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STUDIES ON THE DIELS-ALDER REACTION OF MALEIC ANHYDRIDE AND β-*trans*-OCIMENE[1]

K. T. JOSEPH and G. S. KRISHNA RAO
Organic Chemistry Department, Indian Institute of Science, Bangalore-12, India

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Abstract—The structure of the by-product, obtained in the Diels-Alder condensation of maleic anhydride with β-*trans*-ocimene followed by distillation of the adduct formed, has been established as 2-isopropylidene-4-methyl-7-carboxy-2,3,3a,6,7,7a-hexahydroindanone (IVa) and the mechanism of its formation from the adduct (II) discussed. Some hitherto unreported reactions of the maleic anhydride adduct (II) and its derivatives are described. These throw light on the stereochemistry of the adduct and derived products.

DURING an investigation of the physical constants (Table 1) and the IR spectra of β-*trans*-ocimene (I), the monoterpene fraction from Litsea zeylanica,[2] and its maleic anhydride adduct (II)[3] we discovered that it furnished a bicyclic diene keto-acid (m.p. 210°) as a by-product in the Diels-Alder reaction of the hydrocarbon with maleic anhydride. The structure elucidation of this by-product which escaped detection by earlier workers[3–5] and further investigations on the adduct itself and its derivatives form the subject matter of the present paper.

TABLE 1

S.N.	Principal isomer and its origin	d_4^{30}	n_D^{30}	λ_{max}^{EtOH}	ε
1.	Ocimene derived from *Litsea zeylanica*	0·8000	1·4870	232 mμ	28,210
2.	Reported values for predominantly				
	(a) β-*cis*-Ocimene	0·8002	1·4885	235 mμ	29,240
	(b) β-*trans*-Ocimene	0·7982	1·4865	232·5 mμ	30,056

β-*trans*-Ocimene (I) obtained from the essential oil of *Litsea Zeylanica* was found to react with maleic anhydride[3,5] and fractionation of the reaction mixture yielded an adduct (85%) as a colourless viscous (often turbid) liquid. The residue remaining, on cooling and washing with light petrol, gave a white solid which was crystallized from ethyl acetate to a constant m.p. of 210°; yield 8%. It was observed that the adduct distilled as a turbid liquid. Addition of light petrol to the turbid distillate precipitated a white solid which after crystallization from ethyl acetate gave the same material melting at 210° with no depression in the mixture m.p. with the higher boiling residual material left in the flask, indicating co-distillation to some extent of the 210° melting material with the anhydride adduct.

Solubility in bicarbonate and the IR spectrum (nujol); 2680 (broad, carboxylic

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[1] This paper was presented at the Joint Convention of the Chemical Research Committee and the Indian Chemical Society held at Aligarh (India) on December 26, 1965.

[2] Our findings in the study of the essential oil will be published separately.

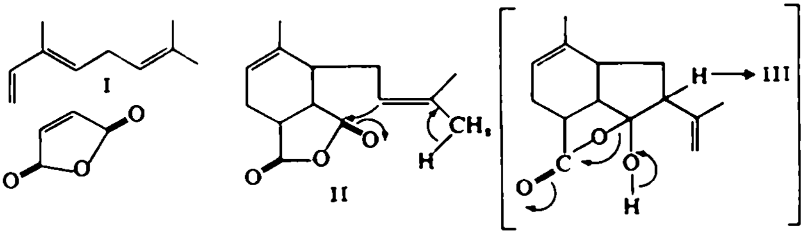
[3] H. Farnow and F. Porsch, *Dragoco Report* 8, 183 (1961).

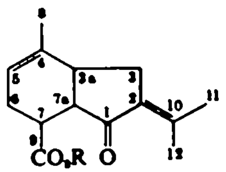
[4] P. Teisseire, *Resherches No.* 3, 33 (1953); *Chem. Abstr.* 49, 961 e (1955).

[5] M. Gunzel-Schumacher and V. Wicker, *Chem. Ber.* 93, 947 (1960).

—OH), 1704 (very strong, unresolved acid and unsaturated ketone carbonyl) and 1637 cm^{-1} (strong due to the double bond of a cisoid enone *et seq.*) indicated that the by-product obtained is an acid. The silver salt[6] showed in the IR spectrum bands due to a 5-membered ketone with a double bond in conjugation IR (nujol): 1704 and 1637 cm^{-1}. The ratio of intensities[7] of the stretching bands of the carbonyl and the —C=C— in conjugation indicated that they have the *cis* relationship. This was further corroborated by the UV absorption spectrum of the acid. UV (EtOH): 254 mμ (ϵ 13,750) which was in complete agreement with the calculated value for the cisoid 5-membered ketone in conjugation with the tetra substituted exocyclic double bond.[8] Elemental analysis agreed with the formula $C_{14}H_{18}O_3$, the three oxygens being accounted for by the presence of the carboxyl and the ketone carbonyl functions. Equivalent weight determination gave a value of 233 which is in close agreement for a monobasic acid of this formula. On catalytic hydrogenation with Adam's catalyst at atmospheric pressure in acetic acid it readily absorbed two mole equivalents of hydrogen indicating the presence of two ethylenic linkages. The IR spectrum of the tetrahydro keto-acid (V) confirmed the presence of carboxyl (2690 and 1698 cm^{-1}), cyclopentanone carbonyl (1729 cm^{-1}) and an isopropyl group[9] (1374, 1357 and 1156 cm^{-1}).

The above data together with the fact that the maleic anhydride adduct, the principal product of this reaction, has the same molecular formula, *viz.*, $C_{14}H_{18}O_3$, indicated that the by-product could result from a rearrangement of the primary Diels-Alder adduct (II). The double bond present in the ω,ω-dimethylallyl side chain at C-3 is ideally situated for participation with the carbonyl on C-2 of the anhydride in the manner shown involving a 6-membered transition state to give the intermediate ring closed keto-unsaturated acid (III) which under the conditions could isomerize to 2-isopropylidene-4-methyl-7-carboxy-2,3,3a,6,7,7a-hexahydroindanone (IVa) with a





IV a, R = H
b, R = Me

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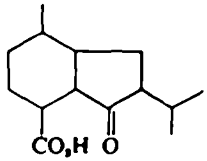
[6] K. Nakanishi, *Infrared Absorption Spectroscopy, Practical* p. 44, Holden-Day, San Francisco (1962).

[7] R. L. Erskine and E. S. Waight, *J. Chem. Soc.* 3425 (1960).

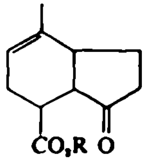
[8] A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products* p. 231. Pergamon Press, Oxford (1964).

[9] H. A. Szymanski, *Interpreted Infrared Spectra* Vol. 1; p. 14. Plenum Press, New York (1964).

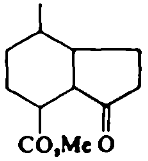
more stable tetrasubstituted double bond in conjugation with the ketonic function.



V



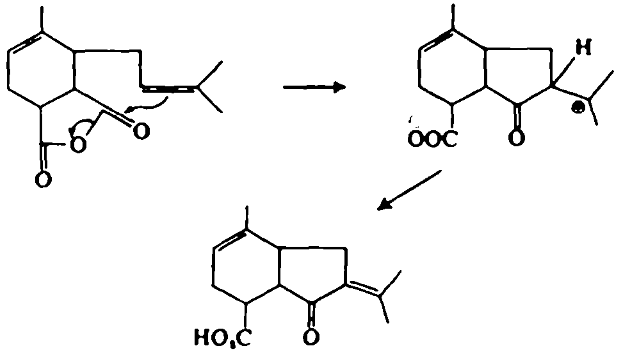
VI a, R = H
b, R = Me



VII

A similar cyclization mechanism has been proposed recently by Sarel and Brauer[10] in the reaction of α-cyclopropyl styrene with maleic anhydride.

A possible alternate mechanism* for the formation of the keto-acid under different conditions is given below. This mechanism is in agreement with the Lewis acid catalysed formation of the same keto-acid (IVa).



IVa

Formation of the by-product (IVa) from the anhydride adduct (II) by rearrangement was clearly demonstrated when II on heating for 1 hr at 210–215° gave IVa in 76% yield. The course of its formation could be conveniently followed by spectral means, as was evident by the progressive disappearance of the anhydride bands of II in the IR spectrum and the appearance of bands characteristic of IVa as heating was continued. The crude Diels-Alder reaction product after removal of the solvent gave the same IR spectrum as that of the purified adduct (II), found superimposable in all detail with the one published,[3] showing that the by-product arises, not during the Diels-Alder reaction itself but in the heat treatment during its distillation. An independent proof for the formation of the by-product IVa from the adduct II was furnished when it was shown that the rearrangement could be smoothly brought about by a Lewis acid, such as anhydrous aluminium chloride. In one single experiment with no attempts to work out optimum conditions, a conversion of 52% was acheived. Analogous formation of cycloalkenones from appropriately substituted olefinic acids in presence of acid catalysts has been recently surveyed by Ansell and Palmer.[11]

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* This alternate mechanism was suggested by the referee.

[10] S. Sarel and E. Brauer, *Chem. & Ind.* 467 (1965).

[11] M. F. Ansell and M. H. Palmer, *Quart. Rev.* **18**, 211 (1964).

The spectral and chemical evidence discussed are in good agreement with the structures assigned to the by-product (IVa) and its tetrahydro derivative (V). The NMR study of the methyl ester (IVb) also fully supports the structural assignment. It shows one olefinic proton (at C-5) at 4·52 τ (poorly resolved multiplet), three methyl groups (at C-4 and C-10) on doubly bonded carbon atoms at 8·20 τ (singlet), 8·31 τ (singlet) and 7·83 τ (merged with methylene protons) and one ester methyl at 6·30 τ (singlet). The down field appearance of methyl protons (C-12) at 7·83 τ is of significance here and is indicative of the proximity of this methyl with the keto group. A similar downfield shift of the β-methyl signal to 7·85 τ has been noticed in citral—a where the methyl and the carbonyl are in *cis*-relationship.[12]

Chemical confirmation for the isopropylidene function adjacent to the ketone in IVa was adduced when it was shown that it could be cleaved readily under retro-aldol conditions by the action of alkali[13] to give the solid 4-methyl-7-carboxy-2,3,3a,6,-7,7a-hexahydroindanone (VIa) and acetone. The modified procedure worked out by us for the retro-aldol reaction proved to be quite convenient and furnished VIa in nearly quantitative yield. The IR spectrum (nujol) of VIa exhibited bands at 1730 (cyclopentanone), 1692 (acid C═O) and 1661 cm^{-1} (—C═C—). The corresponding methyl ester (VIb) also had the expected spectral properties; IR (neat): 1739 (cyclopentanone and ester C═O) and 1661 cm^{-1} (—C═C—) and furnished a yellow 2,4-dinitrophenylhydrazone. On hydrogenation it absorbed one mole equivalent of hydrogen to give the saturated keto-ester (VII), characterized by an orange-red 2,4-dinitrophenylhydrazone.

We next turned our attention to a detailed investigation of the maleic anhydride adduct (II) in order to throw further light on its reactions and stereochemistry.

The adduct (II) readily underwent hydrolysis with aqueous alkali to give the corresponding dicarboxylic acid (VIIIa) m.p. 156° in quantitative yield. On exposure it underwent slow hydrolysis as shown by the clear liquid anhydride becoming increasingly turbid from which the dicarboxylic acid could be precipitated by the addition of light petrol. The dicarboxylic acid could readily be reconverted to the anhydride by refluxing in benzene. Removal of the solvent furnished a viscous liquid which showed strong anhydride bands in the IR spectrum. This shows that the dicarboxylic acid (VIIIa) resulting from the alkaline hydrolysis of the anhydride (II) and consequently its dimethyl ester (VIIId) have the same *cis* stereochemistry.

In conformity with the principle of *endo* addition to acyclic dienes[13,14,15] the addition of the dienophile, maleic anhydride to the *trans* butadiene *viz.*, β-*trans*-ocimene (I) should result in a completely *cis* substituted cyclohexene, to give *cis*-1,2,3,6-tetrahydro-3-ω,ω-dimethylallyl-4-methylphtahlic anhydride of structure II. Consequently the stereochemistry of the dicarboxylic acid should be as indicated (VIIIa). The facile formation of the indanone derivative (IVa) from the anhydride adduct (II) is readily explained on the basis of *cis* substitution pattern at C-2 and C-3. Assuming pesudo equatorial conformation for the bulky alkenyl side chain at C-3 of the substituted cyclohexene, axial and equatorial assignments for the C-2 and C-1 substituents respectively would follow as depicted in the conformational representation VIII. In

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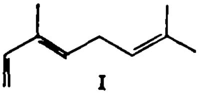
[12] P. B. Venuto and A. R. Day, *J. Org. Chem.* **29**, 2735 (1964).

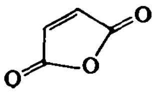
[13] D. H. R. Barton and G. S. Gupta, *J. Chem. Soc.* 1961 (1962).

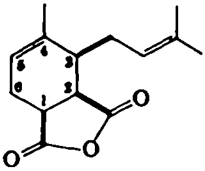
[14] J. G. Martin and R. K. Hill, *Chem. Rev.* **61**, 537 (1961).

[15] J. E. Milks and J. E. Lancastor, *J. Org. Chem.* **30**, 888 (1965).

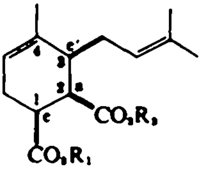


I

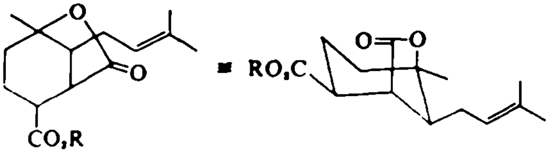




II



VIII a, $R_1 = R_2 = H$
b, $R_1 = Me, R_2 = H$
c, $R_1 = H, R_2 = Me$
d, $R_1 = R_2 = Me$



IX a, $R = H, + H_2O$
b, $R = H$
c, $R = Me$

their studies on the stereochemistry related to the Diels-Alder adducts of 4-methyl-1,3-pentadienes Ichikizaki and Arai[16] made similar assignments for the C-1 and C-2 carboxyls of their products.

Assignment of axial conformation for the C-2 carboxyl was confirmed by the facile formation of a γ-lactone (IXa) by treatment of the dicarboxylic acid (VIIIa) with 1N HCl acid for 1·5 hr. The lactone carboxylic acid (IXa) IR (nujol): 3623 (sharp, unassociated —OH of the hydrate), 2632 (broad, carboxylic —OH), 1770 (γ-lactone) and 1701 cm^{-1} (acid C=O) was obtained as a crystalline hydrate. It could also be obtained directly from the anhydride (II) under identical conditions. It was dehydrated by refluxing in benzene with *p*-toluenesulphonic acid (heating at refluxing toluene temperature for 2 hr did not eliminate the water of hydration) to furnish IXb, the IR spectrum of which exhibited γ-lactone (1760 cm^{-1}) and carboxyl carbonyl (1730 cm^{-1}) bands, but did not show the characteristic sharp band at 3623 cm^{-1} of the hydrate IXa. On esterification with diazomethane, IXb furnished a crystalline lactone ester (IXc) which was found to be identical with the lactone methyl ester (mixture m.p. undepressed and IR spectra superimposable) prepared by an alternate route.

The maleic anhydride adduct (II) on refluxing with absolute methanol furnished a mixture of half esters VIIIb and VIIIc with the former predominating. One of the isomers solidified to give a crystalline material m.p. 81–82° while the other remained as a viscous liquid and could not be crystallized. Attempts to purify the liquid half ester by distillation, only converted it to the anhydride (II) apparently by elimination of methanol at elevated temperature.

The solid half ester exhibited the expected IR bands (nujol): 1736 (ester C=O) 1709 (acid C=O) and 1678 cm^{-1} (C=C). That it corresponded to the structure VIIIb with the methoxy carbonyl in equatorial and carboxyl in axial conformations became evident by its facile conversion to the γ-lactone methyl ester (IXc) on treatment with

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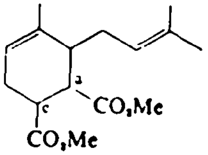
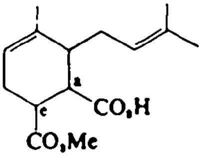
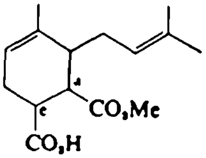
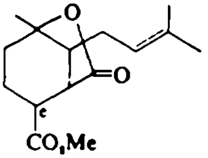
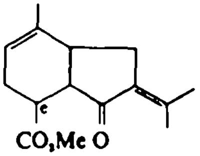
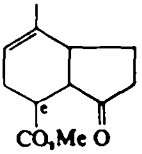
[16] I. Ichikizaki and A. Arai, *Bull. Chem. Soc. Japan* 37, 432 (1964).

Table 2

Structure of the compound		Position of the NMR signal of ester protons	Remarks
VIIId		6·42 τ 6·30 τ	
VIIIb		6·30 τ	
VIIIc		6·41 τ 6·30 τ	Contaminated with the equatorial isomer
IXc		6·28 τ	
IVb		6·30 τ	
VIb		6·30 τ	

p-toluenesulphonic acid in benzene involving the free axial carboxyl at C-2 and the double bond in the Δ^4-position. The IR and NMR spectra of this compound are in complete agreement with the proposed structure [IR (CCl_4): 1779 (γ-lactone) 1742 (ester C=O) and 1639 cm^{-1} (—C=C—); NMR (CCl_4): 4·95 (poorly resolved m—one olefinic proton), 6·28 (s—Me protons of the ester), 8·26 and 8·40 (s—Me, on the double bond) and 8·67 τ (s—Me on the lactone bridge)]. This lactone ester was found to be identical in all respects with the one prepared by the alternate route (VIIIa → IXa → IXb → IXc). The structure isomer relationship of both the half esters (VIIIb and VIIIc) was established by their conversion to the same dimethyl ester (VIIId) identical with the one obtained directly from the dicarboxylic acid VIIIa by esterification with diazomethane.

An examination of the methyl proton signals (Table 2) of the methoxy carbonyl groups in the dimethyl ester VIIId, the isomeric half esters VIIIb and VIIIc (slightly contaminated with VIIIb), the lactone ester IXc and the indanone esters IVb and VIb in their NMR spectra is of some interest. The chemical shift values shown in the Table exhibit an unmistakable trend in the axial *vs* equatorial methyl esters in the series of compounds studied, the methyl signal of the former occurring at a higher field relative to the latter.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra: Perkin-Elmer (Model 137) Infracord spectrophotometer and UV spectra: in EtOH soln, using a Beckman DU spectrophotometer. NMR spectra: a Varian A60 spectrometer in CCl_4 soln with TMS as internal standard. Light petrol refers to the fraction b.p. 40–60°. Microanalyses were carried out by Messrs. B. R. Seetharamiah, D. P. Bose and H. S. Thyagarajan of this department.

Isolation of β-trans-*ocimene* (I) *from the essential oil.* A fresh sample of the essential oil (40 g) of *Litsea Zeylanica*, was carefully fractionated using a Tower's column with a 1:10 reflux ratio. The initial fractions boiling in the range 88–89°/40 mm were combined and refractionated to give I (32·3 g, 81%), b.p. 88–88·5°/40 mm, n_D^{30} 1·4870, d_4^{30} 0·8000, IR (neat): 3175, 3049, 2985, 1639, 1608, 1100, 986, 890 and 826 cm^{-1}; UV (EtOH): 232 mμ (ε 28,210).

Preparation of the Diels-Alder adduct (II).* To a pure sample of maleic anhydride (49 g) in dry benzene (130 ml), freshly distilled I (68 g) was carefully added (30 min) with cooling and constant stirring. The reaction mixture was then refluxed for 4 hr and the solvent removed. The adduct distilled (100 g, 85%) as a colourless viscous liquid, b.p. 160–165°/1 mm. IR (neat): 1845, 1783 (C=O of the anhydride) 1637 (–C=C–) and 1238 cm^{-1} (C—O—C stretching); NMR: 4·33, 4·85 (multiplets, two olefinic protons) 8·30 and 8·20 τ (singlets, 9H, three Me on doubly bonded C atoms). (Found: C, 71·27; H, 7·80. Calc. for $C_{14}H_{18}O_3$: C, 71·77; H, 7·74%.)

Isolation of the by-product IVa

(a) After repeated washings of the remaining residue (15 g) in the distillation flask with light petrol, a clean white solid separated which on crystallization from AcOEt afforded IVa (9·5 g, 8%), m.p. 210°. (Found: C, 71·80; H, 7·65. $C_{14}H_{18}O_3$ requires: C, 71·77; H, 7·74%.)

(b) A freshly distilled sample of II (10 g) was heated under N at 210–215° (bath) for 1 hr. The product, which solidified on cooling, was crystallized from AcOEt, m.p. 210° (7·6 g, 76%) (mixture m.p. with IVa undepressed).

(c) Finely powdered anhydrous $AlCl_3$ (4 g) was added to an ethereal soln (12 ml) of II (2·5 g) with constant stirring and cooling (ice-salt). The stirring was continued for 1 hr keeping the temp of the reaction mixture below 0°, and then for 6 hr at room temp. The reaction mixture was added to crushed ice (50 g) containing conc HCl (5 ml). The product was extracted with AcOEt, washed several times with water, dried and the solvent removed. Crystallization of the crude product from AcOEt afforded a colourless solid (1·3 g, 52%), m.p. 210° (mixture m.p. with IVa undepressed).

The Ag-salt of IVa prepared in the usual manner had IR (nujol) 1704, 1637, 1513 and 1389 cm^{-1}.

Catalytic reduction of IVa. The keto-acid IVa (1 g) in AR AcOH (50 ml) was hydrogenated using PtO_2 catalyst (20 mg) at atm press. Absorption of 2 mole equivs H was complete in 1 hr. Working up of the product gave a gummy material (980 mg) which was purified by short-path distillation to give V, b.p. 95–100° (bath)/2·3 × 10^{-3} mm. (Found: C, 71·03; H, 9·38. $C_{14}H_{22}O_3$ requires: C, 70·53; H, 9·30%.)

Preparation of IVb. To a soln of IVa (1 g) in AcOEt (50 ml) was added an excess of diazomethane soln in ether. The crude methyl ester was crystallized from AcOEt to yield IVb (950 mg), m.p. 93–94°, IR (nujol): 1730 (ester C=O), 1698 (C=O of unsaturated ketone) and 1634 cm^{-1} (s, C=C in *cis* relationship with the ketone) UV (EtOH) 256 mμ (ε 11,870). (Found: C, 72·52; H, 8·06. $C_{15}H_{20}O_3$ requires: C, 72·55; H, 8·12%.)

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* This method is an improvement over the previous reported procedures.[6] High exothermicity of the reaction warranted slow addition of the hydrocarbon under cooling in ice.

Preparation of VIa. The keto-acid IVa (1 g) was mixed with KOHaq (5 g in 5 ml) and ethylene glycol (25 ml) and heated at a bath temp of 120–125° for 4 hr, a continuous stream of N being maintained throughout. The liberation of acetone ceased indicating completion of the reaction (tested by passing the out-going gas through a solution of 2:4 DNP reagent). The reaction mixture was added to water (200 ml), acidified with 2N HCl in the cold and extracted repeatedly with AcOEt, washed with water, dried and the solvent removed. Crystallization of the crude material from AcOEt afforded VIa (700 mg), m.p. 166–168°. (Found: C, 67·61; H, 7·36. $C_{11}H_{14}O_3$ requires: C, 68·02; H, 7·27%.)

Esterification of VIa. To a soln of VIa (1 g) in AcOEt (25 ml) was added an excess of an ethereal soln of diazomethane. Working up gave, in quantitative yield, VIb, b.p. 140–142°/1 mm. NMR: 4·60 (m, olefinic proton), 6·30 (s, ester protons) and 8·28 τ (s, Me on the double bond). (Found: C, 69·01; H, 7·83. $C_{12}H_{16}O_3$ requires: C, 69·21; H, 7·74%.)

The 2:4 *dinitrophenylhydrazone* of VIb had m.p. 178°, IR (nujol) 3521 (N—H), 1730 (ester C═O), 1618 and 1592 cm^{-1} (—C═C— and —C═N—). (Found: C, 55·50; H, 5·21; N, 14·56. $C_{18}H_{20}N_4O_6$ requires: C, 55·66; H, 5·19; N, 14·43%.)

Catalytic hydrogenation of VIb. The keto-ester VIb (1 g) was hydrogenated using PtO_2 catalyst in AcOH (20 ml). Absorption of one mole equiv H was complete in 1 hr. The product was purified by short-path distillation to afford VII (950 mg), b.p. 115–120° (bath)/1 mm, IR (neat): 1736 (unresolved ester and cyclopentanone —C═O) and 1403 cm^{-1} ($-CH_2-\overset{O}{\overset{\|}{C}}-$). (Found: C, 68·62; H, 8·71. $C_{12}H_{18}O_3$ requires: C, 68·54; H, 8·63%.)

The 2:4 *dinitrophenylhydrazone* of VII had m.p. 195°, IR (nujol) 3425 (N—H), 1736 (ester carbonyl), 1613 and 1587 cm^{-1} (—C═C— and —C═N—). (Found: C, 55·67; H, 5·47; N, 14·63. $C_{18}H_{22}N_4O_6$ requires: C, 55·38; H, 5·68; N, 14·35%.)

Alkaline hydrolysis of the Diels-Alder adduct (II). The adduct II (1 g) was heated over a water bath with NaOHaq (5 ml, 25%) for 1 hr. The soln was cooled, diluted with water (10 ml) and acidified with 2N H_2SO_4, when the dicarboxylic acid separated. Crystallization from AcOEt–light petrol afforded VIII a (970 mg), m.p. 156°, IR (nujol): 2681 (broad, —OH of acid), 1709 (acid C═O) and 1672 cm^{-1} (—C═C—). (Found: C, 67·03; H, 8·16. Calc. for $C_{14}H_{20}O_4$: C, 66·67; H, 7·94%.)

Diazomethane esterification of VIIIa. The acid VIIIa (1 g) on esterification with diazomethane, gave VIIId (970 mg), b.p. 145–150° (bath)/1·5 mm, IR (neat): 1739 (ester C═O) and 1667 cm^{-1} (—C═C—), NMR (CCl_4): 4·63 and 4·93 (m—two olefinic protons), 6·42, 6·30 (s—6 ester protons), 8·26 and 8·42 τ (s—3 Me on doubly bonded C atoms). (Found: C, 68·20; H, 8·42. $C_{16}H_{24}O_4$ requires: C, 68·55; H, 8·63%.)

Preparation of the isomeric monomethyl ester acids VIIIb *and* VIIIc. A freshly distilled sample of II (20·5 g) was refluxed with abs MeOH (90 ml) for 24 hr. On removal of the solvent and cooling, partial solidification occurred. Addition of light petrol hastened the process. The solid was washed repeatedly with light petrol and crystallized from AcOEt–light petrol to yield VIIIb (11·5 g) m.p. 81–82°. NMR (CCl_4): 4·60, 4·83 (m, 2 olefinic protons), 6·30 (s, ester protons) 8·30 and 8·42 τ (s, 3 Me on doubly bonded C atoms). (Found: C, 67·58; H, 7·95. $C_{15}H_{22}O_4$ requires: C, 67·64; H, 8·33%.)

Removal of the solvent from the filtrate furnished VIIIc still contaminated with VIIIb, (revealed by the NMR spectrum) as a viscous liquid. IR (CCl_4): 1742 (ester C═O), 1709 (acid C═O) and 1672 cm^{-1} (—C═C—).

Esterification of the isomeric half esters VIIIb *and* VIIIc. Both isomeric ester acids VIIIb and VIIIc were esterified with diazomethane to afford the same diester VIIId with identical physical properties as those of the one prepared from the dicarboxylic acid.

Lactonisation of VIIIa. A mixture of VIIIa (2 g) and 1N HCl (30 ml) was heated for 1·5 hr at 95–100°. Colourless needles separated on cooling, which were filtered off, washed with water and crystallized from AcOEt to furnish IXa (1·80 g) m.p. 180° (hot water). (Found: C, 62·02; H, 8·16. $C_{14}H_{22}O_5$ requires: C, 62·20; H, 8·20%.)

Treatment of IXa *with* p-*toluenesulphonic acid.* *p*-Toluenesulphonic acid (15 mg) was added to IXa (150 mg) in benzene (40 ml) and the reaction mixture refluxed for 8 hr, the water being removed azeotropically. The benzene soln was washed repeatedly with water, dried and the solvent removed.

Crystallization of the crude product from benzene yielded IXb (125 mg) m.p. 112–113°. (Found: C, 66·83; H, 8·01. $C_{14}H_{20}O_4$ requires: C, 66·65; H, 7·99%.)

Esterification of IXb. The above IXb (200 mg) on esterification with diazomethane afforded the methyl ester (195 mg) which was crystallized from AcOEt–petrol to give IXc, m.p. 82–83° (mixture m.p. with the lactone ester prepared by the alternate route undepressed. IR spectra were superimposable).

Lactonization of the solid mono ester acid VIIIb. A mixture of *p*-toluenesulphonic acid (25 mg) and VIIIb (2·5 g) in dry benzene (30 ml) was refluxed for 12 hr. After removal of the solvent, the product was extracted with ether, washed with 5% $NaHCO_3$aq (2 × 25 ml) followed by repeated washing with water, dried and the solvent removed. Crystallization from AcOEt–petrol gave IXc (2 g) as colorless needles, m.p. 82–83°. (Found: C, 67·58; H, 8·29. $C_{15}H_{22}O_4$ requires: C, 67·64; H, 8·33%.)

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