Hydrocyclopropa[b]anthracene Derivatives

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Robinson annelation of the 10-hydroxymethylene derivative of $1\beta,4,4$-trimethyl-$3\alpha,5\alpha$-tricyclo[5.4.0.0^{3,5}]undec-7-en-9-one with methyl and ethyl vinyl ketones has yielded hydrocyclopropa[b]anthracenones whose products of reduction and cyclopropane scission are reported. The stereochemistry of the tetracycles and tricycles are analysed by the ^{13}C n.m.r. spectral and c.d. methods.
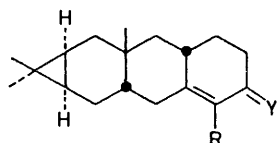
In continuation of studies on the chemistry of cyclopropanodecalins based on the $(-)$-cis-carane skeleton [1-3] tricyclic ketone (1) was exposed to Robinson annelation procedures. Base-induced condensation of (1) with
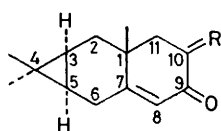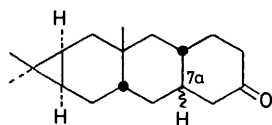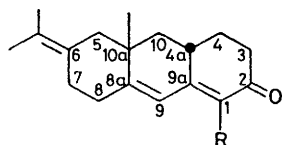

(1) R = H$_2$
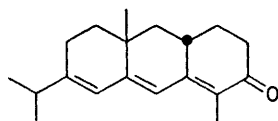(2) R = CHOH
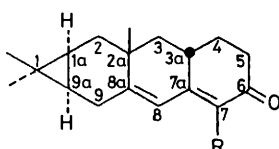
(3) R = H
(4) R = Me

(5) R = H, Y = O
(6) R = Me, Y = O
(9) R = H, Y = H$_2$

(7) 7α β-H
(8) 7α α-H

(10) R = H
(11) R = Me

(12)
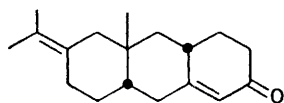
(13)

ethyl formate yielded the α-hydroxymethylene derivative (2). Treatment of the latter with methyl vinyl ketone in t-butyl alcohol in the presence of potassium t-butoxide catalyst and exposure of the product to potassium hydroxide in aqueous dioxan produced dienone (3) in 65% yield. Similar involvement of (2) with ethyl vinyl ketone resulted in the formation of a diketone whose aldol condensation and dehydration under the influence

of sodium methoxide led to the tetracycle (4) in 60% yield. The structures of the dienones and subsequent compounds are based on spectral analysis.

Partial hydrogenation of ketones (3) and (4) over 5% palladium on strontium carbonate support gave enones (5) and (6), respectively, and hydrogenation of (5) over 10% palladium–charcoal yielded saturated ketone (7). Reduction of (5) with lithium in liquid ammonia, however, led to isomer (8). Finally, conversion of ketone (5) into its ethylene thioketal and reduction of the latter with lithium-ammonia afforded an olefin mixture from which the major isomer (9) could be isolated.

The acid-induced cyclopropane cleavage of tetracycles (3)—(5) was investigated next. Treatment of dienone (3) with hydrogen bromide in acetic acid and subsequent dehydrobromination with collidine in dimethylformamide gave a 1 : 1 product mixture from which trienone (10) could be isolated. The same two-reaction sequence imposed on dienone (4) led to a 1.5 : 1 mixture of trienones (11) and (12), respectively. However, the same treatment of enone (5) produced a complex mixture of substances, of which dienone (13) could be identified. As the results of the experiments on (4) especially illustrate, the cyclopropane bond scission is regiounselective in sharp contrast to the behaviour of tricycle (1) [1,4] whose cyclopropane cleavage led predominantly to a bicyclic dienone with an isopropyl side-chain substitution pattern related to structure (12). Since the bond rupture of (1) and (3) or (4) can be expected to lead to similar dimethylcarbonium ions, the difference of transition state stability of the bond-breaking process in the tricyclic and tetracyclic series, permitting the latter a competitive ring opening at a different cyclopropane site, must be associated with the transmission of subtle differences of conformational effects of the two ring systems to the reaction centre.

^{13}C N.m.r. Spectral Analysis.—The ^{13}C n.m.r. spectra of compounds (3)—(6) and (8)—(13) were inspected and the Yb(dpm)$_3$-induced shifts of the key ketones (3), (5), (8), (10), (12), and (13) used for the chemical shift assignment of all substances. The data are listed in Tables 1 and 2.

The stereochemistry of the tetracycles (3)—(9) and tricycles (10)—(13) was determined by ^{13}C n.m.r. spectroscopy, but at some carbon sites could be anticipated on the basis of the following arguments. Since ketones (3)

TABLE 1

Chemical shifts (δ) [a] and lanthanide shift slopes (S) [b] of the tetracycles

	(3) δ	(3) S	(4) δ	(5) δ	(5) S	(6) δ	(9) δ	(8) δ	(8) S
C(1)	18.9	1.6	19.1	16.7	0.8	16.6	16.6	16.6	0.8
C(1a)	26.3	2.6	26.7	16.9	1.2	16.9	17.3	17.0	0.4
C(2)	34.5	4.0	34.6	33.8	2.4	33.4	34.6	34.4	1.9
C(2a)	36.1	6.4	35.5	31.2	4.4	31.3	31.4	31.4	3.2
C(3)	44.0	8.4	44.9	37.8	8.0	37.8	37.4	37.7	5.7
C(3a)	33.2	17.0	33.8	34.2	15.6	34.8	33.4	37.0	12.0
C(4)	30.4	21.6	30.4	30.0	20.0	29.5	31.7	33.6	16.0
C(5)	38.0	42.8	38.3	37.3	44.4	39.4	21.2	41.6	32.4
C(6)	199.4	c	199.0	196.3	c	195.6	25.9	216.3	c
C(7)	121.5	53.6	126.0	127.0	46.4	131.2	122.6	48.2	35.2
C(7a)	159.6	24.4	152.7	165.9	28.0	159.2	137.1	37.0	15.0
C(8)	121.4	9.6	118.7	38.3	6.4	34.8	39.4	35.2	6.0
C(8a)	161.8	7.2	160.7	37.3	3.6	37.1	37.5	35.7	3.2
C(9)	28.4	2.8	29.1	22.4	3.2	22.4	22.4	20.9	1.6
C(9a)	18.9	2.8	19.1	18.6	1.6	18.6	19.1	18.4	0.8
1α-Me	27.8	0.8	28.0	28.6	0.4	28.5	28.8	28.4	0.1
1β-Me	14.5	1.6	14.6	15.3	0.8	15.3	15.5	15.3	0.3
2a-Me	25.6	4.0	25.7	26.6	4.0	26.7	27.0	27.6	2.4
7-Me			10.0			10.7			

[a] In p.p.m. downfield from Me$_4$Si; δ(Me$_4$Si) = δ(CDCl$_3$) +76.9 p.p.m. [b] In p.p.m. per molar equivalent of Yb(dpm)$_3$. [c] Slopes were not computed for the signals of the carbonyl group.

and (4) had been prepared from (2) under equilibrium conditions, these tetracycles and all compounds derived therefrom could be expected to possess the thermodynamically favourable *syn*-diaxial relationship of H(3a) and the angular methyl group. Whereas the stereochemical consequence of the conversion of (3) and (4) into (5) and (6), respectively, on hydrogenation could not be diagnosed, the transformation of (5) into the two isomeric, saturated ketones (7) and (8) by hydrogenation and metal reduction, respectively, could be interpreted in terms of the latter process yielding a *trans*-decalone product, *i.e.* structure (8) or (14).

The total coincidence of the carbon shifts of the carane portion of the saturated ketone with the δ values of like carbons of the cyclopropanodecalin (15) [3] shows the tetracyclic ketone to possess structure (7) in the con-

TABLE 2

Chemical shifts (δ) [a] and lanthanide shift slopes (S) [b] of the tricycles

	(10) δ	(10) S	(11) δ	(13) δ	(13) S	(12) δ	(12) S
C(1)	121.8	39.6	127.9	123.6	50.0	126.7	35.0
C(2)	195.4	c	196.0	195.7	c	196.4	c
C(3)	37.7	39.2	37.6	36.6	46.0	37.9	35.9
C(4)	29.9	16.4	30.8	28.0	21.0	30.1	14.0
C(4a)	31.8	12.8	32.8	33.2	16.1	32.5	11.8
C(5)	44.4	2.4	44.6	31.0	2.2	36.5	2.8
C(6)	127.1	1.6	127.1	126.9	1.8	24.0	2.0
C(7)	30.5	1.6	29.5	25.6	2.2	152.0	3.0
C(8)	33.4	2.0	34.0	31.3	3.8	121.4	3.2
C(8a)	158.0	5.6	156.4	43.7	4.9	151.7	6.0
C(9)	121.8	7.2	123.6	36.5	9.0	119.4	9.0
C(9a)	159.0	18.4	151.8	168.5	22.7	152.2	18.0
C(10)	44.9	6.0	45.8	48.3	8.2	44.6	6.0
C(10a)	39.0	3.2	38.3	33.2	4.8	33.0	4.4
6-C	123.8	1.6	123.8	123.8	1.2		
7-C						35.1	1.4
1-Me			9.8			9.9	24.4
10a-Me	23.1	3.2	23.1	26.6	2.9	22.1	3.0
Me	20.0	0.8	20.0	20.0	0.1	21.3	1.2
	19.9	0.8	19.9	20.0	0.1	20.8	1.2

[a] In p.p.m. downfield from Me$_4$Si; δ(Me$_4$Si) = δ(CDCl$_3$) +76.9 p.p.m. [b] In p.p.m. per molar equivalent of Yb(dpm)$_3$. [c] Slopes were not computed for the signals of the carbonyl group.

formation depicted earlier for hydrocarbon (15).[3] Furthermore, the carbonyl-bearing ring of tetracycle (7) must be fused diequatorially to its neighbouring ring, since the introduction of any axial substituent in the

(14)   (15)
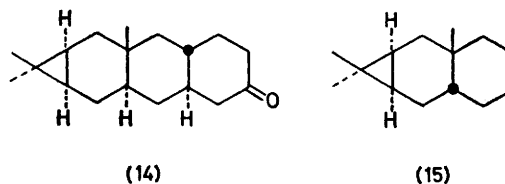
cyclopropanodecalin system would impose δ effects on some carane carbons. The elucidation of the stereostructure (7) for the saturated, polycyclic ketone limits the configuration of all other substances to their depicted formulae.

C.d. Data (*Table 3*).—The c.d. curves for the αβ-unsaturated ketones (5) and (6) in the π→π* region (below 300 nm) were essentially quasi-enantiomeric with those of Δ⁴-3-oxo-steroids,[5] in accord with the absolute configurations assigned to the present compounds. The rather weak bisignate [6] n→π* band above 300 nm for compound (5), and the absence of any c.d. above 300 nm for the methylated derivative (6) are features found occasionally in analogous αβ-unsaturated steroidal ketones,[7] and may be associated with virtual coplanarity of the C=C and C=O bonds. The dienones (3), (4), (10), and (11) likewise gave the c.d. curves expected of compounds quasi-enantiomeric with a steroidal 4,6-dien-3-one,[8] whereas the trienone (12) gave a curve of essentially similar form, red-shifted by the additional conjugation. There is no steroid analogue of the trienone (12).

The saturated ketone (8) showed c.d. behaviour characteristic of a *trans*-2-decalone.[9] Both the magnitude and the negative sign of the n→π* band near 300 nm agreed with the *trans*-fusion of ketonic and adjoining rings, and with the absolute stereochemistry assigned. The *cis*-isomer (7) showed an exceptionally large c.d. at

TABLE 3

C.d. data for tricyclic and tetracyclic ketones

Compound	Δε(nm) [a] Hexane	Methanol
Conjugated enones		
(5)	−0.31 (359)	−0.74 (345)
	+0.22 (322)	+0.42 (301)
	−0.24 (278)	−4.24 (236)
	−6.21 (229)	−1.4! (202!)
	−3.8! (189!)	
(6)	Nil (>300)	Nil (>300)
	−4.77 (238)	−3.56 (246)
	−7! (182!)	
Conjugated dienones		
(3)	−4.69 (365)	−14.28 (337)
	−4.59 (279)	+3.26 (300)
	+9.18 (208)	+5.91 (208)
(4)	−7.00 (364)	−3.65 (345)
	−5.25 (285)	+1.22 (305)
	+13.2 (216)	+1.62 (217)
(10)	Insoluble	−9.7 (337)
		−3.0 (281)
		+3.7 (213)
		−6.0 (196)
(11)	−10.1 (345)	−6.96 (340)
	−20.4 (290)	−4.74 (295)
	+20 (216)	+5.19 (216)
	−25 (197)	−8.0 (196)
Trienone		
(12)	−0.9 (421)	−11.2 (362)
	−6.9 (364)	+1.6 (238)
	−13.5 (326)	+8.8 (203)
	0 (255)	
	+9.6 (214)	
	+12.3 (196)	
Saturated ketones		
(8) (trans-2-decalone type)	−1.50 (302)	−0.68 (288)
	−2.8! (185!)	−0.7! (197!)
(7) (cis-2-decalone type)	+2.45 (299)	+3.2 (290)
	−3.9! (189!)	−4.0! (193!)

[a] ! Indicates the limit of measurement, not a maximum.

the n→π band (Δε ca. +3), when compared with data for the apparently quasi-enantiomeric 3-oxo-5β-steroids (Δε ca. −0.5).[9] The reason was apparent from study of a Dreiding model, which showed that the chair–chair conformation of the cis-decalone unit is excessively strained, so that the middle cyclohexane ring is likely to adopt a twist conformation. An octant projection (Figure) of the molecule in such a conformation indicates a periplanar 'primary zig-zag'[9] of four C–C bonds extending into a 'positive' rear octant. Strain in these bonds, associated with the twisted conformation, would enhance their positive contribution to the c.d.[10]
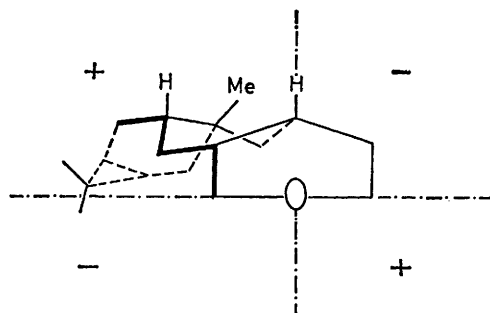
Octant projection of the cis saturated ketone (7), with twisted middle ring: heavy lines indicate 'primary zig-zag' in a 'positive' octant

Both the trans- and the cis-saturated ketones show strongly negative c.d. bands below 200 nm which are attributable to the dimethylcyclopropyl component of structure.[11] This contribution is masked in the unsaturated ketones by strong c.d. associated with the enone or related systems.

EXPERIMENTAL

B.p.s and m.p.s were uncorrected. Column chromatography was carried out on Silal 13 and t.l.c. on silica gel PF_{254} with light petroleum (b.p. 30—60 °C) as elution solvent. (Ligroin corresponds to the petroleum fraction of b.p. 80—100 °C.) A Carlo Erba GI chromatograph and 2 or 3 m 10% Carbowax 20M or 20% LAC 728 columns served for g.l.c. analysis. U.v. (EtOH) and i.r. (CCl_4) spectra were recorded on Beckman OKW-1A and Perkin-Elmer 521 spectrophotometers, respectively. Optical rotations on chloroform solutions were obtained on a Polax polarimeter and c.d. curves were determined on a Cary 61 instrument by Mrs. M. W. Barrett (Westfield). The carbon shifts (in p.p.m. downfield from Me_4Si) were recorded with deuteriochloroform solutions [$\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ p.p.m.] on a Varian XL-100-15 spectrometer operating at 25.20 MHz in the Fourier transform mode.

The carbon shift assignment was made unambiguous by the extensive use of the lanthanide-induced shift technique. On several occasions difficulties of signal designation at zero lanthanide concentration were encountered mainly because of the proximity of three lines with different slopes and the lack of knowledge of the lowest lanthanide concentration with good precision as a consequence of the presence of traces of water despite the care taken for the exclusion of moisture in the solvent and solute prior to any experiment. For this reason a computer program for automatic signal assignment was written and made to work in the following manner. It chooses lines minimizing the distance between the theoretical and experimental δ values for intermediate lanthanide concentrations from among lines connecting chemical shifts associated with zero and maximum lanthanide concentrations. By the use of a general minimization procedure the intermediate concentrations then are adjusted in such a fashion as to minimize the distances between theoretical and experimental chemical shifts for all lines at the same time. This resonance designation and minimization process is repeated a few times, until convergence takes place.[12]

10-Hydroxymethylene-1β,4,4-trimethyl-3α,5α-tricyclo-[5.4.0.0³,⁵]undec-7-en-9-one (2).—Ethyl formate (40 ml) was added dropwise to a stirring mixture of sodium methoxide, from sodium (6.4 g) and dry methanol, in dry benzene (100 ml) under nitrogen at room temperature and the stirring continued for 0.5 h. The mixture was stirred in an ice-bath and a solution of ketone (1) (20.0 g) in dry benzene (70 ml) added dropwise over 0.5 h. More benzene (50 ml) was added and stirring continued at room temperature for 18 h. The mixture was poured into water, the aqueous solution washed with benzene and ether, and the combined organic solutions extracted with ice-cold 5% potassium hydroxide solution. Ice-cold 5% sulphuric acid was added cautiously to the combined aqueous solutions and the acidic mixture extracted with 1 : 1 benzene–ether. The extract was washed with water, dried (Na_2SO_4), and evaporated under vacuum. Crystallization of the residue from ligroin gave the crystalline ketone (2) (16.6 g, 72%), m.p. 73—75°,

$[\alpha]_D^{22}$ 109° (*c* 1.93), $\lambda_{max.}$ 256 nm (ε 11 500), $\nu_{max.}$ (CHCl$_3$) 1 645 (CO) and 1 570 cm^{-1} (C=C) (Found: C, 77.7; H, 8.65. Calc. for C$_{15}$H$_{20}$O$_2$: C, 77.55; H, 8.7%).

1,1aα,2,2a,3,3aβ,4,5,9,9aα-*Decahydro*-1,1,2aβ-*trimethyl*-6H-*cycloprop*[b]*anthracen*-6-*one* (3).—A solution of ketone (2) (11.4 g) and freshly distilled methyl vinyl ketone (4.4 g) in dry t-butyl alcohol (44 ml) was mixed with an ice-cold solution of potassium t-butoxide, from potassium (400 mg), in dry t-butyl alcohol and the mixture left under nitrogen at room temperature for 12 h. It was then diluted with water, acidified with ice-cold 5% sulphuric acid, and extracted with ether and benzene. The combined extracts were washed with 5% potassium hydroxide and water, dried, and evaporated. A mixture of a solution of the solid residue (12.8 g) in dioxan (330 ml) and a solution of potassium hydroxide (12.2 g) in water (330 ml) was stirred under nitrogen at room temperature for 12 h. It was then extracted with benzene and ether and the extracts were washed with water, dried, and evaporated. Chromatography of the residue (12.1 g) and elution with 4:1 light petroleum–ether yielded a solid whose crystallization from ligroin gave crystals of ketone (3) (8.00 g, 65%), m.p. 128—130°, $[\alpha]_D^{22}$ −456° (*c* 0.548), $\lambda_{max.}$ 299 nm (ε 30 300), $\nu_{max.}$ 1 660 (CO) and 1 622 cm^{-1} (C=C) (Found: C, 84.55; H, 9.45. Calc. for C$_{18}$H$_{24}$O: C, 84.3; H, 9.45%).

1,1aα,2,2a,3,3aβ,4,5,9,9aα-*Decahydro*-1,1,2aβ,7-*tetra-methyl*-6H-*cycloprop*[b]*anthracen*-6-*one* (4).—The procedure for the preparation of (3) was applied to ketone (2) (15.0 g) and freshly distilled ethyl vinyl ketone (8.40 g) in dry t-butyl alcohol (60 ml) and potassium t-butoxide, from potassium (600 mg) in dry t-butyl alcohol (80 ml). The above follow-up deformylation step was used on the crude product (24.3 g) in dioxan (450 ml) and potassium hydroxide (24 g) in water (450 mg). A solution of the resultant diketone (17.8 g) in dry methanol (300 ml) mixed with sodium methoxide solution, from sodium (4.00 g) and dry methanol (300 ml), was refluxed for 4 h. A solution of potassium hydroxide (25 g) in water (25 ml) was added and the mixture refluxed for another 5 h. After the usual work-up the product (16 g) was chromatographed and eluted with 4:1 light petroleum–ether. Crystallization of the eluates from ligroin gave crystalline ketone (4) (9.80 g, 60%), m.p. 115—117°, $[\alpha]_D^{22}$ −436° (*c* 2.18), $\lambda_{max.}$ 305 nm (ε 27 900), $\nu_{max.}$ 1 660 (CO) and 1 622 cm^{-1} (C=C) (Found: C, 84.0; H, 9.65. Calc. for C$_{19}$H$_{26}$O: C, 84.4; H, 9.7%).

1,1aα,2,2a,3,3aβ,4,5,8,8aβ,9,9aα-*Dodecahydro*-1,1,2aβ-*tri-methyl*-6H-*cycloprop*[b]*anthracen*-6-*one* (5).—A mixture of ketone (3) (1.0 g) and palladium (5%) on strontium carbonate (0.3 g) was shaken over hydrogen at room temperature and pressure. After the uptake of 4.65 mmol of hydrogen the mixture was filtered and the filtrate evaporated. Crystallization of the residue (1 g) from ligroin gave ketone (5) (0.90 g, 90%), m.p. 112—114°, $[\alpha]_D^{22}$ −57° (*c* 0.96), $\lambda_{max.}$ 240 nm (ε 17 200), $\nu_{max.}$ 1 680 (CO) and 1 622 cm^{-1} (C=C) (Found: C, 83.95; H, 10.25. Calc. for C$_{18}$H$_{26}$O: C, 83.65; H, 10.15%).

1,1aα,2,2a,3,3aβ,4,5,8,8aβ,9,9aα-*Dodecahydro*-1,1,2aβ,7-*tetramethyl*-6H-*cycloprop*[b]*anthracen*-6-*one* (6).—Ketone (4) (6.5 g) was hydrogenated by the above procedure. Distillation of the product (6.0 g) at 128—130 °C and 0.1 Torr gave a crystalline solid (4.8 g, 73%) whose crystallization from light petroleum yielded ketone (6), m.p. 63—65°, $[\alpha]_D^{22}$ −79° (*c* 2.53), $\lambda_{max.}$ 248 nm (ε 14 600), $\nu_{max.}$ 1 670 (CO) and 1 615 cm^{-1} (C=C) (Found: C, 83.5; H, 10.2. Calc. for C$_{19}$H$_{28}$O: C, 83.75; H, 10.35%).

Perhydro-(1aα,3aβ,7aβ,8aβ,9aα)-1,1,2aβ-*trimethylcyclo-prop*[b]*anthracen*-6-*one* (7).—A mixture of ketone (5) (500 mg) and palladium–charcoal (0.2 g, 10%) in dry ethanol (15 ml) and methylcellosolve (0.1 ml) was hydrogenated at room temperature and pressure. Filtration of the catalyst and evaporation of the solvent left a residue, whose benzene solution was washed with water, dried, and evaporated. Crystallization of the residual solid (450 mg, 90%) from light petroleum yielded ketone (7), m.p. 61—62°, $[\alpha]_D^{22}$ 88° (*c* 2.05), $\nu_{max.}$ 1 720 cm^{-1} (CO) (Found: C, 83.5; H, 10.7. Calc. for C$_{18}$H$_{28}$O: C, 83.0; H, 10.85%).

Perhydro-(1aα,3aβ,7aβ,8aβ,9aα)-1,1,2aβ-*trimethylcyclo-prop*[b]*anthracen*-6-*one* (8).—Lithium (600 mg) was supplied in small pieces to liquid ammonia (250 ml) kept at −45 °C. The solution was stirred for 0.2 h, a solution of ketone (5) (2.00 g) and t-butyl alcohol (0.8 g) in dry ether (30 ml) was added over 0.2 h, and stirring continued for 1 h. Enough ammonium chloride was added for the disappearance of the blue solution colour and the solution was permitted to evaporate at room temperature. Ether and water were added and the aqueous solution saturated with sodium chloride and extracted with ether. The combined organic solutions were washed with water and saturated brine, dried, and evaporated. Vacuum distillation of the residue (2.1 g) yielded liquid ketone (8) (1.70 g, 85%), $[\alpha]_D^{22}$ −5° (*c* 3.40), $\nu_{max.}$ 1 720 cm^{-1} (CO) (Found: C, 83.1; H, 10.65. Calc. for C$_{18}$H$_{28}$O: C, 83.0; H, 10.85%).

1,1aα,2,2a,3,3aβ,4,5,8,8aβ,9,9aα-*Dodecahydro*-1,1,2aβ-*tri-methyl*-6H-*cycloprop*[b]*anthracene* (9).—A solution of ketone (5) (3.5 g), ethane-1,2-dithiol (2 ml), and boron trifluoride–ether (2 ml) in absolute methanol (75 ml) was kept at room temperature for 1.5 h. The resultant, crystalline precipitate (3.4 g) was filtered off, showed no i.r. carbonyl absorption, and was used in the next step without further purification. A solution of the thioacetal (3.0 g) in dry ether (30 ml) was added slowly to a stirring solution of lithium (1.5 g) in liquid ammonia (260 ml), the stirring continued for 0.3 h, and the reaction quenched by the addition of ammonium chloride. After the usual work-up the crude product (2 g) was chromatographed. Elution with light petroleum gave liquid olefin (9) (93% pure by g.l.c.) (1.8 g, 55%), $\nu_{max.}$ (film) 1 630 cm^{-1} (C=C).

Cyclopropane Scissions.—A solution of dry hydrogen bromide (2.30 g) in glacial acetic acid (30 ml) was poured dropwise into a stirring solution of ketone (3) (6.00 g) in glacial acetic acid (90 ml) at 10 °C. The mixture was kept at room temperature for 0.3 h and then concentrated under reduced pressure. An ether solution of the residue was washed with water and 5% sodium hydrogencarbonate solution, dried, and evaporated. A solution of the residual oil (8.0 g) and collidine (6 ml) in dimethylformamide (90 ml) was refluxed for 1 h. After the addition of more collidine (8 ml) the heating was continued for 1.5 h. Water was added and the mixture extracted with ether. The extract was washed with cold 5% sulphuric acid solution, 5% potassium hydroxide solution and water, dried, and evaporated. Chromatography of the crude product (6 g), by g.l.c. a 1:1 mixture of two substances, and elution with 4:1 light petroleum–ether yielded a solid (1.80 g) whose crystallization from ligroin gave trienone (10), m.p. 81—83°, $\lambda_{max.}$ 300 nm (ε 16 500), $\nu_{max.}$ (CHCl$_3$) 1 650 (CO) and 1 585 cm^{-1} (C=C) (Found: C, 84.6; H, 9.35. Calc. for C$_{18}$H$_{24}$O: C, 84.35; H, 9.45%).

Treatment of ketone (4) (8.0 g) with hydrogen bromide, followed by dehydrobromination of the resultant bromo-

ketones (13 g), led to a crude product (8 g), by g.l.c. a 1.5 : 1 mixture of two substances, whose chromatography and gradient elution with light petroleum to a 4 : 1 light petroleum–ether mixture yielded as major component liquid trienone (11) (1.50 g), $[\alpha]_D^{22}$ −415° (c 3.08), $\lambda_{max.}$ 302.5 nm (ε 18 000), $\nu_{max.}$ (CHCl$_3$) 1 645 (CO), 1 612 (CO), and 1 582 cm^{-1} (C=C) (Found: C, 84.6; H, 9.65. Calc. for $C_{19}H_{26}O$: C, 84.4; H, 9.7%) and subsequently as minor constituent liquid trienone (12) (500 mg), $[\alpha]_D^{22}$ −595° (c 2.02), $\lambda_{max.}$ 345 nm (ε 30 000), $\nu_{max.}$ (CHCl$_3$) 1 640 (CO) and 1 580 cm^{-1} (C=C) (Found: C, 84.25; H, 9.7. Calc. for $C_{19}H_{26}O$: C, 84.4; H, 9.7%).

Similar treatments of ketone (5) (3.00 g) yielded a crude product (3 g), by g.l.c. a complex mixture, whose chromatography and gradient elution with light petroleum to 4 : 1 light petroleum–ether mixture gave a crystalline solid (400 mg). Crystallization of the latter from ligroin led to dienone (13), m.p. 155—156°, $\nu_{max.}$ 1 675 (CO) and 1 625 cm^{-1} (C=C) (Found: C, 83.65; H, 10.1. Calc. for $C_{18}H_{26}O$: C, 83.65; H, 10.15%).

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