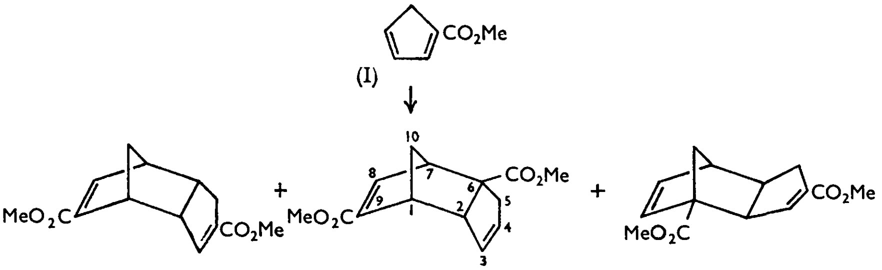
211. *Simple Derivatives of Cyclopentadiene. Part IV.*[1] *The Dimerisation of Methyl Cyclopentadiene-1-carboxylate.*

By David Peters.

Dimerisation of methyl cyclopentadiene-1-carboxylate gives three dimers, whose structures are deduced by combination of chemical and spectroscopic results. The kinetic and spectroscopic evidence does not reveal complexity in the dimerisation, although the suggested structure of the main reaction product implies that the reaction is not simple.

The preceding study[1] of the Diels–Alder reaction between methyl cyclopentadiene-1-carboxylate and cyclopentadiene has been extended to the reaction of this ester with itself. This reaction is summarised in the scheme below.

In the absence of a solvent, methyl cyclopentadiene-1-carboxylate (I) dimerises spontaneously at room temperature, giving Thiele's ester[2] (65%), whose suggested structure is (II), a second solid dimer[3] (10%), to which is assigned a structure such as (III), and a liquid dimer (25%), to which is assigned a structure such as (IV). There are closely related alternatives for each of the suggested structures, and it is not yet possible to discriminate between these: for example, the 6-methoxycarbonyl group in compound (III) * may be on carbon-2 or -5). The structures written here are those that require a minimum of structural reorganisation during the dimerisation.



(II) (65%) (III) (10%) (IV) (25%)

The liquid isomer is easily isolated from the mixture since it does not react with dimethylamine whereas the other two give the adducts (V) and (VI) (see ref. 1). Separation of the isomers (II, III) or (V, VI) was effected by chromatography. The parent esters are regenerated from the amine adducts (V) and (VI) by boiling water.

The structures of the three esters have been deduced by a combination of chemical and spectroscopic evidence. Our first assumption, that addition of dimethylamine is diagnostic

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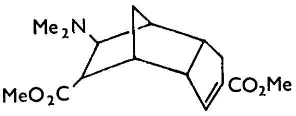
* Throughout this discussion a double bond in the isolated cyclopentene ring is designated 3,4-, the numbering which it has in the parent hydrocarbon. It may be noted that according to strict nomenclature it acquires numbers 4,5 when the ester groups are given priority for lowest numbers; this strict numbering is used in the Experimental section.

[1] Part III, preceding paper.

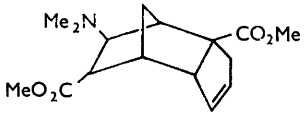
[2] Thiele, *Ber.*, 1901, **34**, 68; 1900, **33**, 666.

[3] Peters, *J.*, 1959, 1761.

of an activated bicycloheptene 8,9-double bond,[4] has been checked, in part, by showing that the adducts (V) and (VI) do not react with phenyl azide, as they should if they contained an 8,9-double bond. If this is correct it is possible to interpret all the other evidence in a consistent fashion.



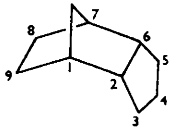
(V)



(VI)

The compounds to be considered and their relevant spectroscopic properties are listed in the Table. We assume that structures (XIII) to (XX) are known to be as shown. The first correlation is that the moderately intense (ε 100—200) infrared bands in the 9—10 μ region are associated with a complex vibration of the methoxycarbonyl group: their position then shows whether there is a double bond conjugated with this group. As shown in the fourth column of the Table there is a singlet or doublet at 9·1—9·2 μ when αβ-unsaturation is present; when there is not, then this band occurs at 9·6—9·8 μ, usually as a doublet, occasionally as a triplet. In only one case (XXIII) is there ambiguity in this interpretation.

Spectroscopic bands for derivatives of bicyclo[5,2,1,$0^{2,6}$]*decane*



No.	Unsatn.	Substituents	9—10 μ	13—15 μ	$\lambda_{max.}$ (m μ)	log ε
XIII	3,4	—	—	13·6s, 14·75m	—	—
XIV	8,9	—	—	13·7s, 14·2m, 14·5w	—	—
XV	3,4; 8,9	—	—	13·3s, 13·8s, 14·2m, 14·85m	—	—
XVI	3,4; 8,9	4-CO_2Me	9·1, 9·2	13·2s, 13·65s, 13·9w, 14·15w	228	3·88
XVII	3,4	4-CO_2Me	9·15, 9·25	13·35s, 14·2w	225	3·78
XVIII	3,4; 8,9	9-CO_2Me (D)	9·2	13·0s, 13·25w, 14·0m, 14·6m	232	3·76
XIX	8,9	9-CO_2Me (D)	9·2	13·05s, 13·7w	236	3·80
XX	3,4	9-CO_2Me 8-NMe_2	9·5, 9·6, 9·7	13·5m, 14·4m	—	—
II	3,4; 8,9	4,9-$(CO_2Me)_2$ (D)	9·1, 9·2	13·05s, 13·7s, 14·0w	220	4·12
XXI	3,4	4,9-$(CO_2Me)_2$ (D)	9·1, 9·2; 9·6, 9·7	13·0m, 13·4s, 13·9w 13·0m, 13·3s, 14·0w	228 227	3·76 3·90
V	3,4	4,9-$(CO_2Me)_2$ 8-NMe_2	9·2; 9·6, 9·7, 9·8	13·4s, 13·8w	228	3·88
XXII	8,9	4,9-$(CO_2Me)_2$ (D)	9·2; 9·7	13·05s	234	3·82
III	3,4; 8,9	6,9-$(CO_2Me)_2$ (D)	9·2; 9·6, 9·7	13·0s, 13·2m, 13·8m, 14·4m	231	3·81
VI	3·4	6,9-$(CO_2Me)_2$ 8-NMe_2	9·6, 9·7	13·5m, 14·2m	—	—
IV	3,4; 8,9	1,4-$(CO_2Me)_2$	9·1; 9·5	13·2s, 13·6s, 14·2w	226	3·95
XXIII	3,4	1,4-$(CO_2Me)_2$	9·2, 9·3	13·4s, 14·1w	225	3·93
XXIV	3,4	4,9-$(CO_2Me)_2$ 8-MeO	9·1, 9·2; 9·7	13·35m, 13·8m	228	3·90
XXV	—	4,9-$(CO_2Me)_2$ 8-NMe_2	9·55, 9·7	—	—	—
XXVI	—	4,9-$(CO_2Me)_2$	9·6, 9·7	—	—	—
XXVII	—	9-CO_2Me	9·6, 9·7	—	—	—
XXVIII	—	9-CO_2Me 8-NMe_2	9·6, 9·7	—	—	—

D denotes that the compound adds dimethylamine. ε values: s = >200; m = 50—200; w = <50.

The second, rather more involved, correlation concerns the olefinic out-of-plane vibrations at 13—15 μ. These bands are the most prominent in the 7·5—15 μ spectrum of the parent hydrocarbons (XIII—XV). When both the 3,4- and the 8,9-double bond are

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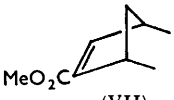
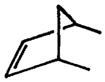
[4] Peters, *J.*, 1960, 1832.

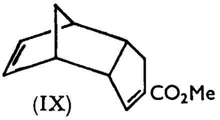
present (XV), interaction between the strong bands of almost equal frequency (13·6 and 13·7 μ) which originate in the separate double bonds of compounds (XIII) and (XIV) gives two new intense bands at 13·3 and 13·8 μ. The 14·75 μ band of (XIII) and the 14·2 μ band of (XIV) [5] survive almost unchanged in the doubly unsaturated compound (XV). Now all the compounds that add dimethylamine (marked D in the Table), but none of those compounds that do not add dimethylamine, have a strong band at 13·00—13·05 μ. Further, those that react with the amine all † show ultraviolet absorption at or above 231 mμ, while those which do not react with it absorb at or below 228 mμ. These three features together are characteristic of the partial structure (VII). The 13·00—13·05 μ band is not affected by the presence or absence of a 3,4-double bond. The compounds that (i) do not react with dimethylamine but (ii) contain an 8,9-double bond (nos. IV, XVI) have a strong band at 13·20—13·25 μ and this is associated with partial structure (VIII). A band occurs at 13·60—13·80 μ when there is an αβ-unsaturated ester group in the isolated cyclopentene ring provided that an 8,9-double bond is also present, *i.e.*, structure (IX) as in compounds (II, III, IV, XVI); when the 8,9-double bond is absent, as in compounds (V, XVII, XXI, XXIII, XXIV), this band moves to 13·30—13·40 μ, *i.e.*, structure (X). Further, any bands of medium intensity at wavelengths longer than 14·2 μ are due to an unsubstituted 3,4-double bond (cases III, XVIII, XIII, XX, VI, XV), but the exact position of this band varies from case to case.

This set of correlations, based originally on the spectra of the known compounds, interprets also the spectra of the new compounds intelligibly and unambiguously. (Additional evidence relating to the structures of various compounds may be found in the Experimental section.)

Several further points about the dimers (II—IV) require mention. First, an earlier inference by the present author [3] about the ultraviolet spectrum of compound (II) must be corrected. When the 8,9-double bond of compound (II) is hydrogenated, a band at about 216 mμ disappears from the ultraviolet spectrum; but it cannot be inferred that this band is due to an *isolated* αβ-unsaturated ester group in the bicycloheptene system, because this group is now known to absorb at 231—236 mμ. Evidently there is interaction between the excited states of the two chromophores, and this is strongest when the two chromophores are identical, as in this case. When the chromophores are not identical, the interaction is small, but not zero (cf. the pairs XVIII/XIX and XVI/XVII). This wrong inference led on to an incorrect structural assignment [3] for compound (III), the 103° isomer. This has the double-bond conjugation in position 8,9, not in 3,4, since it has $\lambda_{max.}$ 231 mμ, it has a strong 13·0 μ band, and *both* the 9·2 and the 9·6—9·7 μ bands of conjugated and unconjugated ester groups. Further, it adds dimethylamine with the disappearance of the ultraviolet maximum, and a medium-intensity band is present at 14·4 μ in the infrared spectrum, suggesting an unsubstituted 3,4-double bond.


(VII)


(VIII)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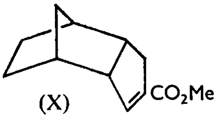
(X)

The third isomer (IV) is assigned an *exo*-structure, as Weise [6] suggested, since it is a liquid. Depolymerisation of this isomer has been found to resemble that of Thiele's ester (II): heating at about 160°/10 mm. causes slow distillation of methyl cyclopentadiene-1-carboxylate, identical with the material obtained by depolymerising Thiele's ester.

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† Except for (II) which has two interacting chromophores.

[5] Cristol and Lalonde, *J. Amer. Chem. Soc.*, 1959, **81**, 5417; Schmerling, Luigi, and Welsh, *ibid.*, 1956, **78**, 2819.

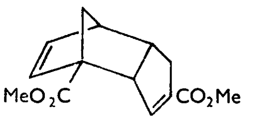
[6] Weise, U.S.P. 2,781,395, 2,716,662.

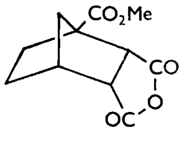
Certain of the derived compounds (XXI—XXVIII) require comment. Compound (XXI), the dihydro-derivative of Thiele's ester, exists in two forms, presumably with different configurations of the 9-ester group. Compound (XXII) is obtained by hydrogenating the dimethylamine adduct (V) of Thiele's ester and then removing the amine; it is a liquid, evidently a mixture of non-isomorphous isomers. Compound (XXIV), in which methanol has been added to the 8,9-double bond of Thiele's ester, is one of the products from the esterification of the crude dimeric cyclopentadienecarboxylic acid.[7] During alkaline hydrolysis of the ester groups the methanol is lost, so that the hydrolysis product is Thiele's acid.

When the two double bonds of dicyclopentadiene and its derivatives are hydrogenated two effects operate. The 8,9-double bond of dicyclopentadiene is more easily hydrogenated than the 3,4-double bond; and the rate of hydrogenation of both double bonds is slowed down by an attached ester group. So, in the parent hydrocarbon (XV), differential hydrogenation of the 8,9-double bond is possible. In compounds (IV) and (XVI), the two effects reinforce each other and selective hydrogenation of the 8,9-double bond is very easy. But in compound (XVIII), the effects are opposed and the rate of hydrogenation of the 8,9-double bond is slowed down so that both bonds are hydrogenated at comparable rates and selective hydrogenation bond is impossible; it is, in fact, possible to hydrogenate the 3,4-double bond of this compound, to give (XIX), by using a method mentioned in the preceding paper.

Another possible structure for Thiele's ester (II) has to be considered, namely, (XI). The situation is like that discussed in the previous paper (the structure of the " new " ester), in that the structural evidence is apparently conflicting. Structure (XI) makes the dimerisation of methyl cyclopentadiene-1-carboxylate easy to understand, but then the addition of dimethylamine and the ultraviolet spectra are very difficult to interpret. Further, if Thiele's ester had structure (XI), then the liquid isomer can hardly have structure (IV): it would presumably have to have its ester group in the 10-position, and this is not likely. Also, the maleic anhydride adduct of methyl cyclopentadienecarboxylate could not have the analogous structure (XII), since it shows no intense ultraviolet absorption above 210 mμ, and requires the ester group in the 10-position. So we retain, for the present, structure (II) for Thiele's ester and accept the consequence that dimerisation is a complex reaction.

(XI)





(XII)

Course of the Dimerisation.—The dimerisation of methyl cyclopentadiene-1-carboxylate has been carried out in the presence and absence of a solvent, at elevated temperatures, and in the presence of 100 moles % of acid. None of these modifications affects the product composition appreciably. The effect of added base (sodium methoxide in methanol) is more complicated, since it ionises the monomer (I); but in small amounts (5 moles %) it does not affect the course of the reaction markedly. It does, however, lead to the formation of a small amount of compound (XXIV) in which methanol has been added to the 8,9-double bond of Thiele's ester.

These results give no indication of the suspected complication in the reaction. Nor do the kinetics, which were followed by measuring the rate of disappearance of the monomer peak at 270 mμ. The reaction is accurately of the second order, the velocity constant being about two hundred times greater than that for cyclopentadiene dimerising under similar conditions.[8] The acceleration is due to both a lower activation energy and

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[7] Ziegler, Kulhorn, and Hafner, *Chem. Ber.*, 1956, **89**, 434.

[8] Wassermann, *J.*, 1936, 1034.

(probably) an increased pre-exponential factor in the Arrhenius equation. During the dimerisation, the growth of the dimer absorption band at 220 mμ is synchronous with the disappearance of the monomer band. There is also a well-formed isobestic point at 246 mμ, showing that there is no appreciable build up of a compound having light absorption different from that of the two main components of the product mixture. This evidence then is also consistent with structure (XI), rather than structure (II), for Thiele's ester.

EXPERIMENTAL

For details of spectral measurements see the preceding paper. Light petroleum was the fraction of b. p. 40—60°, unless otherwise specified.

Preparation of Thiele's Ester (II).—For large-scale preparations of this compound, the method of Ziegler *et al.*[7] (pouring a decalin suspension of sodium cyclopentadienide on to solid carbon dioxide) is more convenient than the Grignard method described earlier. The product is a mixture containing about 60% of Thiele's acid. The crude acid was partly purified by one crystallisation from methanol and the purification completed after the esterification. The impurities (which have not been examined) in the crude acid were a methanol-insoluble solid acid and liquid acids. The partly purified acid was esterified by refluxing its solution in methanol containing a little sulphuric acid for 16 hr. The product was crystallised from light petroleum (b. p. 60—80°): the overall yield of Thiele's ester from sodium cyclopentadienide is about 40%. The filtrate from this crystallisation gives compound (XXIV) (cf. below).

Dimerisation of Methyl Cyclopentadiene-1-*carboxylate* (I).—Depolymerisation of Thiele's ester to methyl cyclopentadiene-1-carboxylate was reported earlier.[3] Reconversion into the dimer is complete in the absence of solvent in an hour at room temperature. The composition of the product mixture (10·05 g.) was determined by first crystallising it from light petroleum (b. p. 60—80°) (100 ml.), to give pure Thiele's ester (5·57 g.), and recovering the oil (3·96 g.) from the filtrate. The composition of this oil was determined by comparison of its infrared spectrum with that of artificial mixtures of Thiele's ester (II), the 103° isomer (III), and the liquid isomer (IV). The overall proportions, which varied slightly in different reactions, were Thiele's ester 65(±3)%; 103° isomer 10(±2)%; liquid isomer 25(±3)%.

Dimerisation of the cyclopentadiene ester (*ca.* 1 g.) in ethanol (20 ml.) at room temperature for 24 hr. and at the b. p. for 1 hr. gave the same product mixture as the above. Dimerisation of the monomer (*ca.* 1 g.) in methanol (10 ml.) containing concentrated hydrochloric acid (0·5 ml.) at room temperature for 3 days also gave the same product mixture. Dimerisation of the monomer (*ca.* 1 g.) in methanol (10 ml.) containing sodium methoxide (5 moles %) gave similar results, except that extra infrared peaks were present in the neutral oil obtained after removal of Thiele's ester and the 103° isomer with dimethylamine. These peaks corresponded with those expected if about 5% of compound (XXIV) was present in the original dimerisation mixture.

Separation of the Dimers.—Separation of the 103° isomer from the dimerisation product mixture has been described.[3] To separate the liquid isomer, the crude product (10·26 g.) was crystallised from light petroleum (b. p. 60—80°) to remove the bulk of the Thiele's ester (5·57 g.), and the oil (3·79 g.) was recovered from the filtrate, dissolved in dimethylamine (20 ml.), and kept at 0° for 16 hr. The neutral product from this reaction is the liquid *isomer* (IV) *dimethyl bicyclo*[5,2,1,0 ^{2,6}]*deca*-3,8-*diene*-1,4-*dicarboxylate* (2·37 g.) (Found: C, 67·6; H, 6·7%; *M*, 252. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5%; *M*, 248). Repeated chromatography of this material on silica gel from light petroleum gave first and last fractions whose infrared spectrum was identical with that of the starting material. The basic product from the dimethylamine treatment is a mixture of the dimethylamine adducts (V) and (VI) from Thiele's ester and the 103° isomer respectively; these adducts are separated by chromatography on silica gel, elution with light petroleum giving first the adduct (VI) (cf. below).

Properties of Thiele's Ester and Derived Compounds.—(*a*) The ester (II) was recovered unchanged after 15 minutes at 100° in absence of a solvent and after refluxing in methanol containing hydrochloric acid (100 moles %).

(*b*) The hydrogenation of the ester over Raney nickel at 1 atm. and room temperature has been described.[3] A dihydro-derivative (XXI), m. p. 86—87°, is obtained. A second dihydro-derivative, *dimethyl bicyclo*[5,2,1,0,^{2,6}]*dec*-4-*ene*-4,8-*dicarboxylate*, is formed when platinum is used as catalyst: this has m. p. 100° (Found: C, 67·1; H, 7·0%; *M*, 235. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%; *M*, 250). A mixture of the two dihydro-derivatives had m. p. 86—95°. Both isomers were crystallised to constant m. p. and infrared spectrum: both were recovered unchanged after reaction with dimethylamine under the usual conditions, and after being dissolved in methanolic sodium methoxide or sulphuric acid. The same tetrahydro-derivative (XXVI), m. p. 77°, was obtained on further hydrogenation of the two dihydro-derivatives.

(*c*) The dimethylamine adduct (V) of Thiele's ester has been described.[4] The parent ester was regenerated in about 50% yield by boiling the adduct with water for 10—15 min.: prolonged boiling gives a mixture.[4] The adduct (0·5 g.) and phenyl azide (0·5 g.) were kept in ethyl acetate (3 ml.) for 7 days, the solvent was removed *in vacuo*, and the residue washed with light petroleum (b. p. below 40°); the solid residue crystallised from light petroleum to give the starting adduct (0·18 g.) (mixed m. p. and infrared spectrum). Hydrogenation of the dimethylamine adduct (V) in ethanol over Raney nickel or platinum led to low and variable hydrogen uptake. Hydrogenation over platinum in dilute hydrochloric acid was better, but still rather erratic. The adduct (2·08 g.) in dilute hydrochloric acid (25 ml.) took up 166 ml. of hydrogen ($1H_2$ = 160 ml.) in 2 hr. The catalyst coagulated at the end of the hydrogenation and was removed from the solution as soon as the reaction was complete. The basic product, 9-*dimethylaminobicyclo*[5,2,1,0^{2,6}]*decane*-4,8-*dicarboxylate* (XXV) had m. p. 82—84° after several crystallisations from light petroleum (Found: C, 65·0; H, 8·4; $C_{16}H_{25}NO_4$ requires C, 65·1; H, 8·5%. Nitrogen analyses were low and variable) and had no intense ultraviolet absorption above 210 mμ. Removal of the dimethylamine by refluxing this dihydro-derivative (1·0 g.) with water (10 ml.) for 15 min. gave as the neutral product, *dimethyl bicyclo*[5,2,1,0^{2,6}]*dec*-8-*ene*-4,8-*dicarboxylate* (XXII), an oil (0·52 g.) (Found: C, 67·35; H, 7·3. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%). The phenyl azide adduct was prepared by keeping a solution of compound (XXII) (0·45 g.) in phenyl azide (0·5 g.) for 24 hr. and then removing the excess of azide by light petroleum (b. p. below 40°). The solid residue of *dimethyl* 9-*phenylazidobicyclo*[5,2,1,0^{2,6}]*decane*-4,8-*dicarboxylate* (0·3 g.), crystallised from a small volume of methyl acetate, had m. p. 125—140° (Found: C, 63·9 H, 6·5 N, 11·8. $C_{20}H_{23}N_3O_4$ requires C, 65·0; H, 6·3; N, 11·4%).

Properties of the Isomer (III) *and its Derivatives.*—The dimethylamine adduct (VI) was prepared by keeping a solution of the 103° isomer (0·15 g.) in dimethylamine (2 ml.) overnight, removing the excess of amine *in vacuo* and crystallising the *product* (0·13 g.) from light petroleum. It had m. p. 127—128° (Found: C, 65·3; H, 7·4; N, 5·4%; *M*, 287. $C_{16}H_{23}NO_4$ requires C, 65·5; H, 7·9; N, 4·8%; *M*, 293) and showed only ester absorption in the ultraviolet region. A solution of this adduct (0·02 g.) in phenyl azide (0·1 g.) was kept for 24 hr.; the infrared spectrum of the basic product from this reaction (0·014 g.) was identical with that of the starting material.

Properties of the Liquid Isomer (IV) *and its Derivatives.*—(*a*) Hydrolysis of the liquid ester (0·55 g.) by refluxing it with sodium hydroxide (0·5 g.) in water (10 ml.) for 45 min. and precipitation of the acid by acidification gave the free acid (0·41 g.), having m. p. 201° (lit.,[6] 201°) after one crystallisation from a large volume of butyl acetate (Found: C, 65·55; H, 5·5%; equiv. 109. Calc. for $C_{12}H_{12}O_4$: C, 65·45; H, 5·55%; equiv., 110). Re-esterification of the acid by refluxing it with methanol containing a little sulphuric acid regenerated the liquid isomer, having the original infrared spectrum.

(*b*) Hydrogenation of the liquid isomer (0·97 g.) in ethanol (20 ml.) over platinum at 1 atm. and room temperature led to the rapid uptake of 92 ml. of hydrogen ($1H_2$ = 87 ml.). The rate of hydrogen uptake then fell markedly. The product (0·84 g.) was *dimethyl bicyclo*[5,2,1,0^{2,6}]-*dec*-3-*ene*-1,4-*dicarboxylate* (XXIII) (Found: C, 66·7; H, 7·4. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·2%). This dihydro-derivative (0·25 g.) was recovered unchanged in infrared spectrum after being kept in phenyl azide (0·25 g.) for 24 hr.

(*c*) The liquid isomer (1·0 g.) was depolymerised quantitatively by distillation at 10 mm. (bath-temp. 160°, vapour-temp. 100—120°) to give a colourless oil whose infrared and ultraviolet spectra were those of methyl cyclopentadiene-1-carboxylate obtained by depolymerising Thiele's ester. After spontaneous dimerisation at room temperature for 24 hr., the product mixture (0·65 g.) had an infrared spectrum identical with that of the dimerisation mixture of methyl cyclopentadiene-1-carboxylate; crystallisation of this mixture from light petroleum gave Thiele's ester (0·30 g.), m. p. and mixed m. p. 83—85°.

Miscellaneous Compounds.—The filtrate from the light petroleum crystallisation of the crude ester (Ziegler *et al.*[7]) gave an oil (18 g.) which was dissolved in dimethylamine and kept for 24 hr. at 0°. The neutral product from this mixture was a semi-solid mixture of the liquid isomer

(IV) and the adduct (XXIV). Washing with light petroleum (b. p. below 40°) removed the oil, leaving *dimethyl 9-methoxybicyclo*[5,2,1,$0^{2,6}$]*dec-4-ene-4,8-carboxylate* (XXIV) (2·5 g.), m. p. 111° (from light petroleum) (Found: C, 64·3; H, 7·1%; *M*, 261. $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·2%; *M*, 280). Mixtures of this compound, the isomer (III), and the dimethylamine adduct of Thiele's ester were molten below 95°. After compound (XXIV) (0·3 g.) had been kept with phenyl azide (0·3 g.) in ethyl acetate (3 ml.) for 7 days, it was recovered (0·22 g.) unchanged in m. p., mixed m. p., and infrared spectrum.

Compound (XXIV) (0·5 g.) and sodium hydroxide (0·5 g.) in water were refluxed for 30 min. Acidification gave Thiele's acid (0·32 g.), m. p. and mixed m. p. 211—212° (from butyl acetate). Esterification of this acid gave Thiele's ester (m. p., mixed m. p., infrared spectrum).

Compound (XXIV) was unaffected when refluxed with water for 30 min.

Compounds (XXV—XXVIII) were obtained by hydrogenation of available compounds. Compound (XIV) was prepared as already described;[9] the product had no 13·05 μ band as reported [8b] for the *exo*-analogue.

Kinetics.—The rate of dimerisation of methyl cyclopentadiene-1-carboxylate was measured by the rate of disappearance of the monomer peak at 270 mμ. It is not possible to determine an accurate ε value for the monomer, since a sample may contain up to 20% of dimer. The ε value was estimated as 7500 at 270 mμ, by distilling Thiele's ester (1·0 g.) into a weighed receiver, adding 20 ml. of ethanol from a calibrated pipette, and weighing the whole before recording its ultraviolet spectrum. The resulting ε value (6250) was increased by 20% since the infrared spectrum of this material showed bands corresponding to this concentration of the dimer. This uncertainty in ε is reflected in the absolute value of the rate constants and so in the pre-exponential Arrhenius *A* factor.

In a typical kinetic run, Thiele's ester (*ca.* 2·0 g.) was distilled into a receiver at −80° and the resulting monomer was made up to 50 ml. and kept at 30° (thermostat). Samples were withdrawn at intervals and diluted 2500 times to produce an optical density of 0·1—0·6 at 270 mμ. Beer's law is obeyed by the monomer over this concentration range. The second-order velocity constants (l. mole^{-1} sec.$^{-1}$) are: at 0°, $2·5 \times 10^{-5}$; at 30°, $3·8 \times 10^{-4}$; at 50°, $1·5 \times 10^{-2}$. The Arrhenius plot is linear; the activation energy is 14·7 kcal. mole^{-1}, and log *A* 7·4. The first- and third-order plots of the kinetic runs are curved. The dimer peak at 220 mμ does not show a simple behaviour during the kinetic run, probably because the monomer also absorbs to an unknown extent at this wavelength.

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[9] (*a*) Bruson and Reiner, *J. Amer. Chem. Soc.*, 1945, **67**, 723; cf. Wilder, Culbertson, and Youngblood, *ibid.*, 1959, **81**, 656; (*b*) Cristol, Seifert, and Soloway, *ibid.*, 1960, **82**, 2351.