A Synthetic Study in the Tricyclovetivene Series

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The total synthesis of racemic tricyclovetivene (**1***a*) and isomers (**1***b* and **26**) is described. The crucial reaction of the synthesis is a cyclization (**iii**) developed in this laboratory.

La synthèse totale du tricyclovetivène (**1***a*) racémique et de ses isomères (**1***b* et **26**) est décrite. L'étape cruciale de la synthèse est une cyclisation (**iii**) mise au point dans ce laboratoire.

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In the course of model studies conducted in preparation to a total synthesis of songorine (**i**), we have discovered (1) a novel route to the C,D ring system of this alkaloid. The synthetic route involved the cyclization of compound **ii** in a basic or compound **iii** in an acidic medium. Both reactions were stereospecific and gave the products **iv** or **v** respectively. In order to explore further the scope and applicability of our method and also in order to ascertain the stereospecificity of the reaction in compounds not including a preformed bicycloheptane system as **ii** or **iii**, we decided to use the method in the synthesis of some sesquiterpene.

It appeared to us that the hydrocarbon tricyclovetivene (2) (**1***a*) might serve as a useful and, at the same time, profitable model for our synthetic scheme.

The readily available starting material, 1-methyl-indan-5-ol (**2**) (3) was converted to its allyl ether (**3**) by alkylation with allyl chloride in the presence of potassium carbonate and potassium iodide. A Claisen rearrangement of compound **3** at 185 °C gave the phenol (**4**) (i.r. hydroxyl at 3615 cm^{-1}; n.m.r., vinyl protons τ 3.96–5.16).[1] Since the rearrangement was expected to prefer the less hindered ortho position and since only one product was observed, it was preliminarily assumed that the product must indeed have the structure **4** (for proof, *vide infra*).

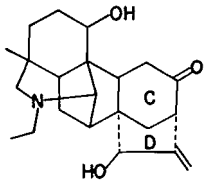
The phenol (**4**) was methylated with dimethyl sulfate and alkali to give the methoxy derivative (**5**). The unsaturated side chain was modified by a series of standard reactions (**6**–**8**) to prepare it for eventual cyclization. Treatment of **5** with sodium chlorate and a catalytic amount of osmium tetroxide gave the diol (**6**) which in turn underwent oxidative cleavage with sodium periodate to furnish directly the aldehyde (**7**) (i.r., aldehyde at 1725 cm^{-1}). Ketalization with ethylene glycol and *p*-toluenesulfonic acid gave the corresponding acetal (**8**).

Modification of the bicyclic system of **8** in preparation for cyclization was accomplished in the following two steps. The acetal (**8**) was subjected to a Birch reduction and the resulting dienol ether (**9**) was immediately hydrolyzed in aqueous methanolic oxalic acid to furnish the β,γ-unsaturated ketone (**10**) (i.r., ketone at 1720 cm^{-1}; n.m.r., no vinyl protons).

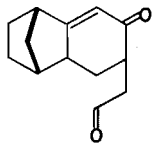
Cyclization of the β,γ-unsaturated ketone (**10**) was accomplished by heating in 80% acetic acid to furnish a mixture of tricyclic epimers (**11***a* and *b*) in a ratio of 2:3.[2] The stereochemistry of the hydroxyl in **11***a* and *b* remains undefined. This is unimportant since the asymmetry of the carbon carrying the hydroxyl will be subsequently removed by its reduction to a methylene. However, only two sharply melting diastereoisomers, **11***a*, m.p. 68–69 °C (ether–hexane) and **11***b*, m.p. 167–168 °C (ether) were isolated by fractional crystallization and thus it was clear that in each case the hydroxyl has a unique configuration. The i.r. spectra of the two epimers (**11***a* and *b*) both showed absorption maxima for the α,β-unsaturated ketone, 1685 cm^{-1} for **11***a* and 1680 cm^{-1} for **11***b* and the hydroxyl, 3625 cm^{-1} for **11***a* and 3615 cm^{-1} for **11***b*, with only minor differences in the fingerprint region. The n.m.r. spectrum showed a distinct difference for position of the methyl

[1]Only relevant spectral data are mentioned in the theoretical; for full spectral and characterization data see Experimental.

[2]Base-catalyzed cyclization of a corresponding β,γ-unsaturated keto aldehyde gave in this case no result.



i



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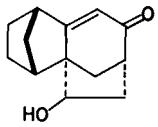

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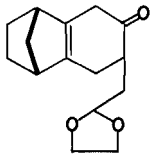

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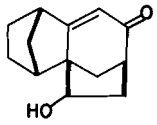

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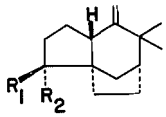
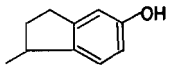


1a R_1 = Me R_2 = H

1b R_1 = H R_2 = Me



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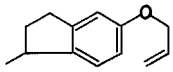

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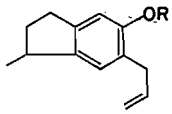
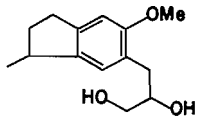


4 R = H

5 R = Me



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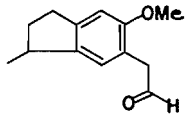

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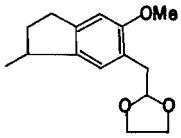

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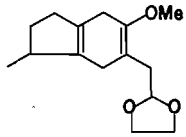

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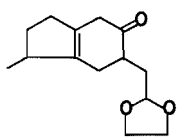

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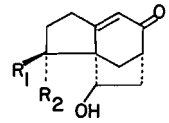
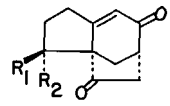


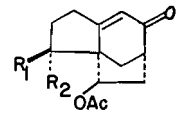
11a R_1 = Me R_2 = H

11b R_1 = H R_2 = Me



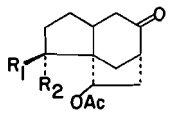
12a R_1 = Me R_2 = H

12b R_1 = H R_2 = Me



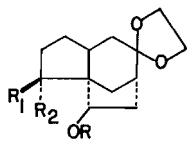
13a R_1 = Me R_2 = H

13b R_1 = H R_2 = Me



14a R_1 = Me R_2 = H

14b R_1 = H R_2 = Me



15a R = Ac R_1 = Me R_2 = H

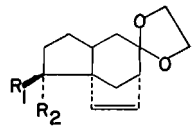
15b R = Ac R_1 = H R_2 = Me

16a R = H R_1 = Me R_2 = H

16b R = H R_1 = H R_2 = Me

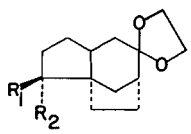
17a R = Xa R_1 = Me R_2 = H

17b R = Xa R_1 = H R_2 = Me



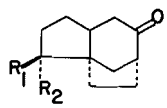
18a R_1 = Me R_2 = H

18b R_1 = H R_2 = Me



19a R_1 = Me R_2 = H

19b R_1 = H R_2 = Me



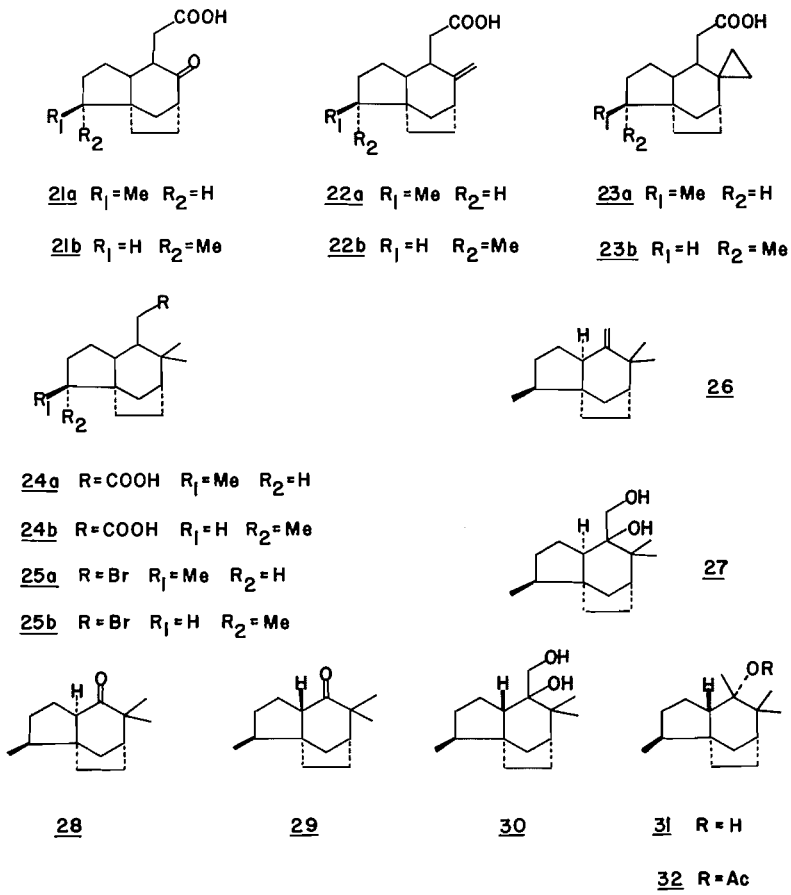
20a R_1 = Me R_2 = H

20b R_1 = H R_2 = Me

doublet, τ 9.04, $J = 7$ Hz for **11***a* and τ 8.85, $J = 7$ Hz for **11***b*.

The configurational assignments of the epimers (**11***a* and *b*) were made by comparing models and spectral data of the diketones (**12***a* and *b*) obtained via Jones' oxidation of the ketones (**11***a* and *b*). Models of these compounds showed that in epimer **12***a* the methyl group was directed away from the ketone while in epimer **12***b* the methyl group lay directly in the deshielding zone of the ketone. Accordingly, the n.m.r. spectra showed the methyl doublet of the ketone (**12***b*), τ 8.82, $J = 7$ Hz, definitely deshielded relative to the methyl doublet of ketone (**12***a*), τ 9.05, $J = 7$ Hz. The i.r. showed absorption maxima for the five-membered ketones, 1748 cm^{-1} for **12***a* and 1745 cm^{-1} for **12***b*. It is thus clear that the cyclization reaction with compound **10** is not stereospecific and that the stereospecificity previously encountered with **iii** must be due to the well known preference of the bicycloheptene system for exo attack by electrophillic reagents. Compounds **12***a* and *b* also provide conclusive evidence for our initial assumption about the course of the Claisen rearrangement, **3** → **4**. The presence in **12***a* and *b* of an α,β-unsaturated ketone (i.r., 1685 cm^{-1} for both) with one vinylic hydrogen which gives a singlet in the n.m.r. spectrum (τ 4.13 for both) does not allow any alternative structures for these two diastereoisomers. Although the alcohol (**11***b*) which has the undesired stereochemistry (for a tricyclovetivene synthesis) comprises 60% of the cyclized product mixture, it was, nevertheless, put to good use to find a possible synthetic pathway to convert the alcohol (**11***a*) to tricyclovetivene.

Acetylation of the alcohol (**11***b*) with acetic



anhydride and pyridine gave the acetate (**13***b*), which easily underwent hydrogenation in ethanol with palladium-on-charcoal to furnish the keto acetate (**14***b*) (m.p. 79–81 °C from hexane). It will be clear from the sequel that the hydrogenation was stereospecific and the hydrogens were added *trans* to the methyl group. Ketalization with ethylene glycol and *p*-toluenesulfonic acid gave the ketal (**15***b*), followed by hydrolysis in aqueous methanolic potassium hydroxide to yield the ketal alcohol (**16***b*). Treatment with carbon disulfide and methyl iodide resulted in formation of the ketal xanthate (**17***b*), which when pyrolyzed at 250 °C gave the unsaturated ketal (**18***b*). Hydrogenation over an excess of Raney nickel and deketalization in 80% acetic acid produced the tricyclic ketone (**20***b*) (DNP; m.p. 148–149 °C).

Stork alkylation of the ketone (**20***b*) with pyrolidine and ethyl bromoacetate followed by hydrolysis in methanolic potassium hydroxide yielded the keto acid (**21***b*). A Wittig reaction with methylidene-phosphorane was performed on the sodium salt of the carboxylic acid to give the unsaturated carboxylic acid (**22***b*), (n.m.r., vinyl protons at τ 5.47, $J = 14$ Hz). Simmons–Smith cyclopropanation of the olefin (**22***b*) with zinc–copper couple and diiodomethane produced the tetracyclic carboxylic acid (**23***b*), (n.m.r., cyclopropane methylenes at τ 9.67–9.87) which on hydrogenation over Adams catalyst gave the *gem*-dimethyl carboxylic acid (**24***b*) (n.m.r., *gem*-dimethyl singlets at τ 9.08 and 9.15).

Bromodecarboxylation using the modified Hunsdiecker method (4) with bromine and red mercuric oxide gave the tricyclic bromide (**25***b*) which when dehydrobrominated with lithium bromide and lithium carbonate in dimethylformamide produced the tricyclic hydrocarbon (**1***b*).

The second epimeric series possessing the natural tricyclovetivene methyl configuration (**11***a* to **25***a*) was processed by steps identical to those just discussed. (See Experimental for yield and physical properties of the compounds.)

Dehydrobromination of the tricyclic bromide (**25***a*) in the same manner used for **25***b* produced the tricyclic hydrocarbon (**26**).

By means of comparing the hydrocarbons **1***b* and **26** to natural tricyclovetivene (**1***a*) (2) it was now possible to establish the stereochemistry of the hydrogenated products (**14***a* and *b*) obtained from hydrogenation of the unsaturated ketones (**13***a* and *b*). The synthetic hydrocarbon (**26**) is not identical with tricyclovetivene (**1***a*) and must differ from it by the stereochemistry of the allylic proton. This is borne out by the fact that in the n.m.r. spectrum the doublets of the vinylic protons for **26** and tricyclovetivene (**1***a*) are significantly different (τ 5.17, $J = 5$ Hz; τ 5.33, $J = 8$ Hz respectively). It appears from models, that the vinylic protons in **26** and **1***a* must be strongly influenced by the configuration of the adjacent asymmetric center.

The synthetic hydrocarbon (**1***b*) is also not identical with tricyclovetivene (**1***a*) but the reason for this nonidentity must be only the configuration of the methyl group. This is borne out by the fact that the vinylic doublet in the n.m.r. spectrum of **1***b* is almost identical (τ 5.33, $J = 11$ Hz) with the same doublet in tricyclovetivene (**1***a*). It is thus clear that the methyl group influences the stereochemistry of the hydrogenation of the acetates (**13***a* and *b*) in such a manner that the hydrogenation proceeds always trans to this group.

Natural tricyclovetivene (**1***a*) and the synthetic epi-tricyclovetivene (**26**) were individually treated with osmium tetroxide to give the diols **30** and **27** respectively and these compounds were in turn cleaved with periodate to furnish the nor-ketones **29** and **28**, respectively. The "natural"[3] nor-ketone (**29**) (2) was epimerized in methanolic sodium methoxide to the "natural" nor-ketone (**28**) and the synthetic nor-ketone (**28**) was epimerized to the synthetic nor-ketone (**29**). The spectral data (i.r. and n.m.r.) of "natural" and synthetic nor-ketones (**28**) were completely superimposable as were the spectral data of "natural" and synthetic nor-ketones (**29**).

Since the Wittig reaction on the nor-ketones (**29**) gave a poor yield, the compounds were treated with methyl lithium yielding the synthetic and "natural" alcohols (**31**). Treatment with acetic anhydride in pyridine gave the unstable synthetic and "natural" acetates (**32**) which pyrolized *in situ* to give respectively synthetic racemic and "natural" tricyclovetivene (**1***a*), both with spectral data completely superimposable with those of natural tricyclovetivene (2). The reason why we have been able to cause elimination of the acetate (**32**) practically exclusively to form an exocyclic methylenic group must be its stereochemistry. The alcohol (**31**) has been produced by the action of methyl lithium on the nor-ketone (**29**) and very probably has the stereochemistry shown. As a consequence of this, a cyclic pyrolytic elimination of the acetate (**32**) to produce an endocyclic olefin is sterically impossible.

[3]"Natural" should be understood to mean "obtained from natural tricyclovetivene".

Experimental

Preparation of the Allyl Ether (3)

A solution of 1-methyl-indan-5-ol (**2**) (3) (14.6 g) in acetone (66 ml) was treated with potassium carbonate (14 g), potassium iodide (8.4 g), allyl chloride (9.6 g) and the mixture refluxed for 20 h. The resulting mixture was diluted with acetone, filtered, stripped of solvent to yield a residue which was dissolved in diethyl ether. The ethereal solution was washed twice with water, dried, and evaporated to yield 18.5 g of oil which was purified by silica gel (600 g, 20% benzene–light petroleum) column chromatography to furnish the allyl ether (**3**) (16.53 g, 88%) as a mobile oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{13}H_{16}O$: 188.1201. Found (mass spectroscopy): 188.1200.

The i.r. (CCl_4): 3080, 3012, 2955, 2860, 1640 (olefinic), 1610 cm^{-1} (aromatic). The n.m.r. (CCl_4): τ 3.07–3.51 (m, 3H, aromatic protons), 3.71–5.00 (m, 3H, vinyl protons), 5.60 (d, 2H, allyl ether methylenes), 8.75 (d, $J = 7$ Hz, 3H, methyl).

Rearrangement of 3 to 4

Allyl ether (**3**) (67 g) divided equally among four Pyrex ampoules, evacuated and sealed, was heated in an oil bath at 180–185 °C for 5 h. The combined contents were purified by silica gel (2 kg, 20% benzene in light petroleum) column chromatography to furnish the phenol (**4**) (38 g, 84%) as an oil homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{13}H_{16}O$: 188. Found (mass spectroscopy): 188.

The i.r. (CCl_4): 3615 (hydroxyl), 3540, 3080, 3010, 2955, 2860, 1630, 1615 cm^{-1}. The n.m.r. (CCl_4): τ 3.96–5.16 (m, 3H, vinyl protons), 6.71 (d, $J = 6$ Hz, 2H, allyl protons), 8.80 (d, $J = 7$ Hz, 3H, methyl).

Preparation of Methyl Ether (5)

A solution of the phenol (**4**) (37 g), sodium hydroxide (12 g), and dimethyl sulfate (22 ml) in water (80 ml) was stirred at room temperature for 1 h followed by addition of sodium hydroxide (2.4 g) in water (20 ml) and dimethyl sulfate (5 ml) and the total stirred of an addition 1 h. The mixture was diluted with diethyl ether and extracted twice with 10% aqueous sodium hydroxide which was in turn back extracted once with diethyl ether. The combined ethereal phases were dried and evaporated to give a residue which was purified on silica gel (1 kg, 20% benzene in light petroleum) column chromatography to yield the allyl methoxy compound (**5**) (33 g, 91%) as an oil homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{18}O$: 202.1358. Found (mass spectroscopy): 202.1352.

The i.r. (CCl_4): 3075, 2990, 2955, 2860, 2845, 1670 (olefinic), 1610 cm^{-1} (aromatic). The n.m.r. (CCl_4): τ 3.92–5.36 (m, 3H, vinyl protons), 6.36 (s, 3H, methoxyl), 6.72 (d, $J = 6$ Hz, 2H, allyl protons), 8.81 (d, $J = 7$ Hz, 3H, methyl).

Preparation of the Diol (6)

A homogeneous solution of the methyl ether (**5**) (2.02 g), tetrahydrofuran (25 ml), sodium chlorate (1.6 g), and water was treated with a solution of osmium tetroxide in tetrahydrofuran (1.0 ml, 80 mg/ml) and the total stirred at room temperature for 3 h. The solution was diluted with water and extracted with ether which in turn was dried and evaporated. The resulting residue was purified by silica gel (100 g, diethyl ether) column chromatography to yield the diol (**6**) (1.80 g, 76%) as an oil homogeneous in t.l.c.

Mol. Wt. for $C_{14}H_{20}O_3$: 236.1413. Found (mass spectroscopy): 236.1408.

The i.r. ($CHCl_3$): 3580 (hydroxyl), 3490, 2995, 2955, 2860, 1612 cm^{-1} (aromatic).

The n.m.r. ($CDCl_3$): τ 2.86–3.34 (m, 2H, aromatic protons), 6.26 (s, methoxyl), 8.80 (d, $J = 7$ Hz, 3H, methyl).

*Cleavage of **6** to the Aldehyde (7)*

A solution of the diol (**6**) (1.55 g) in tetrahydrofuran (20 ml) was treated with a solution of sodium periodate (15 g) in water (20 ml) and the total stirred at room temperature for 20 min. The mixture was filtered, diluted with diethyl ether, washed three times with water, dried, and evaporated to yield pure aldehyde (**7**) (1.32 g, 99%) as an oil, homogeneous in t.l.c.

Mol. Wt. for $C_{13}H_{16}O_2$: 204.1150. Found (mass spectroscopy): 204.1145.

The i.r. (CCl_4): 3000, 2955, 2860, 2840, 2720, 1725 (aldehyde), 1610 cm^{-1} (aromatic). The n.m.r. ($CDCl_3$): τ 0.40 (bs, 1H, aldehydic proton), 2.96–3.44 (m, 2H, aromatic protons), 6.24 (s, 3H, methoxyl), 8.76 (d, $J = 7$ Hz, 3H, methyl).

Preparation of the Acetal (8)

A solution of the aldehyde (**7**) (18 g), ethylene glycol (6.5 g), *p*-toluenesulfonic acid (0.5 g) all in benzene (600 ml) was refluxed over a water separator for 30 min. The cooled solution was washed with saturated sodium bicarbonate solution and water, dried, and evaporated to yield the acetal (**8**) (20.5 g, 100%) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{20}O_3$: 248.1413. Found (mass spectroscopy): 248.1406.

The i.r. (CCl_4): 2955, 2875, 1610 cm^{-1} (aromatic). The n.m.r. ($CDCl_3$): τ 2.90–3.34 (m, 2H, aromatic protons), 4.93 (t, 1H, acetal proton), 6.22 (s, 7H, methoxyl and acetal methylenes), 8.77 (d, $J = 7$ Hz, 3H, methyl).

Preparation of the Diene (9)

A solution of the ketal (**8**) (10 g) in diethyl ether (250 ml) and tertiary butanol (10 ml) was added dropwise over a period of 1/2 h to a stirred solution of lithium metal (20.7 g) in dry liquid ammonia (1000 ml) and the total stirred for 5 min, whereupon a solution of diethyl ether (20 ml) and tertiary butanol (250 ml) was added dropwise and the total stirred for an additional 24 h. Absolute ethanol (300 ml) was added until the blue color disappeared and the mixture was allowed to stand to evaporate the ammonia. The residue was taken up in ether, washed with saturated sodium chloride solution, dried, and evaporated. The resulting residue was purified by silica gel (500 g, benezene–ether) column chromatography to yield the diene (**9**) (6.5 g, 65%), homogeneous in t.l.c.

Mol. Wt. for $C_{15}H_{22}O_3$: 250. Found (mass spectroscopy): 250.

The i.r. (CCl_4): 2955, 2875, 1665 (olefinic), 1650 cm^{-1} (olefinic). The n.m.r. ($CDCl_3$): τ 5.08 (t, $J = 5$ Hz, 1H, acetal proton), 6.16 (s, acetal methylenes), 6.48 (s, 3H, methoxyl), 8.98 (d, $J = 7$ Hz, 3H, methyl).

Preparation of the β,γ-Unsaturated Ketone (10)

A solution of the diene (**9**) (1.0 g) in methanol (50 ml) was treated with a solution of oxalic acid (1.0 g) in water (10 ml) and the total stirred at room temperature for 45 min, followed by dilution with water and extraction with diethyl ether. The ethereal extract was washed with aqueous sodium bicarbonate solution and water, dried, and evaporated to give the ketone (**10**) (0.91 g, 100%) as an oil, homogeneous in t.l.c.

Mol. Wt. for $C_{14}H_{20}O_3$: 236. Found (mass spectroscopy): 236.

The i.r. (CCl_4): 2955, 2925, 2875, 2840, 1720 cm^{-1}, (ketone). The n.m.r. ($CDCl_3$): τ 5.02 (t, $J = 5$ Hz, 1H, acetal proton), 6.17 (s, 4H, acetal methylenes), 8.88 (d, $J = 7$ Hz, 3H, methyl).

Cyclization to the Alcohols (11a and b)

A solution of the ketone (**10**) (300 mg) in 80% acetic acid (3 ml) was heated in an oil bath at 80 °C for 3 h followed by evaporation of the solvent in high vacuum. The residue was purified by silica gel (20 g, benzene–ether) column chromatography to give the epimeric alcohols (**11***a* and *b*) (90 mg, 35%) as a semi-crystalline oil, appearing homogeneous in t.l.c. Dissolution of the mixture of epimeric alcohols in ether resulted in immediate crystallization of the alcohol (**11***b*), m.p. 167–168 °C. Repeated crystallizations succeeded in removing all this epimer from the mother liquors.

Anal. Calcd. for $C_{12}H_{16}O_2$ (mol. wt. 192) (alcohol **11***b*): C, 74.96; H, 8.39. Found (192 (mass spectroscopy)): C, 74.60; H, 8.32.

The i.r. (CCl_4): 3615, 3450, 2955, 2860, 1680 (α,β-unsaturated ketone), 1630 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ 4.14 (s, 1H, vinyl proton), 5.51 (m, 1H, adjacent to OH), 8.85 (d, $J = 7$ Hz, 3H, methyl), λ_{max} (EtOH): 244.5 nm (11 700).

The oily residue from the mother liquors cyrstallized from ether–hexane to give the alcohol (**11***a*) m.p. 68–69 °C. Ratio of alcohols (**11***a* and *b*) was 2:3.

Anal. Calcd. for $C_{12}H_{16}O_2$ (mol. wt. 192) (alcohol **11***a*): C, 74.96; H, 8.39. Found (192 (mass spectroscopy)): C, 75.57; H, 8.35.

The i.r. (CCl_4): 3625, 3425, 2955, 2860, 1685 (α,β-unsaturated ketone), 1630 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ 4.34 (s, 1H, vinyl proton), 6.09 (m, 1H, adjacent to OH), 9.04 (d, $J = 7$ Hz, 3H, methyl), λ_{max} (EtOH): 244.5 nm (11 100).

*Formation of the Diketones (**12***a and b)*

A solution of the alcohol (**11***b*) (150 mg) in acetone at 0 °C was treated dropwise with Jones' reagent to a slight excess followed by evaporation of the solvent. The residue was taken up in water extracted with ether, dried, and evaporated to give an oil which was purified by silica gel (20 g, benzene–ether) column chromatography to furnish the diketone (**12***b*) (99 mg, 66%), homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{12}H_{14}O_2$ (diketone **12***b*): 190.0994. Found (mass spectroscopy): 190.0990.

The i.r. (CCl_4): 2955, 2925, 2860, 1745 (five-membered ketone), 1685 (conjugated ketone), 1625 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ 4.13 (s, 1H, vinyl proton), 8.82 (d, $J = 7$ Hz, 3H, methyl), λ_{max} (EtOH): 228.5 (10 000), 253 nm (7300).

The epimeric diketone (**12***a*) was obtained in the same manner.

Mol. Wt. Calcd. for $C_{12}H_{14}O_2$ (diketone **12***a*): 190.0994 Found (mass spectroscopy): 190.0990.

The i.r. (CCl_4): 2955, 2925, 2860, 1748 (five-membered ketone), 1685 (conjugated ketone), 1630 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ 4.13 (s, 1H, vinyl proton), 9.05 (d, $J = 7$ Hz, 3H, methyl), λ_{max} (EtOH): 226 (9800), 251 nm (7400).

*Preparation of the Acetates (**13***a and b)*

A solution of the alcohol (**11***a*) (1.0 g) in acetic anhydride (4 ml) and pyridine (3 ml) was allowed to stand overnight followed by evaporation under high vacuum to give a thick oil which was purified by silica gel (40 g, 30% diethyl ether in benzene) column chromatography to yield the acetate (**13***a*) (1.22 g, 100%), homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{18}O_3$: 234.1256. Found (mass spectroscopy): 234.1250.

The i.r. (CCl_4): 2955, 2855, 1742 (acetate), 1685 (conjugated ketone), 1630 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ 4.31 (s, 1H, vinyl proton), 5.11 (m, 1H, adjacent to acetate), 7.91 (s, 3H, acetate methyl), 9.01 (d, $J = 7$ Hz, 3H, methyl), λ_{max}(EtOH): 234 nm (13 100).

By the same method, acetylation of alcohol (**11***b*) (3.45 g) gave the acetate (**13***b*) (4.20 g, 100%) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{18}O_3$: 234.1256. Found (mass spectroscopy): 234.1250.

The i.r. (CCl_4): 2955, 2860, 1750 (acetate), 1685 (conjugated ketone), 1630 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ 4.09 (bs, 1H, vinyl proton), 4.70 (m, 1H, proton adjacent to acetate), 8.00 (s, 3H, acetate methyl), 8.91 (d, $J = 6$ Hz, 3H, methyl), λ_{max} (EtOH): 238 nm (12 600).

*Preparation of Keto Acetates (**14***a and b)*

A mixture of the acetate (**13***a*) (1.0 g) and 10% palladium-on-charcoal (0.1 g) all in ethanol (30 ml) was hydrogenated for 3 h followed by filtration and evaporation. The resulting oil was immediately dissolved in acetone (20 ml) and treated with an excess of Jones' reagent followed by dilution with water and extraction with ether. The ethereal extract was dried, evaporated, and the residue purified by silica gel (35 g, 10% ether–benzene) column chromatography to yield the keto acetate (**14***a*) (758 mg, 75%) as a clear oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{20}O_3$: 236.1413. Found (mass spectroscopy): 236.1407.

The i.r. (CCl_4): 2955, 2860, 1740 (acetate), 1715 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 5.03 (m, 1H, adjacent to acetate), 7.95 (s, acetate methyl), 8.95 (d, $J = 6$ Hz, 3H, methyl).

By the same method, reduction of the acetate (**13***b*) (2.23 g) gave the acetate (**14***b*) (1.57 g, 70%) as an oil which crystallized from hexane, m.p. 79–81 °C.

Anal. Calcd. for $C_{14}H_{20}O_3$ (mol. wt. 236): C, 71.15; H, 8.51. Found (236 (mass spectroscopy)): C, 70.97; H, 8.35.

The i.r. (CCl_4): 2955, 2905, 2870, 1740 (acetate), 1715 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 4.60 (m, 1H, proton adjacent to acetate), 7.94 (s, 3H, acetate methyl), 9.01 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Ketal Acetates (**15***a and b)*

A solution of the keto acetate (**14***a*) (1.0 g), ethylene glycol (620 mg), and *p*-toluenesulfonic acid (50 mg) all in dry benzene (25 ml) was refluxed over a water separator for 2 h. The solution was cooled, washed with saturated sodium bicarbonate solution and water, dried, and evaporated to give the ketal acetate (**15***a*) (1.2 g, 100%) homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{16}H_{24}O_4$: 280.1675. Found (mass spectroscopy): 280.1668.

The i.r. (CCl_4): 2955, 2875, 1737 cm^{-1} (acetate). The n.m.r. ($CDCl_3$): τ 5.12 (m, 1H, adjacent to acetate), 6.12 (s, 4H, ketal methylenes), 7.94 (s, acetate methyl), 9.05 (d, $J = 6$ Hz, 3H, methyl).

By the same method, ketalization of the keto acetate (**14***b*) (580 mg) gave the ketal acetate (**15***b*) (678 mg, 97%) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{16}H_{24}O_4$: 280.1675. Found (mass spectroscopy): 280.1670.

The i.r. (CCl_4): 2955, 2905, 2870, 1740 (acetate), 1245, 1045 cm^{-1}. The n.m.r. ($CDCl_3$): τ 4.87 (m, 1H, proton adjacent to acetate), 6.15 (s, 4H, ketal methylenes), 8.00 (s, 3H, acetate methyl), 9.10 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Ketal Alcohols (**16***a and b)*

A solution of the ketal acetate (**15***a*) (560 mg) in 5% methanolic potassium hydroxide (10 ml) was refluxed for 3 h. The solution was cooled, diluted with water, extracted with diethyl ether, dried, and evaporated to furnish the ketal alcohol (**16***a*) (480 mg, 100%) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O_3$: 238. Found (mass spectroscopy): 238.

The i.r. (CCl_4): 3620 (hydroxyl), 3495, 2950, 2875 cm^{-1}. The n.m.r. ($CDCl_3$): τ 6.14 (s, 4H, ketal methylenes), 8.95 (d, $J = 6$ Hz, 3H, methyl).

By the same method, hydrolysis of the ketal acetate (**15***b*) (572 mg) gave the ketal alcohol (**16***b*) (480 mg, 100%) as an oil homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O_3$: 238.1569. Found (mass spectroscopy): 238.1567.

The i.r. (CCl_4): 3625 (hydroxyl), 3500, 2955, 2905, 2870,

1455, 1050 cm^{-1}. The n.m.r. ($CDCl_3$): τ 5.73 (m, 1H, proton adjacent to alcohol), 6.13 (s, 4H, ketal methylenes), 9.05 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of Xanthates (**17a** and **b**)*

A mixture of ketal alcohol (**16***a*) (480 mg), 75% sodium hydride in mineral oil (100 mg) all in tetrahydrofuran (25 ml) was refluxed for 1 h followed by cooling and addition of carbon disulfide (4 ml) with the total being heated for an additional $1\frac{1}{2}$ h. The mixture was again cooled and treated with methyl iodide (4 ml) followed by reflux for 1 h. The solvent was distilled off and the residue dissolved in benzene which in turn was washed with water, dried, and evaporated. Chromatography of the residue on silica gel (25 g, 10% ether–benzene) furnished the xanthate (**17***a*) (560 mg, 85%) as a yellow oil which crystallized from hexane, m.p. 108–109 °C.

Anal. Calcd. for $C_{16}H_{24}O_3S_2$ (mol. wt. 328): C, 58.51; H, 7.37; S, 19.53. Found (328 (mass spectroscopy)): C, 58.66; H, 7.40; S, 19.18.

The i.r. (CCl_4): 2950, 2875, 1230 cm^{-1} (xanthate). The n.m.r. ($CDCl_3$): τ 4.34 (m, 1H, proton adjacent to xanthate), 6.10 (s, 4H, ketal methylenes), 7.44 (s, 3H, xanthate methyl), 8.95 (d, $J = 6$ Hz, 3H, methyl).

By the same method, addition to the ketal alcohol (**16***b*) (770 mg) gave the xanthate (**17***b*) (890 mg, 84%) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{16}H_{24}O_3S_2$: 328. Found (mass spectroscopy): 328.

The i.r. (CCl_4): 2950, 2870, 1220, 1060 cm^{-1}. The n.m.r. ($CDCl_3$): τ 4.13 (m, 1H, proton adjacent to xanthate), 6.10 (s, 4H, ketal methylenes), 7.40 (s, 3H, xanthate methyl), 9.07 (d, $J = 6$ Hz, 3H, methyl).

*Formation of the Olefins (**18a** and **b**)*

The xanthate (**17***a*) (328 mg) was pyrolyzed in an open Pyrex tube at 190 °C for 30 min followed by distillation to yield the olefin (**18***a*) (170 mg, 95%) as an oil b.p. 150 °C/1 mm, appearing homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{20}O_2$: 220. Found (mass spectroscopy): 220.

The i.r. (CCl_4): 3050 (olefin), 2950, 2875, 1650 (olefin), 1120 cm^{-1}. The n.m.r. ($CDCl_3$): τ 4.20 (m, 2H, vinyl protons), 6.10 (s, 4H, ketal methylenes), 9.12 (d, $J = 6$ Hz, 3H, methyl).

By the same method, the xanthate (**17***b*) (730 mg) was pyrolyzed to give the olefin (**18***b*) (502 mg) as a liquid, b.p. 250 °C/16 mm, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{20}O_2$: 220.1463. Found (mass spectroscopy): 220.1458.

The i.r. (CCl_4): 3050 (olefin), 2950, 2860, 1640 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ 3.83–4.27 (m, 2H, vinyl protons), 6.10 (s, 4H, ketal methylenes), 9.10 (d, $J = 6$ Hz, 3H, methyl).

*Hydrogenation of the Olefins, **18a** and **b** to **19a** and **b***

A mixture of the olefin (**18***a*) (1.0 g) in ethanol (150 ml) and Raney nickel (40 g) was hydrogenated for 4 h followed by filtration and evaporation to yield the saturated ketal (**19***a*) (953 mg, 95%), homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O_2$: 222. Found (mass spectroscopy): 222.

The i.r. (CCl_4): 2950, 2875, 1110 cm^{-1} (ketal). The n.m.r. ($CDCl_3$): τ 6.11 (s, 4H, ketal methylenes), 9.18 (d, $J = 6$ Hz, 3H, methyl).

By the same method, hydrogenation of the olefin (**18***b*) (502 mg) gave the saturated ketal (**19***b*) (408 mg) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O_2$: 222. Found (mass spectroscopy): 222.

The i.r. (CCl_4): 2950, 2860, 1102 cm^{-1} (ketal). The n.m.r. ($CDCl_3$): τ 6.09 (s, 4H, ketal methylenes), 9.13 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Tricyclic Ketones (**20a** and **b**)*

A solution of the ketal (**19***a*) (1.0 g) in 80% acetic acid was heated at 80 °C for 30 min followed by dilution with water and extraction with chloroform. The chloroform extract was dried and evaporated to furnish the tricyclic ketone (**20***a*) (802 mg, 100%) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{12}H_{18}O$ (the ketone): 178. Found (mass spectroscopy): 178.

The i.r. (CCl_4): 2955, 2875, 1715 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 7.34, 7.84, 8.07, 8.47, 9.08 (d, $J = 6$ Hz, 3H, methyl).

Anal. Calcd. for $C_{18}H_{22}N_4O_4$ (dinitrophenylhydrazone, m.p. 156–157 °C): C, 60.32; H, 6.18; N, 15.64. Found: C, 59.45; H, 6.09; N, 15.93.

By the same method, deketalization of the ketal (**19***b*) (408 mg) gave the tricyclic ketone (**20***b*) (324 mg, 82% based on the xanthate (**17***b*)) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{12}H_{18}O$: 178. Found (mass spectroscopy): 178.

The i.r. (CCl_4): 2955, 2875, 1715 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 7.33, 7.80, 8.33, 8.47, 9.06 (d, $J = 6$ Hz, 3H, methyl).

Anal. Calcd. for $C_{18}H_{22}N_4O_4$ (dinitrophenylhydrazone, m.p. 148–149 °C): C, 60.32; H, 6.18; N, 15.65. Found: C, 60.50; H, 6.12; N, 15.72.

*Preparation of the Keto Acids (**21a** and **b**)*

A solution of the tricyclic ketone (**20***a*) (600 mg) and pyrrolidine (1.19 g) in dry benzene (20 ml) was refluxed under nitrogen and a water separator for 15 h followed by replacement of the solvent with dry dioxane (15 ml). Ethyl bromoacetate (1.11 g) in dioxane (5 ml) was added dropwise over a period of 1/4 h and the mixture heated at 100 °C under nitrogen for 24 h, followed by evaporation of the solvent and treatment of the residue with water (20 ml) at reflux for 2 h. The cooled aqueous solution was extracted with diethyl ether and in turn washed with water, saturated sodium chloride solution, dried, and evaporated to give a residue (710 mg) which was saponified by refluxing in 1 *N* methanolic potassium hydroxide solution (15 ml) for 2 h. The reaction was stripped of solvent and the residue taken up in water, followed by extraction with diethyl ether which on drying and evaporation yielded starting ketone (**20**) (232 mg). The aqueous solution was acidified with 5% hydrochloric acid and extracted with diethyl ether and in turn washed with water, saturated sodium chloride solution, dried, and evaporated to give the keto acid (**21**) (266 mg, 72% with recovery) as a thick oil, homogeneous in t.l.c. Recycling furnished a 54% overall yield.

Anal. Calcd. for $C_{14}H_{20}O_3$ (mol. wt. 236): C, 71.16; H, 8.53; O, 20.31. Found (236 (mass spectroscopy)): C, 70.95; H, 8.55; O, 20.39.

The i.r. (CCl_4): 3525, 2950, 2860, 1715 (ketone), 1710 cm^{-1} (carboxylic acid). The n.m.r. ($CDCl_3$): τ 0.53 (bs. 1H, carboxylic acid proton), 9.05 (d, $J = 6$ Hz, 3H, methyl).

By the same method, the tricyclic ketone (**20***b*) (340 mg) was alkylated to give the keto acid (**21***b*) (79 mg, 81% with recovery) as an oil, homogeneous in t.l.c. Recycling furnished a total of 225 mg (50%).

Mol. Wt. Calcd. for $C_{14}H_{20}O_3$: 236. Found (mass spectroscopy): 236.

The i.r. (CCl_4): 3530, 2960, 2875, 1715 cm^{-1} (carboxylic acid and ketone). The n.m.r. ($CDCl_3$): τ −0.17 (bs, 1H, carboxylic acid proton), 9.05 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Tricyclic Olefins (**22***a and b)*

A stirred suspension of oil-free sodium hydride (197 mg) in dimethylsulfoxide (20 ml) under nitrogen was treated with methyl triphenylphosphonium iodide (1.26 g) and stirred for 2 h followed by addition of a solution of the keto acid (**21***a*) (369 mg) in dimethylsulfoxide (5 ml) and the total stirred at room temperature for 4 h and at 75 °C for 24 h. The solution, cooled well, was acidified dropwise with 5% hydrochloric solution and in turn taken up in chloroform. The chloroform was washed with water and evaporated to give a residue which was taken up in 5% sodium hydroxide solution, washed with diethyl ether, and acidified with 5% hydrochloric acid. The aqueous mixture was extracted with diethyl ether, washed with water and saturated sodium chloride solution, dried, and evaporated to give the tricyclic olefin (**22***a*) (327 mg, 89%) as a thick oil, homogeneous in t.l.c.

Anal. Calcd. for $C_{15}H_{22}O_2$ (mol. wt. 234): C, 76.88; H, 9.46; O, 13.66. Found (234 (mass spectroscopy)): C, 76.58; H, 9.25; O, 13.71.

The i.r. (CCl_4): 3530, 2950, 2860, 1705 (carboxylic acid), 1640 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ + 0.57 (bs, 1H, carboxylic acid proton), 5.42 (d, $J = 20$ Hz, 2H, vinyl protons), 9.18 (d, $J = 6$ Hz, 3H, methyl).

By the same method, the Wittig reaction on the keto acid (**21***b*) (235 mg) gave the tricyclic olefin (**22***b*) (181 mg, 78%) as a thick oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{22}O_2$: 234.1620. Found (mass spectroscopy): 234.1616.

The i.r. (CCl_4): 3530, 3080, 2950, 2875, 1705 (carboxylic acid), 1635 cm^{-1} (olefin). The n.m.r. ($CDCl_3$): τ −0.83 (bs, 1H, carboxylic acid proton), 5.47 (d, $J = 14$ Hz, 2H, vinyl protons), 9.15 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Tetracyclic Carboxylic Acids (**23***a and b)*

A suspension of zinc–copper couple (338 mg), a few crystals of iodine, and a few drops of diiodomethane all in dry diethyl ether (5 ml) was stirred until the iodine color was absent followed by addition of diiodomethane (1.98 g) and the total refluxed for 1/2 h. The mixture was cooled and treated with a solution of the tricyclic olefin (**22***a*) (290 mg) in dry diethyl ether (5 ml) and the total refluxed for 4 days. The mixture was filtered, diluted with diethyl ether, washed with 5% hydrochloric acid and water followed by extraction with 5% sodium hydroxide solution which was in turn washed with diethyl ether, acidified with 5% hydrochloric acid, and extracted with diethyl ether. The ethereal extract was washed with water, saturated sodium chloride solution, dried, and evaporated to give the tetracyclic carboxylic acid (**23***a*) (214 mg, 70%) as a thick oil, homogeneous in t.l.c.

Anal. Calcd. for $C_{16}H_{24}O_2$ (mol. wt. 248): C, 77.37; H, 9.74; O, 12.88. Found (248 (mass spectroscopy)): C, 76.82; H, 9.61; O, 13.75.

The i.r. (CCl_4): 3525, 2945, 2865, 1705 cm^{-1} (carboxylic acid). The n.m.r. ($CDCl_3$): τ −1.10 (bs, 1H, carboxylic acid proton), 9.15 (d, $J = 6$ Hz, 3H, methyl), 9.65–9.87 (m, 4H, cyclopropane methylenes).

By the same method, from the tricyclic olefin (**22***b*) (152 mg) was prepared the tetracyclic carboxylic acid (**23***b*) (138 mg, 72%) as a thick oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{16}H_{24}O_2$: 248. Found (mass spectroscopy): 248.

The i.r. (CCl_4): 3530, 3075, 3005, 2955, 2875, 1705 cm^{-1} (carboxylic acid). The n.m.r. ($CDCl_3$): τ −0.73 (bs, 1H, carboxylic acid proton), 9.15 (d, $J = 6$ Hz, 3H, methyl), 9.67–9.87 (m, 4H, cyclopropane methylenes).

*Hydrogenation of **23***a and b to the Tricyclic Carboxylic Acids (**24***a and b)*

A mixture of the tetracyclic carboxylic acid (**23***a*) (660 mg) and Adams catalyst (660 mg) all in glacial acetic acid (20 ml) was hydrogenated at 2000 p.s.i. for 24 days at room temperature. The mixture was filtered and evaporated to furnish the tricyclic carboxylic acid (**24***a*) (562 mg, 84%) as a clear, colorless, thick oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{16}H_{26}O_2$: 250.1933. Found (mass spectroscopy): 250.1924.

The i.r. (CCl_4): 2950, 2865, 1705 cm^{-1} (carboxylic acid). The n.m.r. ($CDCl_3$): τ −0.20 (bs, 1H, carboxylic acid proton), 9.10 (s, 6H, two methyls), 9.15 (d, $J = 6$ Hz, 3H, methyl).

By the same method, hydrogenation of the tetracyclic carboxylic acid (**23***b*) (288 mg) gave the tricyclic carboxylic acid (**24***b*) (261 mg, 90%) as a thick oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{16}H_{26}O_2$: 250.1933. Found (mass spectroscopy): 250.1928.

The i.r. (CCl_4): 3530, 2950, 2870, 1705 cm^{-1} (carboxylic acid). The n.m.r. ($CDCl_3$): τ −1.30 (bs, 1H, carboxylic acid proton), 9.08 (s, 3H, methyl), 9.15 (s, 3H, methyl), 9.15 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Tricyclic Bromides (**25***a and b)*

A refluxing mixture of the tricyclic carboxylic acid (**24***a*) (550 mg) and red mercuric oxide (570 mg) in dry carbon tetrachloride (8 ml) was treated dropwise with a solution of bromine (422 mg) in dry carbon tetrachloride (2 ml) and the total refluxed for an additional 1 h. The mixture was filtered, diluted with carbon tetrachloride, washed with 5% sodium hydroxide solution, water, saturated sodium chloride solution, dried, and evaporated. The labile residue (594 mg) was immediately purified by preparative silica gel t.l.c. (light petroleum) to furnish the tricyclic bromide (**25***a*) (156 mg, 25%) as a clear colorless oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{25}Br$: 285. Found (mass spectroscopy): m/e 286, 284.

The i.r. (film): 2950, 2865, 1470, 1235, 760 cm^{-1}. The n.m.r. ($CDCl_3$): τ 6.50 (m, 2H, protons α to bromine), 9.07 (s, 3H, methyl), 9.10 (s, 3H, methyl), 9.15 (d, $J = 6$ Hz, 3H, methyl).

By the same method, bromodecarboxylation of the tricyclic carboxylic acid (**24***b*) (260 mg) gave the tricyclic bromide (**25***b*) (103 mg, 36%) as a clear colorless liquid, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{25}Br$: 285. Found (mass spectroscopy): 284, 286.

The i.r. (film): 2950, 2875, 1460, 1230 cm^{-1}. The n.m.r.

($CDCl_3$): τ 6.33–6.87 (m, 2H, protons α to bromine), 8.97 (s, 3H, methyl), 9.10 (s, 3H, methyl), 9.15 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of epi-Tricyclovetivene (**26**)*

A mixture of the tricyclic bromide (**25**) (150 mg), lithium bromide (277 mg), and lithium carbonate (235 mg) all in dimethylformamide (3 ml) was refluxed under nitrogen for 90 min. The mixture was diluted with ice-cold 5% hydrochloric acid until solution occurred, followed by extraction with diethyl ether. The ethereal extract was washed with 5% hydrochloric acid, water, saturated sodium chloride solution, and the ether fractionally distilled off. The residual liquid was purified by preparative silica gel t.l.c. (light petroleum) to furnish epi-tricyclovetivene (**26**) (92 mg, 85%) as a clear colorless liquid, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{24}$: 204.1878. Found (mass spectroscopy): 204.1872.

The i.r. (film): 3075 (olefin), 2950, 2860, 1630 (olefin), 890 cm^{-1}. The n.m.r. ($CDCl_3$): τ 5.17 (d, $J = 4$ Hz, 2H, vinyl protons), 7.77 (bt, 1H, allyl proton), 8.85 (s, 3H, methyl), 8.92 (s, 3H, methyl), 9.15 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Methyl Epimer (**1b**) of Tricyclovetivene*

A mixture of the tricyclic bromide (**25***b*) (100 mg), lithium bromide (183 mg), and lithium carbonate (155 mg) all in dimethylformamide (2 ml) was refluxed under nitrogen for 90 min. The reaction mixture was cooled, diluted with ice-cold 5% hydrochloric acid until solution occurred, and extracted with ether. The ethereal extract was washed with 5% hydrochloric acid, water, dried, and the solvent fractionally distilled off. The residual liquid was purified by preparative silica gel t.l.c. (light petroleum) to furnish the methyl epimer (**1***b*) (35 mg, 49%) of tricyclovetivene as a clear colorless liquid, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{24}$: 204.1878. Found (mass spectroscopy): 204.1875.

The i.r. (film): 3080 (olefin), 2940, 2860, 1635 (olefin), 1455, 1375, 890, 735 cm^{-1}. The n.m.r. ($CDCl_3$): τ 5.33 (d, $J = 11$ Hz, 2H, vinyl protons), 7.60 (bt, 1H, allyl proton), 8.45, 8.92 (s, 6H, 2 methyls), 9.15 (d, $J = 6$ Hz, 3H, methyl).

*Spectra of Natural Tricyclovetivene (**1a**)*

The i.r. (film): 3080 (olefin), 2940, 2860, 1635 (olefin), 1460, 1375, 890 cm^{-1}. The n.m.r. ($CDCl_3$): τ 5.33 (d, $J = 8$ Hz, 2H, vinyl protons), 7.47 (bt, 1H, allylic proton), 8.23, 8.57, 8.90 (s, 3H, methyl), 8.93 (s, 3H, methyl), 9.05 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Tricyclic Diol (**27**)*

A solution of epi-tricyclovetivene (**26**) (59 mg) in dry pyridine (1.1 ml) was treated with a tetrahydrofuran solution (1 g OsO_4/4 ml) of osmium tetroxide (0.32 ml) and the total stirred at room temperature for 3 h. The resulting black mixture was treated with a solution of sodium bisulfite (134 mg) in water (2.5 ml) and pyridine (1.5 ml) and the total stirred for 30 min at room temperature. The solution was extracted with methylene chloride, washed with saturated sodium chloride solution, dried, and evaporated. The residue was purified by preparative silica gel t.l.c. (chloroform) to give the tricyclic diol (**27**) 56 mg, 81% as a clear, colorless, thick oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{26}O_2$: 238.1933. Found (mass spectroscopy): 238.1938.

The i.r. (film): 3400 (hydroxyl), 2950, 2865, 1465, 1025 cm^{-1}. The n.m.r. ($CDCl_3$): τ 6.50 (s, 2H, methylenes of primary alcohol), 7.83 (bs, 2H, exchanges with D_2O), 8.97 (s, 3H, methyl), 9.07 (s, 3H, methyl) 9.15 (d, $J = 6$ Hz, 3H, methyl).

*Cleavage of **27** to epi-Tricyclovetivene Nor-ketone (**28**)*

A homogeneous solution of the tricyclic diol (**27**) (56 mg) in tetrahydrofuran (1.5 ml) and water (1 ml) was treated with powdered sodium meta periodate (500 mg) and the total stirred at room temperature for 30 min. The mixture was filtered, diluted with diethyl ether, washed with water, saturated sodium chloride solution, dried, and evaporated to give epi-tricyclovetivene nor-ketone (**28**) (43 mg, 90%) as a clear colorless liquid, homogeneous on t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O$: 206.1671. Found (mass spectroscopy): 206.1670.

The i.r. (film): 2950, 2860, 1695 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 7.70 (bt, 1H, proton α to ketone), 8.85 (s, 3H, methyl), 8.92 (s, 3H, methyl), 9.08 (d, $J = 6$ Hz, 3H, methyl).

*Epimerization of **28** to Tricyclovetivene Nor-ketone (**29**)*

A solution of epi-tricyclovetivene nor-ketone (**28**) (30 mg) in 1% methanolic sodium methoxide (1 ml) was refluxed for 15 h followed by evaporation of the solvent. The residue was diluted with water and extracted with diethyl ether which in turn was washed with water, saturated sodium chloride solution, dried, and evaporated. The residual liquid consisting of a 1:1 mixture of epimers (**28** and **29**) was purified and the epimers separated by preparative silica gel t.l.c. (10% diethyl ether–light petroleum). The unepimerized epimer (**28**) was exhaustively epimerized to yield a total of tricyclovetivene nor-ketone (**29**) (19 mg, 63%) as a clear colorless liquid, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O$: 206.1671. Found (mass spectroscopy): 206.1670.

The i.r. (film): 2950, 2860, 1705 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 7.07 (bt, 1H, proton α to ketone), 8.80 (s, 3H, methyl), 8.95 (s, 3H, methyl), 9.01 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the "Natural"[3] Tricyclic Diol (**30**)*

A solution of natural tricyclovetivene (**1a**) (102 mg) in dry pyridine (2 ml) was treated with a solution (0.52 ml) of osmium tetroxide (1 g OsO_4/4 ml tetrahydrofuran) and the total stirred at room temperature for 3 h. The mixture was treated with a solution of sodium bisulfite (230 mg) in water (4 ml) and pyridine (2.5 ml) and stirred for 30 min at room temperature. The solution was extracted with methylene chloride, washed with saturated sodium chloride solution, dried, and evaporated. The residual oil was purified by preparative silica gel chromatography (chloroform) and crystallized from light petroleum to furnish the "natural" tricyclic diol (**30**) (100 mg, 84%) as white prisims, m.p. 86.5–87.0 °C (lit. (2) 84–84.5).

Anal. Calcd. for $C_{15}H_{26}O_2$ (mol. wt. 238: C, 75.58; H, 11.00; O, 13.42. Found (238 (mass spectroscopy)): C, 75.93; H, 10.84; O, 13.33.

The i.r. (film): 3500 (hydroxyl), 2950, 2865, 1465, 1025 cm^{-1}. The n.m.r. ($CDCl_3$): τ 6.20 (d, $J = 5$ Hz, 2H, methylene of primary alcohol), 7.27 (s, 1H, exchanges with D_2O), 7.67 (t, $J = 5$ Hz, 1H, exchanges with D_2O), 8.93 (s, 3H, methyl), 9.03 (s, 3H, methyl), 9.08 (d, $J = 6$ Hz, 3H, methyl).

Cleavage of ***30*** *to "Natural" Tricyclovetivene Nor-ketone (****29****)*

A homogeneous solution of the tricyclic diol (**30**) (90 mg) in tetrahydrofuran (2 ml) and water (1.5 ml) was treated with powdered sodium meta periodate (813 mg) and the total stirred at room temperature for 30 min. The mixture was filtered, diluted with diethyl ether, washed with water, saturated sodium chloride solution, dried, and evaporated to give "natural" tricyclovetivene nor-ketone (**29**) (77 mg, 99%) as a clear colorless liquid, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O$: 206.1671. Found (mass spectroscopy): 206.1670.

The i.r. (film): 2950, 2860, 1705 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 7.07 (t, 1H, proton α to ketone), 8.80 (s, 3H, methyl), 8.95 (s, 3H, methyl), 9.01 (d, $J = 6$ Hz, 3H, methyl).

Epimerization of "Natural" ***29*** *to "Natural" epi-Tricyclovetivene Nor-ketone (****28****)*

A solution of the "natural" tricyclovetivene nor-ketone (**29**) (77 mg) in 1% methanolic sodium ethoxide solution (5 ml) was refluxed for 15 h followed by evaporation of the solvent. The residue was diluted with water, extracted with ether, washed with water, saturated sodium chloride solution, dried, and evaporated to give a 1:1 mixture of the epimers (**28** and **29**). The epimers were separated by preparative silica gel t.l.c. (10% diethyl ether–light petroleum). The unepimerized "natural" nor-ketone (**28**) was recycled to give a total of "natural" epi-tricyclovetivene nor-ketone (**28**) (39 mg, 50%) as a clear colorless oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{14}H_{22}O$: 206.1671. Found (mass spectroscopy): 206.1670.

The i.r. (film): 2950, 2860, 1695 cm^{-1} (ketone). The n.m.r. ($CDCl_3$): τ 7.70 (bt, 1H, proton α to ketone), 8.85 (s, 3H, methyl), 8.92 (s, 3H, methyl), 9.08 (d, $J = 6$ Hz, 3H, methyl).

*Preparation of the Tricyclic Alcohol (****31****)*

A solution of the "natural" nor-ketone (**29**) (60 mg) in anhydrous ether (1 ml) was treated dropwise with an ethereal solution of methyl lithium (excess) and the total refluxed for 1 h. The reaction mixture was diluted with wet ether and in turn washed with water. The ethereal extract was dried and evaporated to yield the "natural" tricyclic alcohol (**31**) (60 mg, 93%) as an oil, homogeneous in t.l.c.

Mol. Wt. Calcd. for $C_{15}H_{26}O$: 222.1984. Found (mass spectroscopy): 222.1977.

The i.r. (CCl_4): 3605 (hydroxyl), 2950, 2860, 1460, 1390, 1370 cm^{-1}. The n.m.r. ($CDCl_3$): τ 8.97 (s, 3H, methyl), 9.02 (s, 3H, methyl), 9.07 (s, 3H, methyl), 9.12 (d, $J = 6$ Hz, 3H, methyl).

By the same method, synthetic nor-ketone (**29**) (5.2 mg) was converted to the synthetic alcohol (**31**) (5.6 mg, 100%).

Analysis: all analytical data (i.r., n.m.r., mass, and t.l.c.) for synthetic alcohol (**31**) were superimposable with that shown above for "natural" alcohol (**31**).

*Conversion of the Alcohol (****31****) to Tricyclovetivene (****1a****)*

A solution of the "natural" alcohol (**31**) (90 mg) in anhydrous acetic anhydride (0.7 ml) and anhydrous pyridine (0.7 ml) was heated at 120 °C for 60 h. After cooling, the reaction mixture was chromatographed on a silica gel column (light petroleum) yielding a mixture of exocyclic and endocyclic olefins which was purified by gas–liquid phase chromatography (15 ft × 1/4 in. column of 30% SE-30 at 225 °C) to give the "natural" tricyclovetivene (**1***a*) (7.5 mg) as an oil, homogeneous in t.l.c.

Analysis: all analytical data (i.r., n.m.r., mass, and t.l.c.) for "natural" tricyclovetivene were superimposable with that of natural tricyclovetivene.

By the same method, synthetic alcohol (**31**) (5.6 mg) was converted to racemic tricyclovetivene (**1***a*) (1.5 mg).

Mol. Wt. Calcd. for $C_{15}H_{24}$: 204.1878. Found (mass spectroscopy): 204.1876.

The remaining recorded spectral data (i.r. and g.l.c.) were completely identical to that of natural tricyclovetivene.

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