Tetrahedron. Vol. 30, pp. 1107 to 1114. Pergamon Press 1974. Printed in Great Britain

MEROTERPENOIDS—IV

ACID-CATALYZED CYCLIZATION OF BAKUCHIOL METHYL ETHER[a,b]

A. S. C. PRAKASA RAO, U. R. NAYAK and SUKH DEV*
National Chemical Laboratory, Poona, India

(*Received in the UK 9 October* 1973; *Accepted for publication 6 December* 1973)

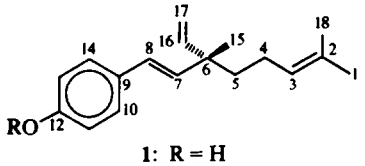
Abstract—Bakuchiol methyl ether cyclizes on acid catalysis to give two major products, which have been suitably correlated. Stereochemistry of these products in relation to the preferred conformations of the transition state is discussed. Direct Wolff-Kishner reduction of 'ozonides' is described.

Cyclization of acyclic terpenes and their derivatives, both under acid-catalysis and solvolysis, has attracted much attention,[1] as at least some of these reactions tend to simulate biogenetic-type synthesis.[2] Furthermore, such reactions were expected to underscore the importance of enzymes for stereospecificity.[3]

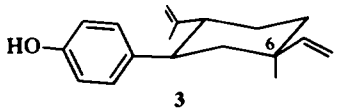
Bakuchiol (**1**), a constituent of the seeds of *Psoralea corylifolia* Linn., is a phenol with an acyclic monoterpene part-structure.[4] Carnduff and Miller[5] noted, in passing, that bakuchiol on a short exposure to *p*-toluenesulphonic acid in refluxing benzene, yielded a mixture of two products, which were not separated, but for which structures **3** and **4** were suggested, on the basis of IR and PMR spectral data. We have now reinvestigated this cyclization on two counts. Firstly, cyclic products were required in pure state to serve as reference compounds in our search for minor constituents of *Psoralea corylifolia* seeds.† And secondly, there is no reason to believe that inversion at C_6 can occur during cyclization (of the same substrate) as is implied by structures **3** and **4** of Carnduff and Miller.

Bakuchiol methyl ether (**2**), on treatment with *p*-toluenesulphonic acid in refluxing $CHCl_3$ (7 h), yielded a product which, on chromatography over SiO_2 gel-$AgNO_3$ furnished in ~ 70% yield two pure compounds, in a ratio of ~ 2:1, hereafter to be referred to as isomer-A and isomer-B respectively. The spectral data (Tables 1, 2) of both of these compounds clearly indicate the involvement of only the *trans*-disubstituted olefinic and tri-substituted olefinic bonds of bakuchiol methyl ether in cyclization; this clearly indicates gross structure **5** for both the compounds. Besides these two compounds, the cyclization reaction gave smaller amounts (least polar material on SiO_2 gel-$AgNO_3$ column) of a product, which from its PMR spectrum (*vide* Experimental) is a mixture of two compounds with the gross structure **6**. This material was not investigated further.

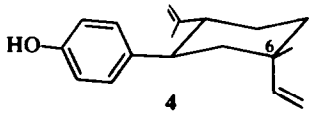
(+)-Bakuchiol methyl ether (**2**) can, in principle, generate four diastereoisomers (**11–14**) with the gross structure **5**. Each one of these will require a distinct stereochemistry of the transition state. Fig 1 depicts, what can be considered as more probable



1: R = H
2: R = Me



3

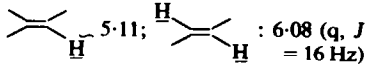
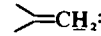
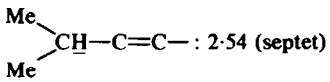
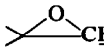
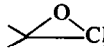


4

conformations of bakuchiol methyl ether, in the transition state, leading to stereochemically distinct products. Making the reasonable assumption that the transition states **8**, **10** are less important, be-

[a]Communication No. 1788, National Chemical Laboratory, Poona, India.
[b]Part III. Ref 4c.
†*cf* e.g. the chemistry of hashish.[6]

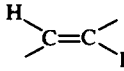
Table 1. PMR spectral (CCl_4) data for bakuchiol methyl ether and cyclic derivatives obtained from it

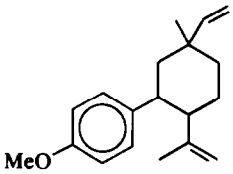
No.	Compound	Chemical shift in ppm					
		C_6-Me[a]	C_2-Me[a]	$\Delta^{16,17}$	Aromatic H's[b]	OMe	Other signals
1	Bakuchiol methyl ether	1·21 (s)	1·60 (s) 1·68 (s)	4·75–5·95 (m)	6·95	3·75 (s)	 5·11; : 6·08 (q, J = 16 Hz)
2	Isomer-A	0·98 (s)	1·45 (d, J = 1·5 Hz)	4·86–6·31 (m)	6·85	3·72 (s)	 4·5 (bs)
3	Isomer-B	1·13 (s)	1·49 (d, J = 1 Hz)	4·68–6·08 (m)	6·85	3·70 (s)	 4·53 (bs)
4	Compound **15**	1·02 (s)	0·84 (d, J = 7 Hz); 0·86 (d, J = 7 Hz)	4·75–6·08 (m)	6·82	3·73 (s)	 : 2·54 (septet)
5	Epoxide from isomer-A	0·98 (s)	1·06 (s)	4·83–6·16 (m)	6·85	3·72 (s)	 1·95 (bs)
6	Epoxide from isomer-B	1·13 (s)	1·13 (s)	4·66–6·07 (m)	6·85	3·72 (s)	 1·93 (d, part of AB quartet).
7	Dihydro deriv. from isomer-A	0·96 (s)	0·62 (d, J = 7 Hz); 0·77 (d, J = 7 Hz).	4·8–6·1 (m)	6·85	3·71 (s)	
8	Dihydro deriv. from isomer-B	1·09 (s)	0·70 (d, J = 6·5 Hz); 0·81 (d, J = 6·5 Hz)	4·65–6·03 (m)	6·85	3·72 (s)	
9	Compound **18**	0·91 (s) 0·97 (s)	0·67 (d, J = 7 Hz); 0·79 (d, J = 7 Hz).		6·83	3·72 (s)	

[a] Each signal is 3H.

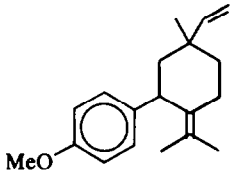
[b] Signal is clearly a typical 'AB' quartet' with two small extra peaks at the base of each of the four main peaks; J = 9 Hz.

Table 2. Relevant IR spectral (liquid phase) data for bakuchiol methyl ether and derived cyclic compounds

No.	Compound	Band (cm^{-1}) assignment			
		—CH=CH₂	Other C=C	OMe	Aromatic ring
1	Bakuchiol methyl ether	925, 1007	 : 980	1050, 1260	1525, 1580, 1605, 825
2	Isomer-A	915, 1002	 : 890, 1640, 3040	1040, 1245	1525, 1580, 1620, 830
3	Isomer-B	915, 1005	 : 890, 1640, 3060	1042, 1250	1525, 1580, 1620, 830
4	Compound **15**	915, 995		1040, 1240	1505, 1570, 1600, 832
5	Epoxide from isomer-A	915, 1000		1040, 1248	1505, 1570, 1600, 832
6	Epoxide from isomer-B	915, 1005		1040, 1248	1510, 1580, 1600, 835
7	Dihydro deriv. from isomer-A	915, 1000		1042, 1250	1515, 1580, 1605, 832
8	Dihydro deriv. from isomer-B	910, 1002		1042, 1250	1515, 1580, 1605, 832
9	Compound **18**			1042, 1250	1515, 1580, 1620, 830



5



6

cause of increased non-bonding interactions, in comparison to **7** and **9**, it can be reasonably safely taken that the two major products of cyclization of bakuchiol methyl ether, are the stereoisomers **11** and **13**. It may be further noted that in **11**, **13**, the configuration at C_6 is the same* and that the configurations at C_3, C_8 have object mirror-image relationship in the two structures.* That, this is indeed so for the two products (isomer-A, isomer-B) from the cyclization of bakuchiol methyl ether, was demonstrated as described below. This clearly proves that of the two structures **3** and **4**, suggested by Carnduff and Miller,[5] one must be in error.

Both isomer-A and isomer-B, when exposed (~ 30°, 24 h) to methane sulphonic acid in CH_2Cl_2 were transformed to products identical in all respects (TLC, IR, PMR), including the sign and approx magnitude of optical rotation. From its spectral characteristics (Tables 1, 2), the isomerised-product is clearly **15** and, it may be noted that this transformation would have generated optical antipodes, had structures differed at C_6 stereochemistry (*cf* **3**, **4**).

*The situation is the same for the pair **12**, **14**.

†Direct Wolff-Kishner reduction of 'ozonides' is a useful short-cut of the usual two-step sequence and, to our knowledge has not been reported earlier.

The next correlation, as depicted in Fig 2, was designed to lead to products, in which asymmetry at C_6 had been eliminated and thus, the end compounds (**18a**, **18b**) would become optical antipodes. Selective hydrogenation of the isomer-A/isomer-B to the dihydroderivative **17** could not be achieved and hence this transformation was accomplished as shown in Fig 2. Both isomers, on interaction with perbenzoic acid in benzene, underwent selective epoxidation to furnish **16** (**a**, **b**) in almost quantitative yields. Structure **16** is in complete accord with the spectral data (Tables 1, 2); however, it may be noted that both compounds (**16a**, **16b**) show the oxirane ring methylene protons at ~ 1·95 ppm (Table 1), which is well above the usual range (3·0–2·3 ppm)[7] for such protons, and this must be due to shielding by the nearby aromatic ring.[8] The epoxides were rearranged in good yield to the corresponding aldehydes (product from each series was in itself a mixture of C_2 epimers), which on Wolff-Kishner (Huang-Minlon modification)[9] reduction yielded the desired dihydro-derivatives **17a**, **17b**. It may be mentioned here that during Wolff-Kishner reduction of aldehyde from isomer-A, almost complete demethylation to the phenol occurred, whereas in the case of aldehyde from isomer-B, practically no demethylation was observed, though reaction conditions in the two cases were the same! The two dihydro derivatives (**17a**, **17b**) were ozonised and the crude 'ozonides' directly subjected to Wolff-Kishner reduction† to furnish the nor derivatives **18a**, **18b**. As expected, the two products have identical IR, PMR and Mass spectra, and have optical rotations of approx the same magnitude, but of opposite sign.

It is not possible to decide, from existing data,

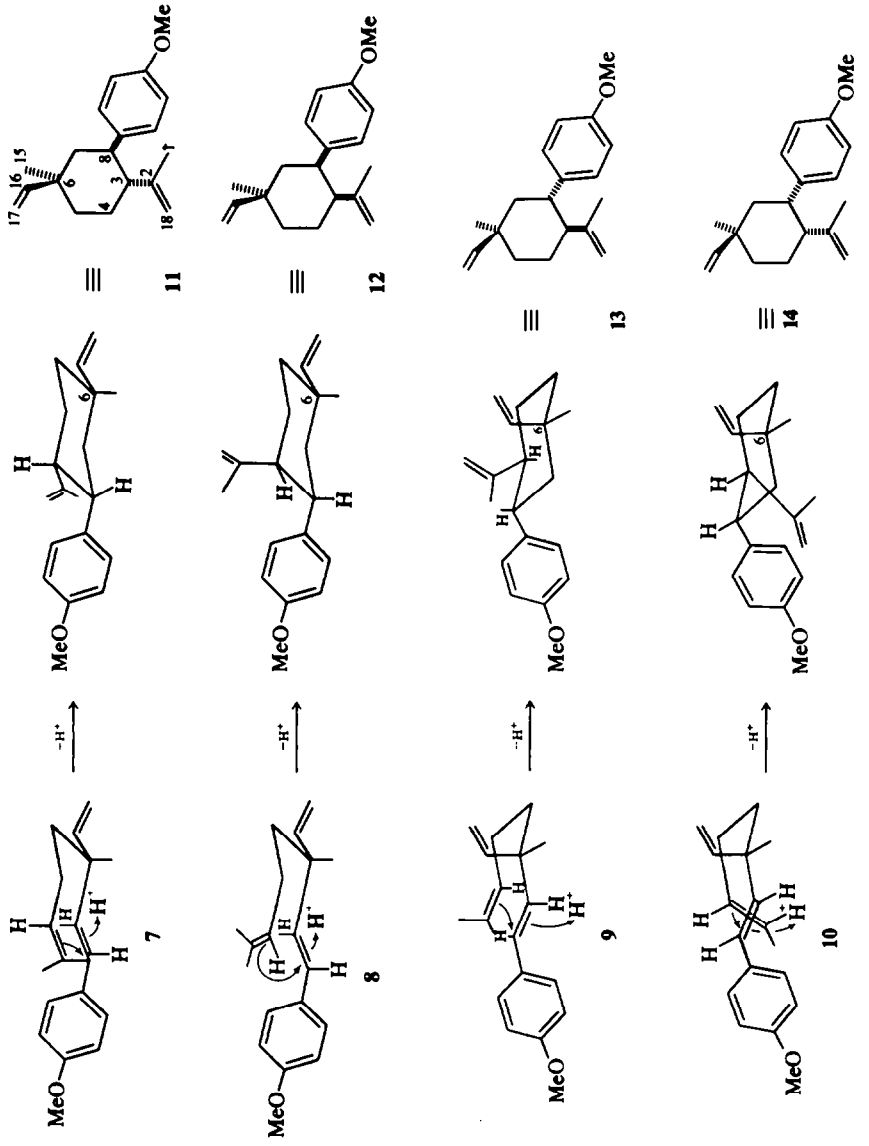


Fig 1. Stereochemistry of acid cyclization of bakuchiol methyl ether.

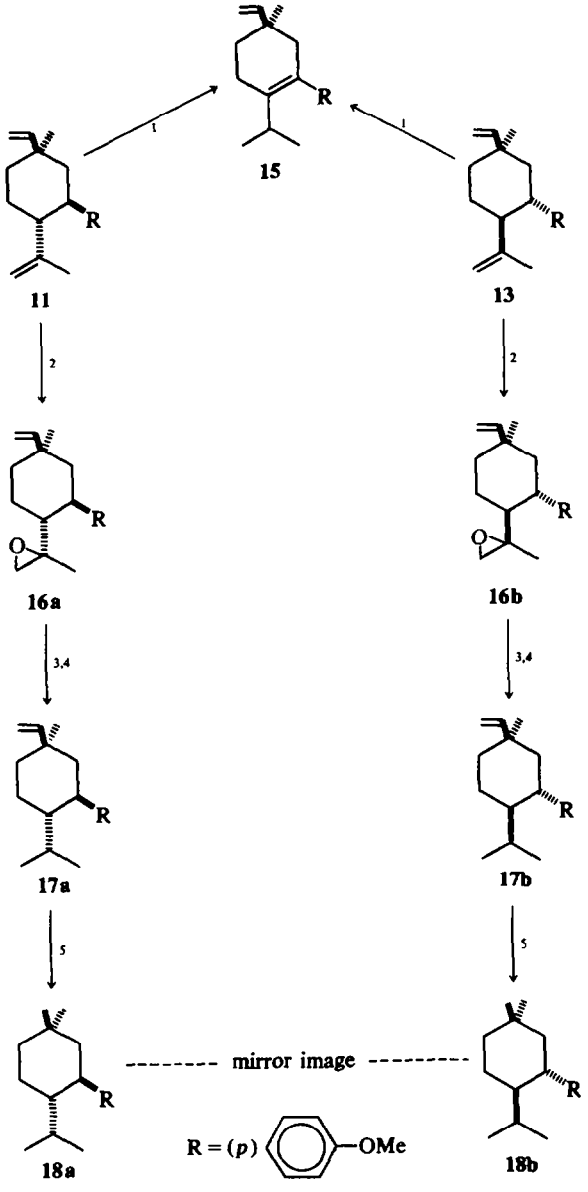
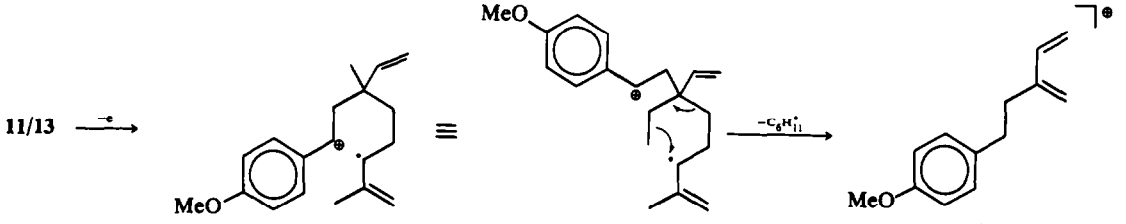


Fig 2. Correlation of isomer-A and isomer-B.

which of the two structures **11**, **13** belongs to which product (isomer-A or isomer-B).

Mass spectral data of compounds investigated during the present study are summarised in Table 3. It may be noted that ion *m/e* 187 is an important fragment for all compounds excepting No. 7 (Table 3). Genesis of this ion, which will explain its formation from the dihydro derivatives (No. 5, 6, Table 3) as well, is shown in **19**, **20**; ion *m/e* 187 can arise from bakuchiol methyl ether by a simple allylic cleavage (*cf* electron impact-induced fragmentation of bakuchiol[4a]).



EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum refers to the fraction b.p. 60–80°. All solvent extracts were dried over Na_2SO_4. Optical rotations were measured in EtOH at room temp (22–30°).

SiO_2-gel for column chromatography was − 100/+ 200 mesh and was washed with hot distilled water till sulphate-free, dried and activated at 125–130° (6–8 h) and standardised.[10] $AgNO_3$-impregnated SiO_2 gel chromatography was carried out according to the method of Gupta and Sukh Dev.[11]

The following instruments were used for spectral data: Perkin-Elmer Infracord model 137-E (IR); Varian Associates A-60 spectrometer (PMR; TMS internal standard); CEC mass spectrometer, model 21-110B (mass; 70 eV, direct inlet system). While citing PMR data following abbreviations have been used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and b (broad); the chemical shift position given is that of the centre of the signal.

Action of p-toluenesulphonic acid on bakuchiol methyl ether

Bakuchiol methyl ether (9·5 g) in $CHCl_3$ (200 ml) was treated with *p*-toluenesulphonic acid (2·0 g) at reflux (7 h). The mixture, after cooling, was washed successively with sat $NaHCO_3$ aq (125 ml × 2), water (125 ml × 2) and brine (125 ml). Drying and removal of solvent gave a dark brown liquid (10 g); TLC ($AgNO_3$–SiO_2 gel; solvent: 10% EtOAc in C_6H_6): 3 spots. The mixture (3·0 g) was chromatographed on $AgNO_3$–SiO_2 gel/IIb (280 g, 130 cm × 2 cm).

Fr. 1	C_6H_6	200 ml × 4	0·527 g	liquid, R_f 0·65 essentially compd. **6**
Fr. 2	2% EtOAc in C_6H_6	200 ml × 4	1·378	liquid, pure isomer-A, R_f 0·46
	5% EtOAc in C_6H_6	200 ml × 6		
Fr. 3	10% EtOAc in C_6H_6	200 ml × 5	0·735	liquid, pure isomer-B, R_f 0·29

Table 3. Relevant mass spectral data for bakuchiol methyl ether and derived cyclic compounds[a]

No.	Compound	*m/e*								
		M^+	1	2	3	4	5	6	7	8
1	Bakuchiol methyl ether	270 (27%)	187 (100%)	172 (9%)	159 (10%)	135 (9%)	121 (30%)	115 (8%)	93 (8%)	91 (7%)
2	Isomer-A	270 (89%)	187 (100%)	159 (9%)	134 (32%)	128 (13%)	121 (70%)	119 (9%)	115 (11%)	77 (6%)
3	Isomer-B	270 (54%)	187 (67%)	159 (6%)	134 (35%)	128 (4%)	121 (100%)	119 (6%)	115 (5%)	77 (5%)
4	Compound **15**	270 (74%)	227 (23%)	187 (36%)	159 (100%)	128 (28%)	123 (31%)	121 (34%)	115 (28%)	91 (21%)
5	Dihydro deriv. from isomer-A	272 (100%)	229 (54%)	187 (82%)	161 (56%)	147 (61%)	134 (59%)	121 (74%)	105 (43%)	95 (38%)
6	Dihydro deriv. from isomer-B	272 (100%)	229 (43%)	187 (76%)	161 (40%)	147 (44%)	134 (57%)	121 (60%)	105 (33%)	95 (17%)
7	Compound **18**	260 (100%)	245 (82%)	201 (43%)	189 (54%)	176 (71%)	161 (62%)	147 (64%)	134 (58%)	121 (54%)

[a] Mol. ion and eight most abundant ions are given. Relative intensities for compounds marked + are not reliable as the spectra were recorded by a pen recorder.

Fr. 1 was distilled: b.p. 140–145° (bath)/0·5 mm. PMR spectrum (CCl_4): tertiary Me (two singlets, total 3H, at 0·73 and 1·00 ppm), vinylic Me (6H, two singlets at 1·53, 1·80 ppm), OMe (s, 3·73 ppm), —CH=CH_2 (3H, m, located between 4·43–6·03 ppm), aromatic protons (4H, m, located between 6·50–7·16 ppm).

Isomer-A was distilled: b.p. 122–124°/0·5 mm, $[\alpha]_D$ + 3·1° (*c*, 0·16%). (Found: C, 84·67; H, 9·73. $C_{19}H_{26}O$ requires: C, 84·39; 9·69%).

Isomer-B was distilled: b.p. 125–128°/0·5 mm, $[\alpha]_D$ − 30·6° (*c*, 0·18%). (Found: C, 84·84; H, 9·87. $C_{19}H_{26}O$ requires: C, 84·39; H, 9·69%).

Action of methane sulphonic acid on isomer-A/isomer-B

(i) *Isomer-A.* Isomer-A (1·5 g) in dry CH_2Cl_2 (10 ml) was treated with 0·3 ml of CH_3SO_3H in CH_2Cl_2 (5 ml) at room temp (~ 30°). After 24 h, the mixture was washed successively with sat $NaHCO_3$ aq (20 ml × 2), water (20 ml) and brine (25 ml). Drying and removal of solvent gave a dark brown liquid (1·45 g); TLC ($AgNO_3$–SiO_2 gel; solvent: 50% light petroleum in $CHCl_3$): 2 spots. This mixture was chromatographed on $AgNO_3$–SiO_2 gel/IIb (65 g, 33 cm × 2 cm) with TLC monitoring:

Fr. 1	10% $CHCl_3$ in light petrol	100 ml × 3	0·095 g	liquid, higher R_f, mixture
Fr. 2	20% $CHCl_3$ in light petrol	100 ml × 2	0·198 g	liquid, mixture
Fr. 3	20% $CHCl_3$ in light petrol	100 ml × 3	0·842 g	liquid, pure compound
Fr. 4	20% $CHCl_3$ in light petrol	100 ml × 1	0·100 g	liquid, mixture
Fr. 5	50% $CHCl_3$ in light petrol	100 ml × 4	0·141 g	liquid, isomer-A
Fr. 6	$CHCl_3$	100 ml × 3	0·041 g	base material (rejected).

Fr. 3 was distilled to give compound **15**, b.p. 140–145° (bath)/0·4 mm, $[\alpha]_D$ − 35·9° (*c*, 0·53%). Mass (Table 3). (Found: C, 84·07; H, 9·71. $C_{19}H_{26}O$ requires: C, 84·39; H, 9·69%).

(ii) *Isomer-B.* Isomer-B (10·0 g) in CH_2Cl_2 (30 ml) was treated with CH_3SO_3H (2 ml) in CH_2Cl_2 (20 ml) exactly as above and worked up to give crude product (10·3 g) which was chromatographed on $AgNO_3$–SiO_2 gel/IIb (500 g, 100 cm × 3 cm) as described under (i) to finally give 6·32 g of **15**, b.p. 155–158°/3 mm, $[\alpha]_D$ − 21·8° (*c*, 0·79%). A small sample was further purified by $AgNO_3$–SiO_2 gel chromatography to remove a trace impurity; this product had $[\alpha]_D$ − 35·75 (*c*, 0·97%). Mass: *m/e* 270 (M^+, 100%), 227 (26%), 187 (40%), 159 (100%), 128 (20%), 123 (39%), 121 (33%), 115 (24%), 91 (20%). (Found: C, 84·72; H, 9·84. $C_{19}H_{26}O$ requires: C, 84·39; H, 9·69%).

Product **15** from isomer-A or isomer-B had the same retention time of GLC (10% silicone SE-30 on Chromosorb W of 60–80 mesh; temp 200°; gas flow: 110 ml H_2/min).

Epoxidation of isomer-A/isomer-B

(i) *Isomer-A.* Isomer-A (0·584 g) in C_6H_6 (10 ml), cooled in ice-water was treated with perbenzoic acid (0·3 g, 1 mole eq. in 9·1 ml of C_6H_6) and kept at 5° overnight. The mixture was washed successively with sat $NaHCO_3$ aq (10 ml × 2), water (10 ml × 2) and brine (10 ml). Removal of solvent and distillation of the residue (0·6 g) gave the monoepoxide: pale yellow liquid, b.p. 180–85° (bath)/0·5 mm, $[\alpha]_D$ + 10·8° (*c*, 1·61%). (Found: C, 79·58; H, 9·06. $C_{19}H_{26}O_2$ requires: C, 79·68; H, 9·15%).

(ii) *Isomer-B.* Isomer-B (0·77 g) in C_6H_6 (10 ml) was epoxidised as in (i) with perbenzoic acid (0·41 g, 1 mole eq. in 13 ml of C_6H_6). The crude product (0·79 g), on distillation, gave the monoepoxide: pale yellow liquid, b.p. 180–185° (bath)/0·5 min, $[\alpha]_D$ − 38·5° (*c*, 0·265%). (Found: C, 79·60; H, 9·20. $C_{19}H_{26}O_2$ requires: C, 79·68; H, 9·15%).

Dihydroderivative from isomer-A/isomer-B

(i) *Isomer-A.* The epoxide from isomer-A (0·5 g) in dry C_6H_6 (10 ml), cooled in ice-water, was treated with $BF_3.Et_2O$ (freshly distilled, 3 drops) and kept for 0·5 h. The mixture was washed successively with sat $NaHCO_3$ aq (10 ml × 2), water (10 ml × 2) and brine (10 ml). Removal of solvent and distillation of the residue gave the epimeric aldehydes: yellowish liquid, b.p. 160–65° (bath)/0·4 mm (0·42 g). IR spectrum (smear): CHO 2700, 1720 cm^{-1}. PMR spectrum (CCl_4): CH.CHO (1H, bs, 9·20 ppm).

The above aldehyde (0·236 g), KOH pellets (0·34 g), hydrazine hydrate (98%, 0·3 ml) and diethylene glycol (5 ml) were mixed and heated (N_2) in an oil bath (*ca* 145°) for 1·5 h. Water and excess of hydrazine were removed by raising the bath temp to *ca* 200° and then refluxed for 5 h. The mixture was poured into water (50 ml), acidified with dil HCl (1:1, Congo red), extracted with ether (50 ml × 3), washed successively with water (25 ml × 2), brine (25 ml) and dried. Removal of solvent gave the demethylated dihydro-derivative as a colourless solid (0·2 g); recrystallises from light petroleum as silky needles m.p. 124–125°. $[\alpha]_D$ + 14·0° (*c*, 0·2%). IR spectrum (Nujol): OH 3250 cm^{-1}; aromatic ring 1615, 1520 cm^{-1}; CH=CH_2 915, 1000 cm^{-1}. PMR spectrum (CCl_4): —CHMe_2 (two 3H doublets centered at 0·63 and 0·78 ppm, each with J = 7 Hz), tertiary Me (3H, s, 0·97 ppm), —CH=CH_2 (3H, m, 4·95–5·80 ppm) aromatic H's (4H, q, 6·80 ppm, J = 9 Hz). (Found: C, 83·83; H, 10·51. $C_{18}H_{26}O$ requires: C, 83·66; H, 10·14%).

The above phenol (0·2 g) was remethylated with MeI (0·2 ml) in dry DMSO (1 ml) and CaO (0·15 g) at room temp (24 h). The product was isolated in the usual manner and distilled to furnish the dihydro isomer-A (0·18 g): b.p. 160–65° (bath)/0·5 mm, $[\alpha]_D$ + 9·3° (*c*, 0·225%). (Found: C, 83·52; H, 10·47. $C_{19}H_{28}O$ requires: C, 83·77; H, 10·36%).

(ii) *Isomer-B.* The epoxide of isomer-B (1·314 g) in dry C_6H_6 (10 ml) was isomerized with $BF_3.Et_2O$ to the aldehyde (epimeric mixture) as described in (i) above: b.p. 160–165° (bath)/0·5 mm. The product (1·036 g) was subjected to Huang-Minlon reduction as in (i) and the dihydroderivative of isomer-B isolated by distillation: b.p. 165° (bath)/0·5 mm, $[\alpha]_D$ − 33·5° (*c*, 0·215%). (Found: C, 83·87; H, 10·53. $C_{19}H_{28}O$ requires: C, 83·77; H, 10·36%).

Nor-derivative of isomer-A/isomer-B

(i) *Isomer-A.* A stream of ozonised oxygen (O_3 conc 0·12 g/h) was passed through a soln of dihydroisomer A (0·173 g) in EtOAc (25 ml) at ~ − 20° for 0·75 h (starch-KI test). After solvent removal at ~ 40°/50 mm the resulting 'ozonide' was treated with 98% hydrazine hydrate (0·25 ml), KOH pellets (0·32 g) and diethylene glycol (5 ml). The mixture was heated (N_2) in an oil bath (150°) for 1·5 h and then to 200° (for removal of water and excess of N_2H_4) followed by 3 h at reflux temp. The mixture was poured into water (50 ml), acidified with dil HCl (1:1, Congo red) washed consecutively with water (25 ml × 2), brine (25 ml) and dried. The crude product (TLC: solvent system, 10% EtOAc in C_6H_6, 3 spots) (0·14 g) was

chromatographed on SiO_2-gel/I (20 g, 35 cm × 1·3 cm):

Fr. 1	C_6H_6	10 ml × 10	0·088 g	liquid, pure nor-derivative
Fr. 2	5% EtOAc in C_6H_6	10 ml × 5	0·020 g	glassy solid, pure demethylated nor-derivative
Fr. 3	5% EtOAc in C_6H_6	10 ml × 10	0·036 g	mixture (rejected).

Fr. 1 was distilled to give a colourless liquid, b.p. 160–165° (bath)/0·5 mm, $[\alpha]_D$ + 32·7° (*c*, 0·51%). (Found: C, 83·39; H, 11·14. $C_{18}H_{28}O$ requires: C, 83·02; H, 10·84%).

(ii) *Isomer-B.* Dihydro isomer-B (0·273 g) in EtOAc (25 ml) was subjected to ozonolysis and the resulting 'ozonide' directly reduced with hydrazine-KOH under Huang-Minlon conditions as described under (i). The crude product (0·29 g) (TLC: 3 spots; solvent 10% EtOAc in C_6H_6) was chromatographed on SiO_2-gel/I (20 g; 35 cm × 1·3 cm).

Fr. 1	C_6H_6	10 ml × 5	0·068 g	liquid, pure, nor-derivative
Fr. 2	2% EtOAc in C_6H_6	10 ml × 5	0·032 g	gum, demethylated nor-derivative(?)
Fr. 3	25% EtOAc in C_6H_6	10 ml × 6	0·132 g	gum, not investigated.

Fr. 1 was distilled: colourless liquid, b.p. 150–155° (bath)/0·4 mm, $[\alpha]_D$ − 35·26° (*c*, 0·59%). (Found: C, 83·32; H, 10·82. $C_{18}H_{28}O$ requires: C, 83·02; H, 10·84%).

REFERENCES

[1]See e.g.: [a]J. F. King and P. de Mayo in *Molecular Rearrangements* (Editor: P. de Mayo) Vol. 2, pp. 834–840. Interscience, New York (1964); [b]W. Rittersdorf and F. Cramer, *Tetrahedron* **24**, 43 (1968); [c]C. A. Bunton, J. P. Leresche and D. Hachey, *Tetrahedron Letters* 2431 (1972)

[2][a]E. E. van Tamelen, *Fortschr. Chem. Org. Naturstoffe* **19**, 245 (1961); [b]W. S. Johnson, *Accounts Chem. Res.* **1**, 1 (1968); [c]E. E. van Tamelen, *Ibid.* **1**, 111 (1968)

[3]See e.g.: Ref 2*b*

[4][a]G. Mehta, U. R. Nayak and Sukh Dev, *Tetrahedron* **29**, 1119 (1973); [b]A. S. C. Prakasa Rao, V. K. Bhalla, U. R. Nayak and Sukh Dev, *Ibid.* **29**, 1127 (1973); [c]N. P. Damodaran and Sukh Dev, *Ibid.* **29**, 1209 (1973)

[5]J. Carnduff and J. A. Miller, *J. Chem. Soc.* (C) 2671 (1968)

[6]R. Mechoulam and Y. Gaoni, *Fortschr. Chem. Org. Naturstoffe.* **25**, 175 (1967)

[7]L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 228. Pergamon, London (1969)

[8]Ref 7, p. 94

[9]Huang-Minlon, *J. Am. Chem. Soc.* **68**, 2487 (1946); **71**, 3301 (1949)

[10]R. Hernandez, R. Hernandez, Jr. and L. R. Axelrod, *Analyt. Chem.* **33**, 370 (1961)

[11]A. S. Gupta and Sukh Dev, *J. Chromatog.* **12**, 189 (1963)