

210. *Simple Derivatives of Cyclopentadiene. Part III.*¹ *The Adducts of Methyl Cyclopentadienecarboxylate and Cyclopentadiene.*

By DAVID PETERS.

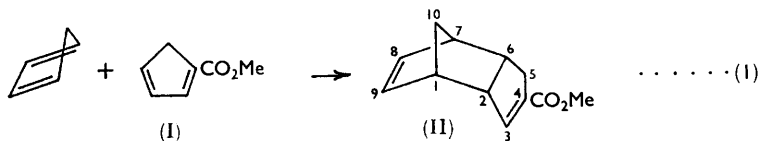
The Diels–Alder reaction between methyl cyclopentadienecarboxylate and cyclopentadiene, known to give 60–70% of compound (II), gives also 30–40% of a second isomer. It is suggested, but not proved, that this has one of four structures (IIIa–d).

IN this and the following paper, some of the reactions of methyl cyclopentadiene-1-carboxylate (I) are reported in greater detail than before. Alder, Flock, Hausweiler, and Reiber² have shown that this ester with cyclopentadiene, in a typical Diels–Alder reaction, gives methyl tricyclo[5,2,1,0^{2,6}]deca-3,8-diene-4-carboxylate (II) in about 70% yield, the ester (I) apparently acting as dienophile. From this and other evidence, they suggested that the substituent on the cyclopentadiene ring is at position 1, as depicted in structure (I), and

¹ Part II, *J.*, 1960, 1832.

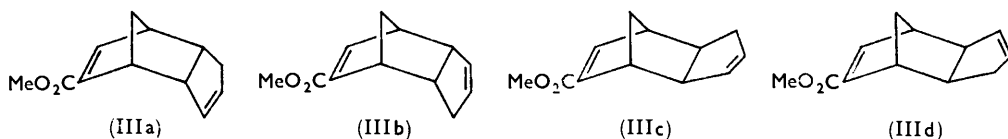
² Alder, Flock, Hausweiler, and Reiber, *Chem. Ber.*, 1954, **87**, 1752.

this has been supported by further evidence.³ It is now shown that the remaining 30% of the product of reaction (1) is an isomer of (II), which, it is suggested, has one of the



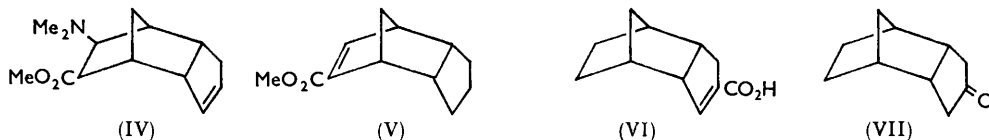
structures (IIIa—d) (a further possibility is discussed but rejected below). It is not yet possible to discriminate between these four structures, so for simplicity only formula (IIIa) is used in this discussion. In the present paper the separation of the two esters and the structure of the new ester are discussed: infrared and ultraviolet spectra are reported in the following paper.

The two esters may be separated in two ways. The first uses the difference in the rate of hydrolysis by hydroxide ion, k for (II) being 0.06 and for (III) 0.005 l. mole⁻¹ min.⁻¹ at 50°. The German workers² apparently used this method but do not mention the second ester. It has been established that the new ester is a genuine product of reaction (I) and is not formed from the ester (II) during the separation. The second method is based on the addition of dimethylamine to the 8,9-double bond of the new ester to give the adduct (IV). Compound (II), in which this double bond carries no activating methoxy-



carbonyl group, is inert to the amine. The amine may be removed again from the adduct to regenerate the doubly unsaturated ester (III) in about 50% yield, simply by boiling water: no elimination occurs in acid solution, so the reaction occurs through the hydroxide. This addition of amine and its removal do not involve rearrangement. This second method is smooth and (in its first stage) complete and has proved useful also with the more complex analogues discussed in the following paper.

The structure (III) has not been established beyond doubt but is supported by the following evidence: (a) The dihydro-derivative (V), in which the 3,4-double bond has been saturated, forms a phenyl azide adduct. The dimethylamine adduct (IV) does not form a phenyl azide adduct. These two facts confirm the expectation that the amine adds to the reactive 8,9- and not to the 3,4-double bond. (b) Dimethylamine does not add to an unsubstituted 8,9-double bond, nor to the 3,4-double bond even when this carries a methoxy-carbonyl group as in (II). It is a reasonable assumption, then, that addition of dimethylamine is diagnostic of an activated 8,9-double bond. (c) The ultraviolet spectra

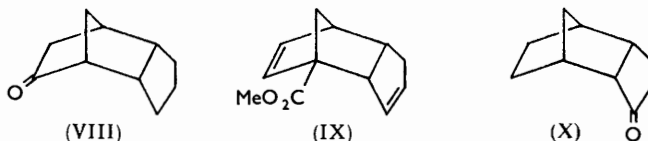


of compounds (III) and (V) are very similar, with intense maxima at 232 and 236 $m\mu$ respectively. The responsible chromophore, also present in compound (II), is often assumed to be $\alpha\beta$ -unsaturated carboxyl group (cf. following paper). Its removal by addition of dimethylamine, as in compounds (IV) and the dimethylamine adduct of (V), removes this maximum. (d) The infrared spectra of compounds (III) and (V) include a

³ Peters, *J.*, 1959, 1761.

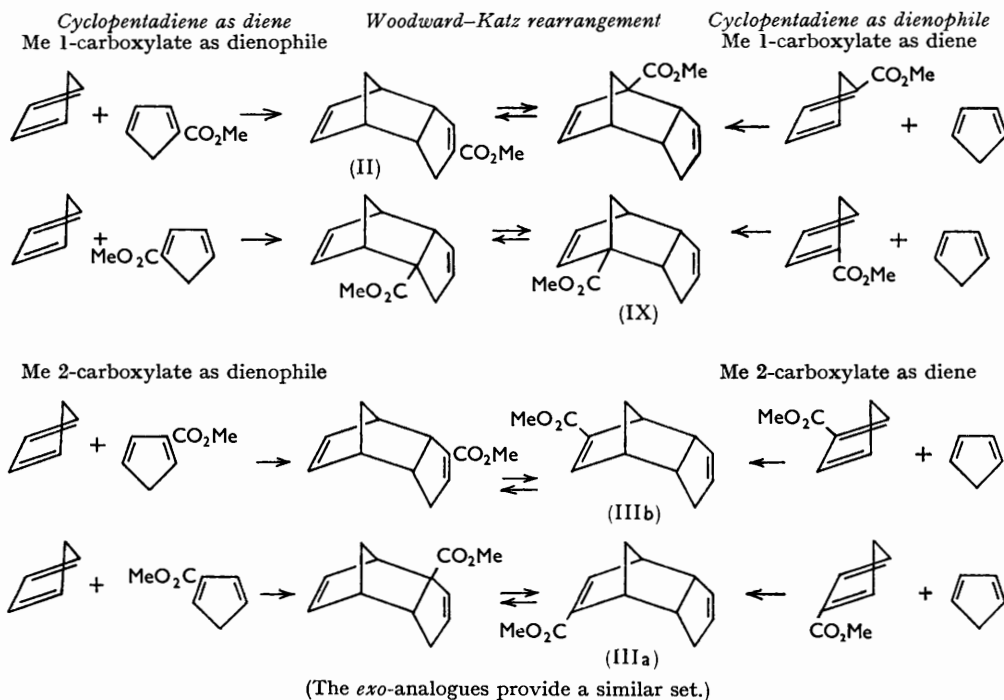
strong band at 9.2μ that seems to belong to the $\alpha\beta$ -unsaturated methoxycarbonyl group (cf. following paper). When the double bond of compound (V) is removed by hydrogenation, or by addition of dimethylamine, this band moves to $9.6\text{--}9.8 \mu$. The infrared spectra of compounds (IV) and (V) in the $13\text{--}15 \mu$ region are also consistent with structure (III) for the new ester.

This evidence, while indicative, is not conclusive, but repeated attempts to confirm it by degradation failed. The German workers² degraded the acid (VI) to ketone (VII) through the azide and isocyanate. We have confirmed and improved this degradation but, despite this experience, attempts to degrade compound (V) to the known ketone (VIII) failed, apparently at or after the rearrangement of the azide stage. An alternative proof by oxidation of the double bond of compound (V) failed when this was found to give complex mixtures of acids.



Structure (IX) (or one of its three obvious variants) has advantages over structure (III) in that it accounts for the formation (see below) of the new ester from (I), for the failure of the Curtius degradation, and for the relatively slow hydrolysis of the ester: it is, however, considered to be excluded, at least temporarily, by the evidence that the ester group is attached to a double bond.

Acceptance of structure (III) creates the problem of how it is formed from the ester (I).



The problem would not arise if methyl cyclopentadienecarboxylate were a mixture of 1- and 2-isomers, but the evidence against this³ still seems convincing and we must assume that it is a single compound, the 1-isomer. The annexed charts show all the possible

Diels–Alder reactions between cyclopentadiene and methyl cyclopentadiene-1- and -2-carboxylate, as well as the rearrangements by the Woodward–Katz mechanism.⁴ They show that compound (III) cannot be formed from the 1-ester: only if a hydrogen atom shifts at some stage can structure (III) result. This shift can, in principle, occur before or during the Diels–Alder reaction.

Depolymerisation of compounds (II) and (III) has been examined: it follows the expected pattern. Compound (II) behaves very much like cyclopentadiene, in that it distils largely unchanged from a bath at 180°/100 mm. Evidently the methoxycarbonyl group on the 3,4-double bond has little or no effect on the rate of depolymerisation, as is to be expected since it is remote from the reaction centre. Compound (III), however, depolymerises almost completely under these conditions and methyl cyclopentadiene-1-carboxylate is obtained (the cyclopentadiene is lost at the low pressure used); so the ester group on [as in (III) or near as in (IX)] the 8,9-double bond accelerates depolymerisation. This is important in that it is the reason for the earlier successful syntheses of substituted cyclopentadienes.¹ Provided the dimer depolymerises at about 150°, quantitative yields of the monomers can be obtained: if a higher temperature is required, as with compound (II), the monomers repolymerise in the distilling flask and the yield of monomer is lowered.

EXPERIMENTAL

Spectra were recorded on a Hilger Uvispek instrument for solutions in absolute ethanol (unless otherwise specified) and on an Infracord Infrared spectrometer (1 mm. path-length, with solvent compensation) for CS₂ solutions.

Preparation of Esters.—The reaction between methyl cyclopentadiene-1-carboxylate and cyclopentadiene was carried out as described by Alder *et al.*² The mixed product had b. p. 76–86°/0.1 mm. (lit.,² 62–70°/0.05 mm.) (Found: C, 76.1; H, 7.6. Calc. for C₁₂H₁₄O₂: C, 75.8; H, 7.4%). Comparison of the infrared spectrum of this mixture with that of an artificial mixture of the two esters indicated the presence of 35 ± 5% of the new ester.

The mixture (20 g.) was dissolved in dimethylamine (50 ml.) and kept at 0° for 16 hr. The oil which remained after removal of the excess of amine *in vacuo* was taken up in ether, extracted with dilute hydrochloric acid (from 25 ml. of concentrated acid), dried, and distilled, to give ester (II) (13.0 g.), b. p. 76–84°/0.1 mm., m. p. 39–41° (Found: C, 76.5; H, 7.7%), λ_{max} 228 mμ (log ε 3.88), ν_{max} (strong) 9.1, 9.2 (conjugated CO₂R), 13.2, and 13.65 μ. The completeness of the reaction was shown by treating this material again with dimethylamine. The acidic aqueous layers were made alkaline and extracted with ether. Removal of the solvent from the dried extract gave the dimethylamine *adduct* (IV) (6.65 g.) as a colourless oil (Found: C, 71.4; H, 9.1; N, 5.8. C₁₄H₂₁NO₂ requires C, 71.45; H, 9.0; N, 5.95%). The ultraviolet spectrum of this compound showed only weak absorption in the 220 mμ region and the infrared spectrum had strong bands at 9.5, 9.6, and 9.7 (unconjugated CO₂Me) and at 13.5 and 14.4 μ.

The amine adduct (6.6 g.) was refluxed with water (50 ml.) for 15 min., then cooled, acidified, and extracted with ether. Removal of the solvent from the dry extract gave the new *ester* (3.1 g.), b. p. 60–62°/0.1 mm., m. p. 30–33° (Found: C, 76.1; H, 7.4%), λ_{max} 232 mμ (log ε 3.76), ν_{max} (strong) 9.2 (conjugated CO₂Me), 13.0, 14.0, and 14.6 μ.

Reactions of Ester (II).—(a) Alkaline hydrolysis of the ester (6.7 g.) was complete in 10 min. in a 50% excess of refluxing 10% sodium hydroxide solution. The acid (5.86 g.) was precipitated on acidification and, crystallised from ethyl acetate, had m. p. 148° (lit.,² 148°) (Found: C, 75.2; H, 7.0%; M, 178. Calc. for C₁₁H₁₂O₂: C, 75.0; H, 6.9%; M, 176), λ_{max} 224 mμ (log ε 3.96). Re-esterification with refluxing methanol containing sulphuric acid gave an oil whose infrared spectrum was identical with that of the starting ester.

(b) Hydrogenation of the acid (4.0 g.) in ethanol over platinum at room temperature and 1 atm. led to rapid uptake of 505 ml. of hydrogen (1H₂ = 512 ml.). Crystallisation of the product from ethyl acetate gave the dihydro-acid (VI), m. p. 152–153° (lit.,² 153°) (Found: C, 74.0; H, 7.9%; M, 177. Calc. for C₁₁H₁₄O₂: C, 74.1; H, 7.9%; M, 178), λ_{max} 226 mμ (log ε 3.97). A mixture of this dihydro-acid and the unsaturated acid (m. p. 148°) had m. p. 147–148°. Selective hydrogenation of the ester (II) to its dihydro-derivative (strong infrared bands at 9.2, 9.3, and 13.35 μ) followed by hydrolysis gave the same dihydro-acid.

⁴ Woodward and Katz, *Tetrahedron*, 1959, 5, 70.

(c) Curtius degradation of the dihydro-acid (VI) was carried out as follows. The *acid chloride*, prepared by refluxing the acid (1.39 g.) with an excess of thionyl chloride for 30 min., was an oil (1.41 g.) (Found: C, 67.4; H, 6.8; Cl, 17.7. $C_{11}H_{13}ClO$ requires C, 67.2; H, 6.6; Cl, 18.1%), λ_{max} 246 μ ($\log \epsilon$ 4.02) in spectroscopic hexane. Reaction of the acid chloride with methanol regenerated the methyl ester, and aqueous hydrolysis regenerated the acid. The azide was prepared by shaking a solution of the acid chloride (1.37 g.) in acetone (20 ml.) with a solution of sodium azide (0.75 g.) in water (3 ml.) for 10 min.; extraction with ether then gave the azide (1.16 g.) as a white solid, λ_{max} 256 μ ($\log \epsilon$ 4.07). The azide (1.15 g.) was heated in toluene (30 ml.) to 100° for 30 min. (170 ml. of gas evolved; $1N_2 = 127$ ml.). Removal of the toluene *in vacuo* left the oily *isocyanate* (0.98 g.) (Found: C, 76.8; H, 7.6; N, 9.0. $C_{11}H_{13}NO$ requires C, 75.4; H, 7.5; N, 8.0%). The isocyanate (0.94 g.) was refluxed with concentrated hydrochloric acid (10 ml.) for 10 min.; the neutral product was a wax (0.81 g.) which was repeatedly sublimed at 10 mm. to give ketone (VII), m. p. 105–106° (lit.,² 115°) (Found: C, 79.3; H, 9.1. Calc. for $C_{10}H_{14}O$: C, 79.95; H, 9.4%), for which the carbonyl band is at 5.7 μ and, as the only strong band above 7.5 μ , there is a band at 8.6 μ . A mixture of ketone (VII) and ketone (X), m. p. 102–104°, had m. p. 103–105°. The semicarbazone of ketone (VII) had m. p. 205–206° (lit.,² 215°) after several crystallisations from ethanol (Found: C, 63.8; H, 8.3. Calc. for $C_{11}H_{17}N_3O$: C, 63.7; H, 8.3%). A mixture of this semicarbazone and the semicarbazone of ketone (X) (m. p. 196–197°) had m. p. 180–185°. The infrared spectra of ketones (VII) and (X) are distinct. Hydrolysis of the isocyanate by refluxing it with water for 30 min. gave impure ketone (VII). The infrared spectrum and the preparation of the semicarbazone showed that ketone (VII) was the main constituent of the mixture.

Reactions of the New Ester.—(a) Alkaline hydrolysis of the ester (0.96 g.) with a 50% excess of refluxing 10% sodium hydroxide solution required 60 min. for completion. The *acid* (0.7 g.) precipitated by acidification had m. p. 128–129° (from ethyl acetate) (Found: C, 75.4; H, 7.4%; M, 180), λ_{max} 230 μ ($\log \epsilon$ 3.78). Re-esterification as above gave an oil whose infrared spectrum was identical with that of the starting ester.

(b) A mixture of the dimethylamine adduct (IV) (0.25 g.) and phenyl azide (0.25 g.) was kept for 24 hr. at room temperature. The basic product was an oil (0.22 g.) whose infrared spectrum was identical with that of compound (IV).

(c) Hydrogenation of the new ester and its acid does not proceed selectively at the 8,9-double bond: both double bonds of ester (III) are hydrogenated at comparable rates. Selective hydrogenation of the 3,4-double bond is possible before the removal of the amine from the adduct (IV). Hydrogenation of the adduct (IV) (6.8 g.) in dilute hydrochloric acid over platinum at room temperature and 1 atm. led to the uptake of 665 ml. ($1H_2 = 650$ ml.). An ethereal extract of the alkaline aqueous solution gave the *dimethylamine adduct* (5.85 g.) of the dihydro-derivative as an oil (Found: C, 70.7; H, 9.8; N, 5.9. $C_{14}H_{23}NO_2$ requires C, 70.85; H, 9.8; N, 5.9%), which had no intense absorption in the ultraviolet above 210 μ and no olefinic band in the 13–15 μ region. Removal of the dimethylamine from the adduct (5.8 g.) by boiling water in 20 min. gave the *dihydro-ester* (V) (2.5 g.), b. p. 70–72°/0.1 mm. (Found: C, 74.9; H, 8.3. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%), λ_{max} 236 μ ($\log \epsilon$ 3.83), ν_{max} (strong) 9.1, 9.2 (conjugated CO_2Me), and 13.05 μ . Further hydrogenation of compound (V), to the tetrahydro-stage, gave an oil whose infrared spectrum was identical with that obtained by complete hydrogenation of ester (III).

(d) Alkaline hydrolysis of ester (V) (1.7 g.) with refluxing sodium hydroxide solution required 60 min. for completion. Acidification gave the *acid* (1.42 g.), m. p. 121–122° (from ethyl acetate) (Found: C, 73.6; H, 7.95%). Re-esterification as above gave an oil whose infrared spectrum was identical with that of the starting ester (V).

Rates of Hydrolysis of the Two Esters.—The ester (~ 0.4 g.) was warmed in methanol (~ 15 ml.) to 50°. *n*-Sodium hydroxide (3 ml.) was added (time zero) and the solution immediately made up to 20 ml. with methanol. Samples (2 ml.) were withdrawn at intervals and titrated against 0.1*N*-hydrochloric acid (Bromothymol Blue). The second-order plots were straight lines: the velocity constants are reported in the discussion.

Depolymerisation.—(a) Compound (II) (2.0 g.) was distilled at 100 mm. (bath-temp. 180°, vapour-temp. 140–150°), to give a distillate (1.4 g.) whose infrared spectrum resembled that of compound (II). The intensity of the strong monomer band at 14.8 μ suggested that some 15% of monomer was present in the distillate.

(b) Compound (III) (1.96 g.) was distilled at 100 mm. (bath-temp. 180°, vapour-temp.

120—125°), to give a colourless oil (0.83 g.) whose infrared spectrum (band at 14.8 μ) resembled that of the monomer (I). After spontaneous dimerisation of this product at room temperature for 24 hr., the spectrum changed to that of the mixed tricyclodecadiene esters and crystallisation from light petroleum (b. p. 40—60°) gave Thiele's ester³ (0.37 g.), identical in m. p., mixed m. p., and infrared spectrum with an authentic sample.

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[Received, August 5th, 1960.]
