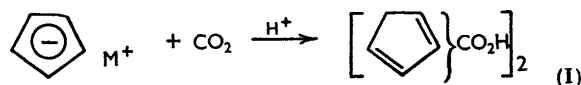


350. Cyclopentadienecarboxylic Acid. The Structure of the Monomer and the Dimers.

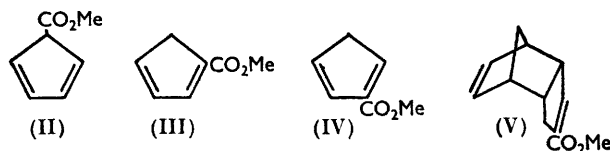
By DAVID PETERS.

Spectroscopic evidence suggests that Thiele's dimer^{1a} of cyclopentadiene-carboxylic acid has a structure in which each carboxyl group is conjugated with a double bond. An isomeric dimer with one conjugated and one unconjugated carboxyl group has been isolated. The spectroscopic data support the chemical evidence² that methyl cyclopentadienecarboxylate exists exclusively or very largely as the 1:3-diene. It is suggested that a reversible prototropic shift occurs in the dimerisation and depolymerisation.

SIMPLE derivatives of cyclopentadiene are attractive as intermediates for the synthesis of non-alternant hydrocarbons containing five-membered rings, an approach used by Hafner³ in his azulene synthesis. A number of such derivatives is already known^{1,4} and of these, the most promising for further synthetic work is the carboxylic acid (I) or its esters, first prepared by Thiele.^{1a} The free acid is readily obtained by carboxylating

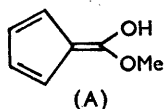


the potassium,^{1a,5} sodium,⁶ or Grignard⁴ derivative of the cyclopentadienyl anion ($M = \text{K}$, Na , or MgX). The point of attachment of the carboxyl group is one of the subjects of this paper. The carboxylic acid is not isolated as such but as the dimer, formed by Diels-Alder dimerisation analogous to that which cyclopentadiene itself undergoes. The dimethyl ester of the dimeric acid is easily obtained by the conventional acid-catalysed esterification: an alternative preparation is described in the following paper.



It is known that the dimeric ester, like cyclopentadiene itself, may be depolymerised thermally to the monomeric ester and it has now been shown that this monomer can be stored as a solid at -70° or in dilute solution in organic solvents at room temperature, for several hours. Chemical evidence for the structure of this monomer has been presented by Alder *et al.*,² and spectroscopic evidence is now provided which supports their findings. Spectroscopic evidence for the structure of the dimer has also been obtained and these results suggest that the relation between the monomer and the dimer is not simple.

Structure of the Monomeric Ester.—That the monomer is the ester of a cyclopentadiene-carboxylic acid is probable from its preparation and this has been confirmed by its hydrogenation to methylcyclopentanecarboxylate. The ultraviolet spectra



of the monomer and the dimer confirm that polymerisation and depolymerisation do occur. As Alder and Holtzrichter point out,⁷ there are three possibilities (II—IV) for the monomer and it must also be established that it is not a mixture. Alder *et al.*² treated this monomer with cyclopentadiene and obtained compound (V), suggesting that the monomer is (III). The ultraviolet spectrum of the monomer provides further evidence for this structure (Fig. 1).

¹ Thiele, *Ber.*, (a) 1901, **34**, 68; (b) 1900, **33**, 666.

² Alder, Flock, Hausweiler, and Reeber, *Chem. Ber.*, 1954, **87**, 1752.

³ Hafner, *Annalen*, 1957, **606**, 79.

⁴ Courtot, *Ann. Chim. (France)*, 1915, **4**, 75.

⁵ Süss, *Annalen*, 1944, **556**, 85.

⁶ Ziegler, Kuhlhorn, and Hafner, *Chem. Ber.*, 1956, **89**, 434.

⁷ Alder and Holtzrichter, *Annalen*, 1936, **524**, 147.

The single smooth peak at $274\text{ m}\mu$ * suggests that only one compound is present: the bathochromic shift of $36\text{ m}\mu$ from the peak of cyclopentadiene itself cannot be reconciled with structure (II) since this should show little or no shift. The examples in the Table show that a bathochromic shift of $27\text{--}33\text{ m}\mu$ is usual for a carboxyl group in the 1-position of the butadienyl system, so structure (III) is acceptable. To exclude structure (IV) is more difficult, since only one example (*H* in the Table) is available with the carboxyl group in the 2-position. This case gives a bathochromic shift of 3 to $8\text{ m}\mu$ and it can be predicted ⁹

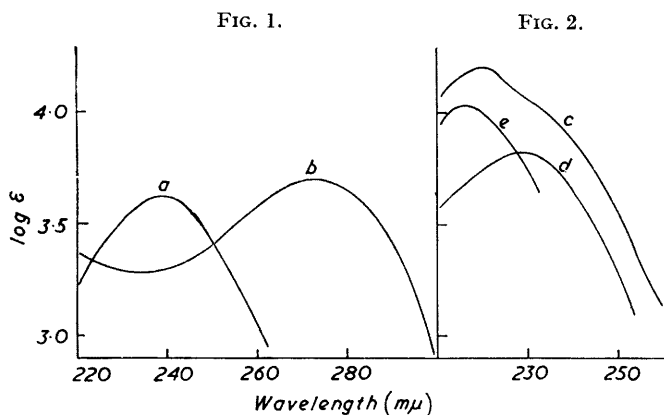


FIG. 1. Absorption spectra of (a) cyclopentadiene and (b) methyl cyclopenta-1,3-dienecarboxylate.

FIG. 2. Adsorption spectra of: (c) Thiele's ester (VII) and acid; (d) the dihydro-derivative (IX), the second isomer (X), the compound (V) and its dihydro-derivative (the spectra of these compounds are essentially the same: exact values for λ and ϵ are in the Experimental section); and (e) resolved peak in Thiele's ester (from curve c and curve d).

on theoretical grounds that the bathochromic shifts of simple substituents in the 1- and the 2-position of the butadienyl system are in the ratio $3 : 1$,† so that the 2-carboxyl substituent should have a bathochromic shift of $5\text{--}10\text{ m}\mu$.

Compound	$\lambda_{\text{max.}}$ (mμ) (solvent)	ϵ	Shift (mμ)	Ref.
(A) $\text{Me}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}_2$	223 (EtOH)	23,000	—	a
(B) $\text{Me}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$	254 (EtOH)	26,000	31	b
(C) Cyclohexa-1,3-diene	256 (C_6H_{14})	8000	—	c
(D) 6-Methylcyclohexa-1,3-dienecarboxylic acid	283	—	27	d
(E) 4-Methylcyclohexa-4,6-diene-1,2-dicarboxylic acid ...	296 (EtOH)	8750	32 *	e
(F) 2,6,6-Trimethylcyclohexa-1,3-dienecarboxylic acid ...	291	—	32 †	d
(G) Cyclohexa-1,3-diene-1,4-dicarboxylic acid	309 (EtOH)	27,300	27 ‡	f
(H) 5-Methylcyclohexa-1,3-diene-1,3,5-tricarboxylic acid	291 (EtOH)	3080	30; 5 ¶	g

* Assumptions: the 1-methyl group contributes $7\text{ m}\mu$; † the 2-methyl group contributes $3\text{ m}\mu$; ‡ the shifts are additive; ¶ the 1-carboxyl group contributes $30\text{ m}\mu$, then the 2-carboxyl group contributes $5\text{ m}\mu$.

References: (a) Booker, Evans, and Gillam, *J.*, 1940, 1453. (b) Allan, Jones, and Whiting, *J.*, 1955, 1865. (c) Henri and Pickett, *J. Chem. Phys.*, 1939, 7, 439. (d) Wendt, *Ber.*, 1941, 74B, 1242. (e) Hennion, Sheehan, and Maloney, *J. Amer. Chem. Soc.*, 1950, 72, 3545. (f) Burnell and Taylor, *J.*, 1954, 3637. (g) Prepared as described by Woolf and Heip, *Annalen*, 1899, 305, 135.

Further confirmation of the structure of the monomeric ester was obtained from the spectrum of the maleic anhydride adduct. The adduct previously reported ^{2,11} was

* The substance is transparent in the $350\text{--}400\text{ m}\mu$ region where simple fulvenes have a band of moderate intensity (ϵ 300).⁸ This fact excludes the fulvenoid structure (A).

† This ratio is correct for the methyl derivatives (7 and $3\text{ m}\mu$ respectively).¹⁰

⁸ Bergmann, "Progress in Organic Chemistry," Vol. III, p. 103, Butterworths Scientific Publications, London, 1955.

⁹ Longuet-Higgins and Sowden, *J.*, 1952, 1404; Coulson, *Proc. Phys. Soc.*, 1952, 65, A, 933; Peters, *J.*, 1957, 646, 1993.

¹⁰ Booker, Evans, and Gillam, *J.*, 1940, 1453.

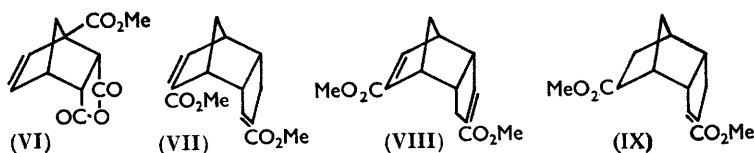
¹¹ Alder and Stein, *Annalen*, 1934, 514, 1.

precipitated in 40% yield from equimolar quantities in ether at room temperature. Examination of the mother-liquors for a second isomer gave only the dimeric ester in some 45% yield, showing that reconversion into the dimer competes with reaction with maleic anhydride. The spectrum of the adduct shows only ethylenic and carboxyl adsorption in the 220 $m\mu$ region, so the adduct is (VI), rather than the isomer from (II) or (IV).

Both the chemical and the spectroscopic evidence indicate that the monomer is methyl cyclopenta-1,3-dienecarboxylate (III).

Structure of the Dimeric Ester.—If structure (III) is accepted for the monomer, several reasonable structures can be written for the dimer. None of these is in agreement with the structure suggested by the following evidence.

The ultraviolet spectrum of the dimeric acid and ester (Fig. 2) shows intense adsorption in the 220 $m\mu$ region, an indication¹² that one or both of the carboxyl groups are conjugated with a double bond. In addition, there is a point of inflection in the 225—230 $m\mu$ region, which suggests that there are two chromophores which have similar but not identical adsorptions: if so, both carboxyl groups are conjugated with double bonds, giving a structure such as (VII) or (VIII). Day¹³ reached the same conclusion. It was confirmed by catalytic hydrogenation to the known dihydro-compound, to be written as (IX) or its isomer from (VIII) since the double bond in the bicycloheptene ring is hydrogenated preferentially. The spectrum of this compound (Fig. 2, λ_{max} , 228 $m\mu$) shows that reduction has destroyed one, but not both, of the chromophores. If the second peak is resolved out of the spectrum of the dimeric ester, a single peak at 216 $m\mu$ remains. The tetrahydro-derivative shows only the carboxyl adsorption. We infer that the 216 $m\mu$ peak is due to the $\alpha\beta$ -unsaturated carboxyl group in the bicycloheptene system, while the peak of lower intensity, at 228 $m\mu$, is due to the $\alpha\beta$ -unsaturated carboxyl group in the cyclopentene ring. Confirmation is provided by the spectrum of compound (V) and its dihydro-derivative, which show only the 228 $m\mu$ peak.



Additional evidence was obtained from oxidation of the dimeric ester with perbenzoic acid. It is known¹⁴ that both double bonds in di(cyclopentadiene) are epoxidised at the same rate: treatment of the dimeric ester with two equivalents of perbenzoic acid led to very slow oxidation of *both* double bonds. It is known¹⁵ that $\alpha\beta$ -unsaturated carboxyl groups are oxidised relatively slowly, so we conclude again that both double bonds carry carboxyl groups.

It is clear that if structures (III) and (VII) are accepted, the depolymerisation and polymerisation are not simple reactions. It has now been shown that the former is straightforward, the monomeric ester being obtained in some 90% yield, but that the latter reaction is complex. The dimeric ester is contaminated with an oil, and chromatography gave a small quantity of a second dimer, whose ultraviolet spectrum (Fig. 2) shows that only the carboxyl group in the cyclopentene ring is conjugated with a double bond. This isomer has formula (X), the dimer which is readily obtained from two molecules of (III). Weise¹⁶ isolated an *exo*-isomer of the dimer of cyclopentadienecarboxylic acid which is not identical with the present isomer. The spectrum of the original oil shows that some 20% of this material is formed in the dimerisation.

¹² Nielsen, *J. Org. Chem.*, 1957, **22**, 1539; Jones, Mansfield, and Whiting, *J.*, 1956, 4073.

¹³ Day, *Diss. Abs.*, 1958, **19**, 39.

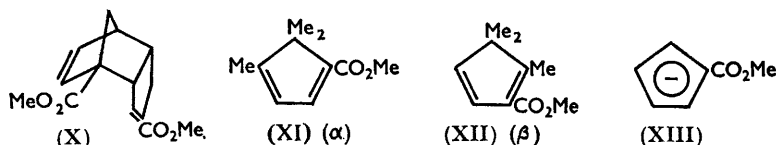
¹⁴ Alder and Stein, *Annalen*, 1931, **485**, 223.

¹⁵ Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692.

¹⁶ Weise, U.S.P., 2,781,395.

It is now clear that a hydrogen shift occurs in the dimerisation and in the depolymerisation. A possible explanation is that (III) and (IV) are in reversible thermodynamic equilibrium. Isomer (III) would be expected to predominate under normal conditions since the π -electron energy of the straight-chain system should be greater than that of the cross-conjugated system. As a diene in the Diels-Alder reaction, however, isomer (IV) should be more reactive since conjugation is preserved in the product and presumably in the transition state: Braude and Evans¹⁷ have shown that butadienyl systems with 2-carboxyl groups are very good dienes in the Diels-Alder reaction. The effect of this situation is to cause most, but not all, of the dimerisation to occur with one molecule each of (III) and (IV) to give the dimer (VII).

The postulated rearrangement has a close precedent in the α - and β -camphylic acids (XI, XII),¹⁸ which are interconvertible,¹⁹ with the α as the more stable, and it is tempting to postulate that the driving force for the rearrangement is provided by the partial development of the stable cyclopentadienyl anion in the transition state. In other words, the anion (XIII) is a major contributor to the valence-bond wave function of the transition state.



One difficulty remains. Maleic anhydride reacts with the monomeric ester to give a compound derived from (III), not from (IV). Our supposition that equilibration of (III) and (IV) leads to diene reaction through the latter form is only partly true since some dimer from two molecules of (III) is formed and it seems that the rates of several reactions are quite similar, so that detailed kinetic studies would be required before a firm decision could be made.

EXPERIMENTAL

Ultraviolet spectra refer to absolute ethanol solutions in a Hilger Uvispek spectrophotometer. Raney nickel was prepared as described by Paul and Hilly.²⁰

Thiele's Dimeric Acid.—Cyclopentadienylmagnesium bromide (4 moles) in dry ether (2.5 l.) was prepared by refluxing ethylmagnesium bromide (4 moles) with cyclopentadiene (4.2 moles) until evolution of ethane ceased (12 hr.). Dry carbon dioxide was passed into the clear dark solution for 2 hr., after which a thick green oil had separated, leaving a clear yellow ethereal layer. Water, followed by dilute sulphuric acid, was added, the ether layer not reacting and the oil reacting vigorously. Stirring was continued until two clear layers containing a suspended solid were obtained. After filtration, the precipitate was taken up in aqueous ammonia, and after filtration was reprecipitated with acid, to give Thiele's dimeric acid (28%), m. p. 197—199°. Crystallisation from methanol (charcoal) gave material of m. p. 208° (lit.,^{1a} 212°), λ_{max} 220 m μ (log ϵ 4.2). The aqueous layers were extracted with chloroform, and the combined organic layers extracted with sodium carbonate solution. Acidification of the aqueous extracts gave a further 0.2 mole of Thiele's acid contaminated with a brown impurity and 49 g. of a water-insoluble oil. Extraction of the acidified aqueous layers gave a water-soluble yellow acid (17 g.) which evolved carbon dioxide in boiling water, precipitating Thiele's acid.

The acid (60 g.) and concentrated sulphuric acid (50 c.c.) were refluxed in methanol (1 l.) for 12 hr. The acid was neutralised, the solvent evaporated, and water added, to give a white ester which, crystallised from light petroleum (b. p. 60—80°), had m. p. 85° (lit.,^{1a} 85°) (50.5 g.,

¹⁷ Braude and Evans, *J.*, 1956, 3238.

¹⁸ Lewis and Simonsen, *J.*, 1936, 734; 1937, 457.

¹⁹ Alder and Windemuth, *Annalen*, 1939, 543, 28.

²⁰ Paul and Hilly, "Newer Methods of Organic Chemistry," Interscience Publ. Inc., New York, 1948, p. 65.

75%) [Found: C, 67·8; H, 6·9; *M* (Rast), 209, (cryoscopic in H_2O), 241. Calc. for $\text{C}_{14}\text{H}_{16}\text{O}_4$: C, 67·7; H, 6·5; *M*, 248], λ_{max} 220 μ ($\log \epsilon$ 4·2). This compound does not decolorise bromine in carbon tetrachloride, but decolorises potassium permanganate in acetone immediately.

The Monomeric Ester and the Second Dimer.—Thiele's ester (12 g.) was distilled into a receiver at -70° (b. p. $110-120^\circ/14$ mm.), giving crystals (10·9 g.), λ_{max} 274 μ ($\log \epsilon$ 3·71). Cyclopentadiene under the same conditions had λ_{max} 238 μ ($\log \epsilon$ 3·62). On warming to room temperature, the white solid first melted and then resolidified exothermally, to a white wax, in a few minutes. Crystallisation from light petroleum (b. p. $60-80^\circ$) gave Thiele's ester (5·2 g.): the mother-liquors gave an oil (5·0 g.) which was chromatographed on silica gel. Elution with 1% of ether in light petroleum (b. p. $40-60^\circ$) gave the second isomer (0·35 g.), m. p. $103-104^\circ$ [from light petroleum (b. p. $<40^\circ$)] [Found: C, 67·6; H, 6·4%; *M* (Rast), 188, (cryoscopic in benzene), 277], λ_{max} 230 μ ($\log \epsilon$ 3·81).

Hydrogenation of Methyl Cyclopentadienecarboxylate.—Thiele's ester (5·0 g.) was distilled at 10 mm. into a cold receiver, and the distillate (4·4 g.) hydrogenated in ethanol (100 c.c.) over Raney nickel at atmospheric pressure until uptake ceased (1200 c.c.; 2H_2 , 1570 c.c.). Distillation of the product gave methyl cyclopentanecarboxylate (0·9 g.), b. p. $142-146^\circ$. Hydrolysis with refluxing aqueous sodium hydroxide gave cyclopentanecarboxylic acid whose *p*-bromophenacyl ester had m. p. 75° (lit.²¹ m. p. $75-76^\circ$) alone or mixed with a specimen prepared by carboxylating the Grignard derivative from cyclopentyl bromide (Found: C, 53·8; H, 5·1; Br, 24·7. Calc. for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{Br}$: C, 54·0; H, 4·8; Br, 25·7%).

Hydrogenation of Thiele's Ester to the Dihydro- and the Tetrahydro-derivative.—The ester (2·0 g.) was hydrogenated in ethanol with freshly prepared Raney nickel at atmospheric pressure. There was a rapid uptake of hydrogen for 2 hr. (250 c.c.; 1H_2 , 220 c.c.), then the rate fell sharply. Filtration and evaporation gave the *dihydro-ester*, m. p. 88° [from light petroleum (b. p. $60-80^\circ$; charcoal)] (Found: C, 67·2; H, 7·8. $\text{C}_{14}\text{H}_{18}\text{O}_4$ requires C, 67·2; H, 7·25%), λ_{max} 228 μ ($\log \epsilon$ 3·76). The m. p. was depressed on admixture of the compound with Thiele's ester. The dihydro-ester decolorised potassium permanganate in acetone immediately. Hydrogenation for 16 hr. under the same conditions gave the tetrahydro-derivative, m. p. $77-78^\circ$ (Found: C, 66·4; H, 8·1. $\text{C}_{14}\text{H}_{20}\text{O}_4$ requires C, 66·6; H, 8·0%), $\log \epsilon_{220}$ 2·21. This compound also depressed the m. p. of Thiele's ester but a mixture with the dihydro-derivative had m. p. $80-82^\circ$. This compound does not decolorise potassium permanganate in acetone.

Maleic Anhydride Derivative of Methyl Cyclopentadienecarboxylate.—The distilled cyclopentadiene ester (4·4 g.) was taken up in dry ether containing maleic anhydride (3·2 g.). The adduct crystallised from the solution in 2 hr. It (3·1 g., 40%) had m. p. 150° (lit.¹¹ $151-152^\circ$) $\log \epsilon_{220}$ 2·30. The mother-liquors were evaporated to an oil (4·5 g.) which was chromatographed on silica gel. Elution with 15% of ether in light petroleum (b. p. $40-60^\circ$) gave Thiele's ester (0·9 g.) contaminated with an oil (1·0 g.). Elution with pure ether gave maleic acid, m. p. and mixed m. p. $136-137^\circ$ (1·65 g.).

Methyl Tricyclo[5,2,0^{2,6}]deca-3,8-diene- and -3-ene-carboxylate.—These compounds were prepared as described by Alder *et al.*² Compound (V) had λ_{max} 230 μ ($\log \epsilon$ 3·83); the monoene had λ_{max} 230 μ ($\log \epsilon$ 3·82). Compound (V) decolorised bromine in carbon tetrachloride immediately; the monoene did not. Both compounds decolorised potassium permanganate in acetone immediately.

Epoxidation of Thiele's Ester.—Di(cyclopentadiene) (0·0033 mole) and perbenzoic acid (0·0066 mole) in chloroform (10 c.c.) reacted exothermally at 0° . Titration after 30 min. showed that 96% of the oxidant had been consumed. Thiele's ester under the same conditions consumed 20% of the total oxidant in 16 hr.

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²¹ Mitsui and Inagaki, *J. Agric. Chem. Soc. Japan*, 1951, **25**, 63; *Chem. Abs.*, 1953, **47**, 9303 f.