-bromobenzyl salt (XIVd) with cold formic acid produced a colourless pseudo-acid, analogous to those from (XIVa, b, and c), but its markedly greater solubility allowed it to be examined better. The molecular weight (in chloroform) showed that it was indeed dimeric. Its ultraviolet ($\lambda_{max.}$ 223, 250, and 319 nm, ε 34000, 11000, and 270) and infrared spectra ($\nu_{max.}$ 2300, 1755, 1720, 1650w., 1600, and 1500 cm.$^{-1}$) resembled those of the other pseudo-acids. Its ^{1}H n.m.r. spectrum in deuteriochloroform had singlets at τ 6·12, 6·19, 6·38, 6·45, and 6·51 (methoxy groups), a singlet at τ 4·79 (benzyl methylene groups) and two doublets with centre at τ 2·62 (aromatic protons). There were also two apparent doublets, at τ 4·70 and 4·23, but the splitting could not have been due to coupling, for the separations were 1·7 and 1·0 c./sec. The substance must be a mixture of at least two isomers, neither of them a dimer of the cyclopentadienone

(XVIII). On treatment with base the blue, monomeric anion was rapidly formed.

EXPERIMENTAL

Unless stated otherwise, ultraviolet spectra are of solutions in 95% ethanol, infrared spectra of Nujol mulls, and ^1H n.m.r. spectra of solutions in deuteriochloroform containing tetramethylsilane. Molecular weights were measured (benzene as solvent) with a thermoelectric osmometer calibrated against known concentrations of benzil.

Reaction between Malonic Esters and Dimethyl Acetylenedicarboxylate.—Octamethyl cyclohepta-1,3-triene-1,2,3,4,5,6,6,7-octacarboxylate (IIIa), m. p. 225—226·5°, made as already described,[1,5] had $\lambda_{max.}$ (methanol) 202 (?) and 286 nm (ε 9090 and 3260), $\nu_{max.}$ 1745, 1730, 1635, and 1620 cm.$^{-1}$ (Found: C, 49·0; H, 4·8; OMe, 44·4. Calc. for $C_{23}H_{26}O_{16}$: C, 49·5; H, 4·7; OMe, 44·4%). The tautomer (IVa), m. p. 186°, was formed (*ca.* 10%) in the absence of solvent.[1]

The mixed ethyl heptamethyl ester (IIIb), synthesised in the same way from methyl ethyl malonate (prepared from ethyl hydrogen malonate and diazomethane), had m. p. 200° and similar absorption spectra to the octamethyl ester (IIIa) (Found: C, 50·1; H, 5·0%; *M*, 572. Calc. for $C_{24}H_{28}O_{16}$: C, 50·35; H, 4·9%; *M*, 572). The diethyl hexamethyl ester (IIIc) had m. p. 156—158° (Found: C, 51·15; H, 5·3; O, 43·15. Calc. for $C_{25}H_{30}O_{16}$: C, 51·2; H, 5·2; O, 43·6%).

1,2,3,4,5-*Pentamethoxycarbonylcyclopentadiene* [(Va) *or* (X)].—The ester (IIIa) (16 g.), anhydrous potassium acetate (45 g.), and water (45 ml.) were boiled together under reflux for 2 hr. to give a clear solution. The mixture was cooled to 15° and the crystallised salt was filtered off, pressed well down, and drained but not washed. The crude salt was dissolved in warm water (18 ml.) and conc. hydrochloric acid (*ca.* 3 ml.) was added until the yellow colour had disappeared. The mixture was cooled to room temperature and more hydrochloric acid (7 ml.) was added. The solution was warmed to 60°. The acid [(Va) or (X)] (8·0 g.) separated, was filtered off from the cooled solutions, and dried *in vacuo*. It gave prisms, m. p. 150—151° (from benzene–light petroleum) (Found: C, 50·6; H, 4·55; O, 44·7; OMe, 43·25. Calc. for $C_{15}H_{16}O_{10}$: C, 50·55; H, 4·5; O, 44·9; OMe, 43·5%). Alternatively, the ester [(IIIa, b, or c) or (IV)] and dry potassium acetate were boiled in dry dioxan for 1 or 2 hr. The solid was filtered off, dissolved in water, and acidified as before. All four esters gave the same salt (VIa) and acid [(IX) or (X)].

Potassium Salt (VIa).—The crude *salt* obtained as already described gave solvated fluffy needles from acetonitrile–benzene. A sample was melted and the resultant glass was powdered and dried at 100° to constant weight, m. p. 220—222° (Found: C, 46·3; H, 3·7; OMe, 39·35. $C_{15}H_{15}KO_{10}$ requires C, 45·7; H, 3·8; OMe, 39·35%). The salt is best recrystallised from ethanol.

Tetra-n-butylammonium Salt (VIb).—The adduct (IIIa) (2 g.), potassium acetate (3·5 g.), and water (10 ml.) were boiled together for 2 hr.; the mixture was then diluted with water (10 ml.). A solution of tetra-n-butylammonium iodide (2 g.) in methanol (10 ml.) was added, and the new *salt* of the cyclopentadienide anion (1·5 g.) separated from the cooled solution. It gave needles, m. p. 244° (from aqueous methanol) (Found: C, 62·3; H, 8·4; O, 26·6. $C_{31}H_{51}NO_{10}$ requires C, 62·3; H, 8·5; O, 26·8%).

Ferrous Salt (VIc).—A mixture of iron powder (3 g.), the cyclopentadiene (1 g.), and water (10 ml.) was heated on the steam-bath for 12 hr. in the absence of air. The mixture was filtered and evaporated to dryness, and the yellow powder was ground several times with boiling acetone (yield 1·0 g.). An aqueous solution had the ultraviolet spectrum of the cyclopentadienide anion and responded to tests for ferrous iron.

1,2,3,4,5-*Pentamethoxycarbonyl*-1-*methylcyclopentadiene* (Vb).—The crude 1,2,3,4,5-pentamethoxycarbonylcyclopentadiene (10 g.) was dissolved in benzene (150 ml.). The solution was filtered (charcoal), boiled to remove water, and cooled to 10°. A diazomethane solution [from *N*-methyl-*N*-nitrosourea (10 g.) and 40% NaOH (35 ml.) in benzene (125 ml.)] was slowly added at <10°. After 5 min aqueous acetic acid was added and the separated benzene layer was washed free of acid ($NaHCO_3$) and dried. The solution was evaporated to dryness to give the *product* (Vb) (7 g.) as plates, m. p. 102—103° (from dipropyl ether) (Found: C, 52·1; H, 4·75; O, 43·0. $C_{16}H_{18}O_{10}$ requires C, 51·9; H, 4·9; O, 43·25%), $\nu_{max.}$ 1750, 1725, 1640, and 1590 cm.$^{-1}$.

1,2,3,4-*Tetramethoxycarbonyl*-5-*methylcyclopentadiene* [(IX) *or tautomer*].—The methylcyclopentadiene (Vb) (1·0 g.) was dissolved in a sodium methoxide solution [from sodium (0·3 g.) in methanol (12 ml.)] and heated under reflux for 3 hr. The solvent was evaporated under reduced pressure, the residue was dissolved in ice–water (10 ml.), and hydrochloric acid was added dropwise until no further solid separated. The product (0·66 g.) was collected and dried *in vacuo*; it was unstable to heat and was crystallised as follows. The compound (0·66 g.) was dissolved in boiling di-isopropyl ether (20 ml.) containing sodium hydrogen carbonate (1 g.) in suspension, quickly filtered into cold light petroleum (b. p. 60—80°) (60 ml.), and rapidly cooled. The *methylcyclopentadiene* (IX) separated as fluffy needles, m. p. 86° (Found: C, 53·85; H, 5·25; O, 42·6. $C_{14}H_{16}O_8$ requires C, 53·85; H, 5·15; O, 43·2%), $\nu_{max.}$ 1740, 1710, 1600 cm.$^{-1}$ (vs).

Charge-transfer Complexes of 1,2,3,4,5-*Pentamethoxycarbonylcyclopentadiene*.—(a) *With maleic anhydride*. The cyclopentadiene [(Va) or (X)] (2 g.) and maleic anhydride (1 g.) were dissolved in boiling benzene (3 ml.). The solution was set aside for 60 hr., then decanted from unchanged cyclopentadiene, and diluted with light petroleum (2·0 ml.). A product crystallised, m. p. 85° (Diels [1] quotes 87°), with ultraviolet absorption in various solvents identical with that of the starting material.

(b) *With tetracyanoethylene*. The cyclopentadiene [(Va) or (X)] (350 mg.) and tetracyanoethylene (150 mg.) were dissolved in boiling benzene and the solution was evaporated to small volume. The *product* separated from the cooled solution gave golden fluffy needles which turned black in contact with metals, m. p. 178—179° (from benzene–petroleum) (Found: C, 52·1; H, 3·6; N, 11·6. $C_{19}H_{11}N_4O_{10}$ requires C, 49·6; H, 3·5; N, 12·1%). Ultraviolet absorption in hydroxylic solvents was the same as that of the cyclopentadiene itself.

1-*Bromo*-1,2,3,4,5-*pentamethoxycarbonylcyclopentadiene* (Ve).—The unsubstituted penta-ester [(Va) or (X)] (2·1 g.) was dissolved in water (30 ml.) containing potassium carbonate (0·45 g., anhydrous). A solution of bromine (36 ml.) [from bromine (1·0 ml.) and potassium bromide solution (90 ml.)] was added dropwise. The *product* separated as an oil, crystallised (2·5 g.), and gave fine needles,

m. p. 98—100° (from aqueous methanol) (Found: C, 41·25; H, 3·8; Br, 18·6. $C_{15}H_{15}BrO_{10}$ requires C, 41·4; H, 3·5; Br, 18·4%), ultraviolet absorption (methanol) identical with that of the starting material.

1-*Chloro*-1,2,3,4,5-*pentamethoxycarbonylcyclopentadiene* (Vd).—Chlorine was bubbled into a solution of the penta-ester [(Va) or (X)] (0·35 g.) in water (10 ml.) containing potassium carbonate (0·07 g.). The *chloro-derivative* immediately separated and formed needles, m. p. 83—85° (from aqueous methanol) (Found: C, 46·2; H, 3·85; Cl, 9·4. $C_{15}H_{15}ClO_{10}$ requires C, 46·1; H, 3·85; Cl, 9·1%).

Reactions of 1-*Bromo*-1,2,3,4,5-*pentamethoxycarbonylcyclopentadiene* (Ve).— (a) *With potassium iodide.* The bromo-compound (0·4 g.) was added to a solution of potassium iodide (3·2 g., 2 equiv.) in water (10 ml.) at 50°. There was an immediate precipitation of iodine and the solution was filtered, then warmed on the steam-bath while a stream of air was blown through it. The last traces of iodine were thus removed and conc. hydrochloric acid (8 ml.) was added. The acid [(Va) or (X)] separated as prisms (0·28 g.; 95%), m. p. 150—151°.

(b) *With quinolin-8-ol.* Oxine (0·3 g.) was dissolved in a solution of potassium hydroxide (1·3 g.) in methanol (10 ml.) and the bromo-pentaester (Ve) (0·8 g.) was added slowly with stirring. The solution was diluted with water (35 ml.) and the separated 5,7-dibromo-derivative was filtered off and washed; it gave pale lemon needles, m. p. 195° (from light petroleum) (b. p. 80—100°)].

1,2,3,4-*Tetramethoxycarbonyl*-5-*phenylazocyclopentadiene* (XI).—The pentamethoxycarbonylcyclopentadiene [(Va) or (X)] (1·0 g.) was dissolved in water (150 ml.) containing conc. hydrochloric acid (5 ml.). A solution of benzenediazonium chloride [from aniline (0·75 g.) in water (50 ml.) and conc. hydrochloric acid (5 ml.) with sodium nitrite (0·5 g.)] was added and the solution was left for several weeks at 5°. The dye obtained was filtered off and recrystallised from propan-2-ol. Further recrystallisation from benzene–petroleum showed the presence of a colourless material (see next experiment). The *dye* separated as deep red prismatic needles, m. p. 185° (Found: C, 56·85; H, 4·45; N, 7·3. $C_{19}H_{18}N_2O_8$ requires C, 56·75; H, 4·5; N, 7·0%), $\lambda_{max.}$ 284 and 408 nm (ε 19,500 and 14,620), unchanged when sodium hydroxide was added.

1,2,3,4,5-*Pentamethoxycarbonyl*-1-*phenylcyclopentadiene* (Vc).—The colourless material isolated from the foregoing experiment yielded the *phenyl derivative* (Vc) as plates, m. p. 123—125° (from aqueous methanol) (Found: C, 58·35; H, 4·75; O, 37·1. $C_{21}H_{20}O_{10}$ requires C, 58·35; H, 4·65; O, 37·05%), $\lambda_{max.}$ (methanol) *ca.* 208, 230sh, and 280sh nm (ε 17,600, 9600, and 3100).

1,2,3,4-*Tetramethoxycarbonyl*-5-(*p*-*nitrophenylazo*)*cyclopentadiene.*—The compound was prepared like the unsubstituted derivative, from diazotised *p*-nitroaniline (3 equiv.). The products were recrystallised from benzene. The *dye* was obtained as red needles, m. p. 251° (Found: C, 51·2; H, 3·8; N, 9·4. $C_{19}H_{17}N_3O_{10}$ requires C, 51·0; H, 3·8; N, 9·4%), $\lambda_{max.}$ 244, 278, and 465 nm (ε 15,200, 12,250, and 23,450), shifted to 278 and 488 nm (ε 17,500 and 23,500) in ethanol containing sodium hydroxide.

Potassium 1,2,3,4,5-*Pentacarbamoylcyclopentadienide* (XII).—The potassium salt of the penta-ester (VIa) (3 g.) was dissolved in ammonium hydroxide solution (50 ml.; *d* 0·880) and left at room temperature for 3 months. A product slowly crystallised. It was collected, washed with water, and recrystallised by dissolution in boiling ethylene glycol which was filtered into boiling ethanol, m. p. <300° (Found: C, 37·6; H, 2·85; N, 19·3; OMe, 1·6. $C_{10}H_{10}KN_5O_5$ requires C, 37·5; H, 3·1; N, 21·8; OMe, 0·0%).

Pyridinium 1-*Cyano*-1-*ethoxycarbonyl*-2,3,4,5-*tetramethoxycarbonylpentadienide* (*Diels'* "*Golden Adduct*") (XIIIa).—Ethyl cyanoacetate (4·5 g.) and dimethyl acetylenedicarboxylate (10 g.) in methanol (25 ml.) cooled in ice were treated with a mixture of pyridine and acetic acid (10 ml; 1 : 1) in portions. The adduct separated and was collected after 30 min. and washed with methanol. It yielded golden prisms, m. p. 127° (from methanol) (Found: C, 55·7; H, 5·2; N, 5·6. Calc. for $C_{22}H_{24}N_2O_{10}$: C, 55·5; H, 5·05; N, 5·9%), $\nu_{max.}$ 2170 (low frequency indicates CN conjugated), 1750, 1740, 1730, and 1640 cm.$^{-1}$ and characteristic pyridinium bands, $\lambda_{max.}$ (methanol) 227, 253, and 370 nm (ε 11,400, 9060, and 14,800).

Pyridinium 2-*Cyano*(*ethoxycarbonyl*)*methylene*-3,4,5-*trimethoxycarbonylcyclopentadienolate* (XIVa).—The procedure for (XIIIa) was followed except that the mixture was heated under reflux for 1 hr. after separation of the golden adduct. The excess of solvent was evaporated, hot propan-2-ol (50 ml.) was added, and the mixture was left to crystallise. The product (24 g.) was collected when cold and washed with propan-2-ol; it gave blue–black prisms, m. p. 175° (from aqueous ethanol) (Found: C, 56·85; H, 4·65; N, 6·4; O, 32·1. Calc. for $C_{21}H_{20}N_2O_9$: C, 56·75; H, 4·5; N, 6·3; O, 32·45%), $\nu_{max.}$ 2200, 1735, 1700, 1680, 1640, and 1580—90 cm.$^{-1}$, $\lambda_{max.}$ (acetonitrile) 318 and 610 nm (ε 25,100 and 3170). One mole of methanol (estimated by gas chromatography) was produced when the golden adduct (XIVa) (0·4 g.) in benzene (0·5 ml.) was heated in a sealed tube at 100° for 1 hr.

Pyridinium 2-*Cyano*(*methoxycarbonyl*)*methylene*-3,4,5-*trimethoxycarbonylcyclopentadienolate* (XIVb).—This was prepared in an analogous manner to the blue dye (XIVa) but from methyl cyanoacetate. Surprisingly, the new dye was much more soluble than Diels' product. It gave blue *needles*, m. p. 147—148° (from propan-2-ol) (Found: C, 56·1; H, 4·6; O, 33·1. $C_{20}H_{18}N_2O_9$ requires C, 55·8; H, 4·2; O, 33·5%).

Pyridinium 2-*Dicyanomethylene*-3,4,5-*trimethoxycarbonylcyclopentadienolate* (XIVc).—By the method of Diels [1] the dark blue salt (50%) was obtained, m. p. 201—202° (Found: C, 56·1; H, 4·3; N, 10·7. Calc. for $C_{19}H_{15}N_3O_7$: C, 55·8; H, 4·2; N, 10·6%).

Pseudo-acid from the Blue Dye (XIVa).—The blue dye (XIVa) (2 g.) was dissolved in cold formic acid (4 ml.) and then heated on a steam-bath for 10 min. The colourless product that separated was filtered off and gave prisms of the dimer (1·0 g.), m. p. 218° (decomp.) (from formic acid) (lit.,[1] 219°) (Found: C, 52·2; H, 3·9; O, 38·25. Calc. for $C_{32}H_{30}N_2O_{18}$: C, 52·6; H, 4·1; O, 38·05%), $\nu_{max.}$ 2270, 1755, and 1730 cm.$^{-1}$, (in equilibrium with the blue dye in solution) $\lambda_{max.}$ (methanol) 265, 309, and 325 nm (ε 14,000, 14,000, and 13,000). Alternatively the blue dye (XIVa), just covered with formic acid, was stirred overnight; the product had m. p. 220° (decomp.) (from formic acid) (Found: C, 52·4; H, 4·0%).

Potassium Salt of Blue Dye (XIVa).—The dimer just described (1·8 g.) was suspended in methanol (50 ml.) and a solution of potassium (0·2 g.) in methanol was added dropwise. The solid dissolved with the formation of a blue solution which was evaporated. This solution turned green; the blue colour was restored by the addition of a few drops of acetic acid. The solution was evaporated to dryness and the residue was dissolved in acetone which was evaporated off *in vacuo*. For analysis the *dye* was ground with potassium carbonate and re-extracted with acetone, which was evaporated off to leave a powdered glass (Found: on material dried to constant weight: C, 47·8; H, 3·7; N, 3·65. $C_{16}H_{14}KNO_9$ requires C, 47·55; H, 3·5; N, 3·5%), $\nu_{max.}$ 2210, 1580, and 12 bands 1650—1750 cm.$^{-1}$.

Silver Salt of the Blue Dye (XIVa).—The pyridine salt (XIVa) (5 g.) was dissolved in boiling water (75 ml.) and methanol (70 ml.). Silver nitrate (2·5 g.) in water (10 ml.) was added to the hot solution. The *salt* (4·5 g.) separated on addition of a seed crystal, was collected and dried *in vacuo*, and gave feathery blue-green needles, m. p. 195° (decomp.) (from water) (Found: C, 40·7; H, 3·2; N, 2·9. $C_{16}H_{14}AgNO_9$ requires C, 40·7; H, 3·0; N, 3·0%).

p-*Bromobenzyl Cyanoacetate*.—*p*-Bromobenzyl alcohol (8·7 g.) and cyanoacetic acid (5 g.) were azeotropically refluxed together in dry benzene (250 ml.) with toluene-*p*-sulphonic acid (0·2 g.). The benzene solution was washed successively with sodium hydrogen carbonate solution and water and dried ($MgSO_4$), and the benzene was removed. The crystalline residue was recrystallised from benzene–light petroleum (yield 10 g.).

Pyridinium 2-(p-*Bromobenzyloxycarbonyl)cyanomethylene*-3,4,5-*trimethoxycarbonylcyclopentadienolate* (XIVd).—Pyridine–acetic acid (50 ml.; 1 : 1) was cautiously added to *p*-bromobenzyl cyanoacetate (35 g.) and dimethyl acetylenedicarboxylate (39·5 g.) in ether (200 ml.). The mixture was refluxed overnight; the blue crystalline *precipitate* (65 g.) had m. p. 136—137° (Found: C, 53·3; H, 3·5; Br, 14·0; N, 4·6. $C_{26}H_{21}BrN_2O_9$ requires C, 53·3; H, 3·6; Br, 13·7; N, 4·8%), $\lambda_{max.}$ (methanol) 250, 256, 312·5, and 628 nm, ε 20,300, 21,300, 19,600, 20,800, and 2640.

p-*Bromobenzyl* 2-*Cyano*-3-*ethoxycarboxyl*-4,5,6-*bimethoxycarbonylhexa*-2,4-*dienoate* (XXVIa).—The blue dye (XIVd) (7·7 g.) was refluxed with absolute ethanol (40 ml.) for 3 hr. The alcohol was then removed and the blue, oily, residue was extracted several times with ether. The ethereal extract was reduced in volume and chromatographed on silica gel (300 g.). Elution with ether gave a greenish oil (3·7 g.) which deposited *crystals* from benzene–light petroleum, m. p. 133—135°. Unreacted blue dye (3·7 g.) was also recovered.

Alternatively, the hot alcoholic solution was left to crystallise and crystals of (XXVIa) were separated by hand (Found: C, 50·2; H, 4·0; Br, 13·7; N, 2·5%. *M*, 550. $C_{23}H_{22}BrNO_{10}$ requires C, 50·0; H, 4·0; Br, 14·5; N, 2·5%; *M*, 552), $\nu_{max.}$ 2200, 1735, 1640, and 1600 cm.$^{-1}$, $\lambda_{max.}$ 224 and 250sh nm (ε 23,000 and 13,000).

Methyl Ester (XXVIb).—Treatment of the blue dye (XIVd) (7 g.) with refluxing methanol for 24 hr. gave a yellow oil (3·7 g.), isolated like the ethyl compound. Sublimation of this oil (steam-bath; 15 mm.) gave *p*-bromobenzyl alcohol (2·2 g.).

Small amounts of the *methyl ester* (XXVIb), m. p. 127—129°, were crystallised from the yellow oil with benzene–light petroleum (Found: C, 49·15; H, 3·75; Br, 14·6; N, 2·5. $C_{22}H_{20}BrNO_{10}$ requires C, 49·05; H, 3·7; Br, 14·9; N, 2·6%), $\nu_{max.}$ 2200, 1735, 1645, and 1699 cm.$^{-1}$, $\lambda_{max.}$ 224 and 250sh nm (ε 20,000 and 10,500).

Pseudo-acid from the Blue Dye (XIVd).—Treatment of the blue dye (XIVd) (3·5 g.) with formic acid (10 ml.) at room temperature overnight, gave the colourless *pseudo-acid* (1·6 g.), m. p. 218—220° (decomp.) (Found: C, 49·5; H, 3·0; Br, 15·3; N, 2·8. $C_{42}H_{32}N_2Br_2O_{18}$ requires C, 49·8; H, 3·2; Br, 15·8; N, 2·8%), *M* (in chloroform), 1035 (calc. 1012).

Ethyl 2-*Carbamoyl*-3,4,5,6-*tetramethoxycarbonylhexa*-3,5-*dienoate* (XVIIa).—This was prepared[1] by hydrolysis of the golden adduct (XIIIa) with formic acid, which gave the product, m. p. 146°, in poor yield.

A better yield was obtained by dissolving the golden adduct (XIIIa) (16 g.) in sulphuric acid (20 ml. of concentrate and 4 ml. of water). The solution was left at 17° overnight, poured into ice–water (200 ml.), and set aside for 72 hr. The product (5 g.) was filtered off, washed, and dried. It yielded prisms, m. p. 147—148° (from methanol) (Found: C, 49·2; H, 5·1; O, 42·8. Calc. for $C_{17}H_{21}NO_{11}$: C, 49·15; H, 5·1; O, 42·4%), $\nu_{max.}$ 3425, 3325, 1730, 1710, 1680, 1650, and 1590 cm.$^{-1}$, $\lambda_{max.}$ (methanol) 227 nm (ε 11,200).

Pentamethyl 5-*Carbamoylpenta*-1,3-*diene*-1,2,3,4,5-*pentacarboxylate* (XVIIb).—The *amide* (1·4 g.) was prepared from the corresponding adduct (XIIIb) (4 g.) in 80% sulphuric acid. It separated as prisms from methanol, m. p. 150—152° (Found: C, 47·5; H, 4·85; O, 44·3. $C_{16}H_{19}NO_{11}$ requires: C, 47·9; H, 4·74; O, 43·9%).

4-*Hydroxy*-2,5-*dimethoxycarbonyl*-3,4-*diphenylcyclopent*-2-*enone* (XXIIa).—Benzil (21 g., 0·1 mole) and dimethyl acetonedicarboxylate (17·4 g., 0·1 mole) were dissolved in absolute methyl alcohol (200 ml.) and the solution was cooled in ice. A methanolic solution of sodium hydroxide (4 g. in 20 ml.) was then slowly added with stirring below 10°. The mixture was stirred overnight at room temperature and the yellow sodium salt was filtered off. It was dissolved in hot acetic acid and water was added to give the *product* (XXIIa) in good yield, m. p. 147—148° (Found: C, 69·0; H, 4·9. $C_{21}H_{18}O_6$ requires C, 68·8; H, 4·9%), $\nu_{max.}$ 3600, 3400, 1735, 1705, 1610, and 1240 cm.$^{-1}$, $\lambda_{max.}$ 290 nm (ε 14,000), τ ($CDCl_3$) 6·82, 6·23, and 6·15 (singlets; 1, 6, and 1H, respectively) and 2·67 (multiplet, 10H).

2,5-*Dimethoxycarbonyl*-3,4-*diphenylcyclopentadienone* (XXIIIa).—The alcohol (XXIIa), in benzene containing a trace of toluene-*p*-sulphonic acid, was refluxed azeotropically for 24 hr. to give, after work-up, orange crystals of the *cyclopentadienone* (XXIIIa). Recrystallisation from benzene–light petroleum gave two crystalline forms, one yellow, m. p. 169°, the other orange, m. p. 175°. When melted, both forms partially resolidified and then reclarified with evolution of carbon monoxide (Found: C, 72·7; H, 4·8%; *M*, 390. $C_{21}H_{16}O_5$ requires C, 72·4; H, 4·5%; *M*, 348).

Dimerisation. The orange monomer (XXIIIa) was heated at 200° for 1 hr. The white *dimer* (XXIVa) was broken up and washed with boiling ethyl acetate. It was only sparingly soluble in common organic solvents, m. p. 249—250° (sealed tube) (Found: C, 72·3; H, 4·4. $C_{42}H_{32}O_{10}$ requires C, 72·4; H, 4·5%), $\nu_{max.}$ 1800, 1745, 1700, 1610, and 1250 cm.$^{-1}$.

Tetramethyl 5,6-*Diphenylbenzene*-1,2,3,4-*tetracarboxylate* (XXVa).—Either the monomer or dimer of (XXIIIa) when refluxed in toluene with a twofold excess of dimethyl acetylenedicarboxylate for 5 hr. gave, on addition of light petroleum, white crystals of the tetra-ester (XXVa), m. p. 223—224°, identical with an authentic sample from Dr. K. A. Huebel.[15]

2,5-*Dimethoxycarbonyl*-3,4-*dimethylcyclopentadienone Dimer* (XXIVb).—Dimethyl acetonedicarboxylate (6·96 g.,

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[15] K. A. Huebel, B.P. 889,993.

0·04 mole) and biacetyl (3·44 g., 0·04 mole) were dissolved in absolute methanol (20 ml.). The solution was cooled to 0° and a methanolic solution of potassium hydroxide (2·24 g. in 50 ml.) was slowly added below 5°. The solution was kept at 0° for 36 hr. before the yellow *potassium salt* (7 g.) was filtered off and recrystallised from ethanol (Found: C, 46·6; H, 4·4. $C_{11}H_{13}KO_6$ requires C, 47·1; H, 4·6%). It was dissolved in water (50 ml.) and the pH of the solution was adjusted to 1 with 4N-sulphuric acid. The turbid solution was continuously extracted with ether for 24 hr. The ethereal extract was washed with water (3 × 50 ml.) and dried ($MgSO_4$); the solvent was removed to leave a pale yellow oil (XXIIb), $\nu_{max.}$ 3500, 1740, 1715, and 1628 cm.$^{-1}$.

The oil was dissolved in dry benzene and refluxed azeotropically in the presence of toluene-*p*-sulphonic acid for 24 hr. The benzene solution was washed with water (3 × 50 ml.) and dried ($MgSO_4$), and the benzene was removed to leave a pale yellow oil which slowly crystallised. It gave the white *dimer* (XXIVb), m. p. *ca.* 155° (with decarbonylation) (from benzene–light petroleum) (Found: C, 58·85; H, 5·3%; *M*, 460. $C_{22}H_{24}O_{10}$ requires C, 58·9; H, 5·35%; *M*, 448), $\nu_{max.}$ 1795, 1730, 1705, and 1620 cm.$^{-1}$.

Tetramethyl 5,6-*Dimethylbenzene*-1,2,3,4-*tetracarboxylate*.—The dimer (XXIVb) (80 mg.) was refluxed overnight with dimethyl acetylenedicarboxylate (130 mg.) in toluene (3 ml.). The residue after removal of the toluene gave white *crystals*, m. p. 142—144° (from benzene–light petroleum) (Found: C, 56·95; H, 5·3%; *M*, 340. $C_{16}H_{18}O_8$ requires C, 56·8; H, 5·3%; *M*, 338).

Dimethyl Dioxosuccinate.—This compound was prepared by the method of Anschutz and Parlato.[16] The last traces of methanol and hydrochloric acid were evaporated off under high vacuum (0·1 mm.) for several days in order to avoid extensive decomposition of the ester when distilled. The ester had b. p. 105—110°/15 mm., and rapidly hydrates in air.

Tetramethoxycarbonylcyclopentadienone Dimer (XXIVc).—As for the preparation of (XXIVb), equimolar quantities of dimethyl dioxosuccinate and dimethyl acetonedicarboxylate were condensed together in methanolic potassium hydroxide solution. The yellow potassium salt obtained was treated with dilute sulphuric acid to liberate (XXIIc) which was azeotropically refluxed in benzene to dehydrate it. The yellow oil isolated from the benzene solution crystallised after several weeks, and gave white *crystals*, m. p. 182—183° (from benzene) (Found: C, 49·8; H, 3·7%; *M*, 635. $C_{26}H_{24}O_{18}$ requires C, 50·0; H, 3·8%; *M*, 624), $\nu_{max.}$ 1835, 1755, 1730, 1650, and 1610 cm.$^{-1}$, n.m.r. singlets (60 Mc./sec.) ($CDCl_3$) at 232, 231, 230, 224·5, and 223 c./sec.

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