ATROPODIASTEREOISOMERISM AND PSEUDOASYMMETRY WITH AXIAL CHIRALITY OF LIGANDS IN BIS(2-METHYL-1-NAPHTHYL)METHANOLS

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On reduction of bis(2-methyl-1-naphthyl) ketone (I) with lithium aluminium hydride alcohol VI was formed which isomerized into alcohol VII. Both alcohols, the configuration of which were proved using ¹H-NMR spectra and X-ray diffraction, represent the first example of compounds having a centrum of pseudoasymmetry and axial chirality of ligands.

Any molecule whose unsubstituted skeleton is of D_n or C_n symmetry $(n > 1)$ can be regarded as a molecular propeller. Such a molecule must possess two or more sub-units (blades), radiating from an axis of rotation, each blade being twisted in the same sense. Several examples of systems which can be regarded as molecular propellers are described in literature[1]. This paper, dealing with preparation and stereochemistry of dinaphthyl ketone derivatives provides further examples of this type.

Preparation of Materials

Bis(2-methyl-1-naphthyl) ketone (I) has been prepared from 2-methyl-1-naphthoyl chloride[2] and 2-methyl-1-naphthylmagnesium bromide. From the reaction mixture ketone I, m.p. 108 – 110°C, has been isolated (Scheme 1). A by-product, m.p. 271 to 273°C, was identified as diketone using infrared spectroscopy and elemental analysis. We failed in asymmetric reduction of ketone I, but an isomeric ketone II, m.p. 207 to 209°C, was obtained by column chromatography of the reaction mixture, exhibiting the same elemental composition and R_F, but different IR, UV and ¹H-NMR spectra (Table I).

To obtain ketone II in better yields, we tried synthesis starting from 2-methyl-1-naphthonitrile and 2-methyl-1-naphthylmagnesium bromide. Hydrolysis of ketimine hydrochloride III was unsuccessful, which is not unusual with this structural type[3]. Reduction of III using lithium aluminium hydride and subsequent acetylation

afforded N-acetyl-bis(2-methyl-1-naphthyl)methylamine (*IV*), m.p. 154—157°C. ^{1}H-NMR spectra of the two compounds are given in Table II.
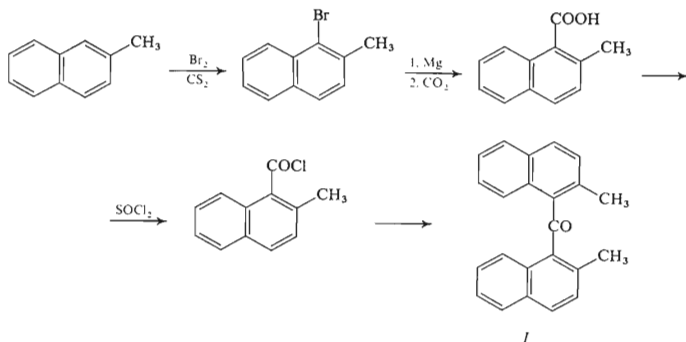
SCHEME 1

Pyrolysis of thorium 2-methylnaphthoate failed to afford the ketone, the calcium salt yielded 2-methylnaphthalene as product of decarboxylation. Reaction of 2-methyl-1-naphthyllithium with lithium 2-methyl-1-naphthoate did not afford the ketone, even though good yields of ketones are reported[4,5] in similar cases. 2-Methyl-1-naphthyllithium with carbon dioxide afforded 2-methyl-1-naphthoic acid only, in higher yields than with the organomagnesium derivative[6]. Finally, treatment of

TABLE I
Characteristic Properties of Ketones *I* and *II*

Ketone	M.w.	R_F	M.p., °C	$\nu(C=O)$ cm^{-1}	δ ppm^a (CH$_3$)	λ_{max}^{b}	ε
I	310·4	0·65	108—110	1 648	2·18	314	9 870
II	310·4	0·65	207—209	1 691	1·94	290	6 240
					2·34		

^{a} In chloroform; ^{b} in tetrachloromethane.

2-methyl-1-naphthyllithium with carbon monoxide led to 2,2'-dimethyl-1,1'-bi-naphthoyl (*V*) whose structure was shown by elemental analysis, infrared, ¹H-NMR and mass spectra.
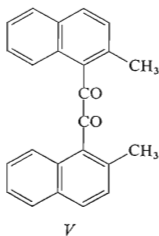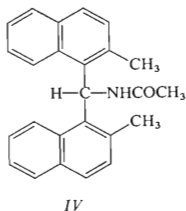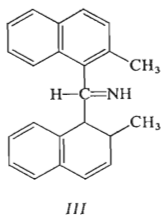

III

IV

V

Table II

Chemical Shifts of Bis(2-methyl-1-naphthyl) Ketimine Derivatives

δ ppm	Hydrochloride[a]	N-Acetyl ketimine[b]	N-Acetyl derivative of the reduction product
CH$_3$	2·62	2·20	2·25
NH	2·48	—	—
COCH$_3$	—	1·99	1·24
Ar—H	7·27—8·10	7·14—8·27	7·15—8·27

[a] In CH$_3$COOD; [b] in CDCl$_3$.

Further experiments to obtain ketone *II* were based on considerations about its formation during the attempted asymmetric reaction. The photochemical reduction, involving a ketyl-radical[7], led to destruction of the ketone *I* molecule. Our attempts on reduction of ketone *I* either with magnesium amalgame or by a modified Meerwein–Ponndorf–Verley method[8] failed.

Reduction of ketone *I* with lithium aluminium hydride afforded bis(2-methyl-1--naphthyl)methanol (*VI*) m.p. 58–60°C, which yielded an isomeric alcohol *VII*, m.p. 105–108°C after standing at room temperature for about six weeks. The two isomers exhibit identical R_F and elemental analysis. ¹H-NMR-spectra of both were measured (Table III) and X-ray analysis performed. The isomerization of alcohol *VI* to alcohol *VII* is possibly iniciated by trace amounts of acid during isolation. Isomerisation in the opposite direction occured by heating alcohol *VI* in methanol and subsequent evaporation. An attempted photochemical isomerisation failed. The reaction of alcohol *VII* with acetic anhydride in pyridine proceeds rapidly to afford acetate *IX*, m.p. 120–121°C. Acetylation of alcohol *VI* was more difficult, an acetate *VIII*, m.p. 105–107°C, was obtained using acetyl chloride in pyridine. Both acetates exhibit equal R_F values. Both alcohols *VI* and *VII* afforded ketone *I* by chromic acid oxidation. In order to establish the position of the methine proton in ¹H-NMR spectrum, ketone *I* was reduced using lithium aluminium deuteride.

Stereochemical Analyses

Two stable conformations *A* and *B* may be derived from space filling models by partial rotation about the $C_{(1)}$—C=O bond. The steric hindrance observed between methyl groups at $C_{(2)}$ and $C'_{(2)}$ and hydrogen atoms at $C_{(8)}$ and $C'_{(8)}$ could possibly be sufficient to allow the isolation of both isomers.

TABLE III
Chemical Shifts of Protons in Alcohols *VI* and *VII* and Acetates *VIII* and *IX*

Proton	Alcohol *VI*	Alcohol *VII*	Acetate *VIII*	Acetate *IX*
CH₃	2·21	2·31	2·26	2·28
C—OH	2·34	2·30[a]	—	—
H—C	7·30[b]	—	7·30	—
C—OCOCH₃	—	—	1·30	2·10
Ar—H	7·08–8·27	7·16–8·37	7·12–8·34	7·14–8·15

[a] At 60°C. [b] The signal of the methine proton in the alcohol *VI* was determined on the base of comparison with the spectrum of the deuterated alcohol. The aromatic protons region was measured with greater accuracy (200 Hz).

The crucial factor for conformation assignement of ketone *I* are the results of X-ray measurement of ketone *I*. The conformation angles $C_{(10)}C_{(11)}C_{(12)}O$ and $OC_{(12)}C_{(13)}C_{(14)}$ are practically corresponding in absolute value and sign (Fig. 7). Thus, ketone *I* is consistent with conformation formula *A*, representing a chiral system having a two-fold rotation axis passing through the carbonyl group. The ^{1}H-NMR spectrum of ketone *I* shows only one signal of six methyl protons (2·18 ppm) while the spectrum of ketone *II* exhibits two signals (1·94 and 2·34 ppm), each of three methyl protons. The data hintherto obtained about ketone *II* are unsufffcient for a detailed structure assignement. This will be the subject of further study.

B   A

I

C   D
VI, R = H   *VII*, R = H
VIII, B = COCH₃   *IX*, R = COCH₃
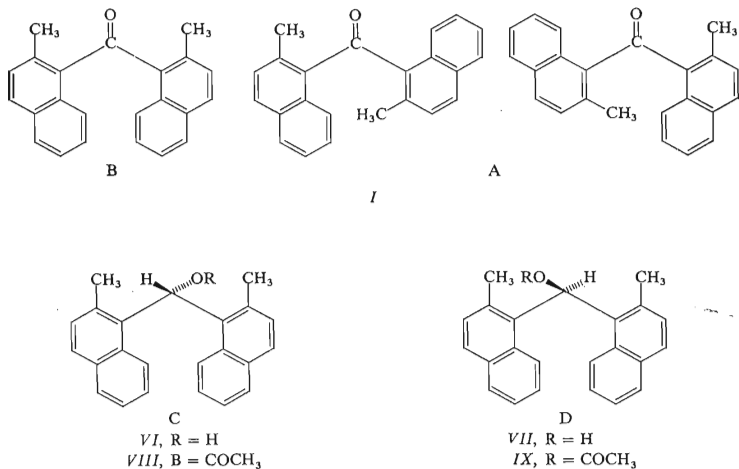
On reduction of ketone *I* alcohol *VI* was formed which transmuted into alcohol *VII*. The assignement of formulas *C*, *D* to both isomers *VI* and *VII* was accomplished by ^{1}H-NMR spectra analysis of the alcohols and their acetates (Table III). The hydroxy group of alcohol *VI* is sterically less accessible than in alcohol *VII*. This fact is consistent with the easier acetylation of alcohol *VII*. The chemical shift of the acetoxy group protons of acetate *IX* is usual for such a type of protons, no influence of the aromatic nuclei can be observed in this case. On the other hand, the signal of acetoxy group protons in acetate *VIII* is shifted considerably upfield, undoubtedly with respect to the greater proximity of the acetoxy group and the aromatic rings.

TABLE IV

Data from Diffractograms of Alcohols *VI* and *VII* (Anode: Cu, filter: Ni, 1 — 50°)

		Alcohol *VI*[a]	
Θ		4·22	14·20
d		10·45	3·13
I		1·00	0·44

			Alcohol *VII*[a]				
Θ	3·72	4·18	4·64	5·42	7·31	8·14	9·30	11·19
d	11·85	10·55	9·50	8·14	6·06	5·43	4·76	3·79
I	0·38	0·69	1·00	0·65	0·48	0·35	0·35	0·31

[a] d the inter-plane distances corresponding with the appropriate angle; I relative intensity of the signal.
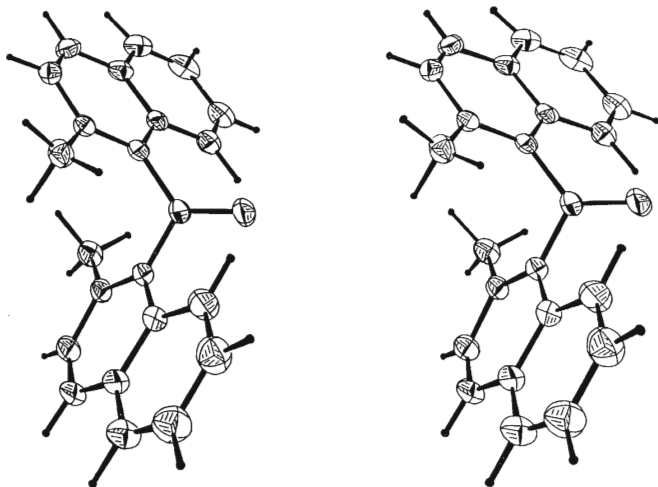

FIG. 1

Stereo-View of the Ketone *I*

We suggest therefore conformation *C* (with the hydroxy group oriented toward the naphthalene rings) for the lower melting alcohol *VI*. The hydroxy group of the diastereoisomeric alcohol *VII* is on the periphery of the molecule (conformation *D*). Both alcohols represent atropodiastereoisomeric compounds. This configuration assignement has been unequivocally confirmed by measurement of X-ray diffraction of the acetate *IX*. The planes of both naphthalene rings are practically perpendicular. As shown in the figure visualising the conformation angles around the central atom, the acetoxy group is orientated out of the space delimited by the planes of the aromatic rings. Thus, acetate *IX*, which most closely resembles a *meso* form in that the two conformational angles have opposite signs, is a derivative of the alcohol represented by conformation formula *D*. Both alcohols *VI* and *VII* afforded ketone *I* by MnO$_2$ or chromic acid oxidation. Thus, they are consistent with the conformation formulas *C* and *D*, differing in configuration at the central atom only. The central atom represents a centrum of pseudoasymmetry according Prelog's definition[9–11]. The results of roentgenometric analysis of alcohols *VI* and *VII* are given in Table IV. Alcohols *VI* and *VII* represent the first case of compounds described with a centrum of pseudoasymmetry and axial chirality of ligands.

Stereo views of molecules are shown in figures 1 and 2. Conformations of the two molecules of ketone *I* are similar enough to warrant only one drawing. Thus Fig. 1 is a view of molecule *E* of ketone *I*. Bond lengths and bond angles are shown in

Fɪɢ. 2
Stereo-View of the Acetate *IX*

Figures 3−6. The six independent naphthalene ring systems are approximately identical within experimental error. The largest variation in bond lengths is observed for the $C_{(6)}$—$C_{(7)}$ and $C_{(17)}$—$C_{(18)}$ bond types ranging from 1·338 to 1·366A. This is a difference of about 4·5 times the standard deviation of the bond length for room temperature data. For bond angles, the $C_{(3)}$—$C_{(4)}$—$C_{(5)}$ and $C_{(19)}$—$C_{(20)}$—$C_{(21)}$ angles show the largest variation, 119·8−122·0°, a difference of 5·5σ.

The pattern of bond length and angles in the naphthalene rings is compared with previously reported values[12−14], as shown in Table V. In each case, the 1−2 bond is considerably shorter than the others, with a value of 1·359A for this study. The order of increasing bond length in this study is identical to the results reported by for 1,5- and 1,8-difluoronaphthalene[13] and for 1,8-bis(dimethylamino)naphthalene[14]. The bond length in the crystal structure of naphthalene[12] show a different pattern with

FIG. 3
Bond Lengths in the Ketone *I*

FIG. 4
Bond Lengths in the Acetate *IX*

bond 3-3' being shorter than bonds 1-1' and 2-3. The angle γ is the smallest average bond angle in each case while the external angle δ has the largest value. Least-squares planes fitted to the carbon atoms of the naphthalene rings show less distortion from planarity for ketone I than in acetate IX, with average deviations of 0·012 and 0·032A, respectively. The exocyclic atoms are definitely out of the least squares planes.

The intramolecular crowding in ketone I forces any approximate symmetrical distortion around the $C_{(11)}$—$C_{(12)}$ and $C_{(12)}$—$C_{(13)}$ bonds. Figures 7 and 8 show some conformational angles and intramolecular close-contact distances. The two molecules of ketone I are similar but not the same. A progression from $C_{(1)}$ to $C_{(23)}$

Fig. 5
Bond Angles in the Ketone I
Standard deviations are between 0·3 and 0·4°.

Fig. 6
Bond Angles in the Acetate IX
    Standard deviations are 0·1°.

through the five intermediate carbon atoms is accompanied by only positive dihedral angles. In each molecule, the planes of the two naphthalene systems intersect at nearly right angles and the closest contacts are between the methyl carbon atom of one ring and the naphthyl carbon atom bonded to the carbonyl group of the other ring. The distances range from 3·029 to 3·131 Å.

However, there are small differences in the conformation of the two molecules of ketone I. For instance the intersection angles for the naphthalene planes is 87·5° for molecule E and 77·7° for molecule F which is primarily the result of the larger rotation around the $C_{(11)}$—$C_{(12)}$ bond in molecule E. Molecule F is more symmetric, as can be

Fig. 7

Ketone I Conformational Angles and Close Contacts

Fig. 8

Acetate IX Conformational Angles and Close Contacts

seen from the dihedral angles and intramolecular contacts. There are many other intramolecular contacts in the ketone *I* molecules and they are listed in Table VI, and it is interesting to note that these involve, as well, carbon atoms $C_{(9)}$, $C_{(10)}$, $C_{(12)}$, $C_{(14)}$, $C_{(15)}$ and hydrogen atoms $H—C_{(9)}$ and $H—C_{(15)}$. There may be weak interactions of the last two atoms with the oxygen atom in both molecules in agreement with a slight elongation of the $C{=}O$ bond.

In the acetate *IX* molecule where there is free rotation around the $C_{(11)}—C_{(12)}$ and $C_{(12)}—C_{(13)}$ bonds the naphthalene moieties are rotated into an orientation where they are almost perfectly perpendicular to each other (89·5°). The rotations are asymmetric as can be seen from the conformational angles in figure 8; the figure which also indicates some intramolecular contacts. Many other intramolecular contacts exist in the molecule which are listed in Table VI and it is interesting to note those involving $H—C_{(9)}$, $H—C_{(12)}$ and $H—C_{(10)}$.

Thus the results of X-ray analysis are consistent with chemical behavior and spectral data.

TABLE V

Comparison of Average Bond Lengths and Angles

Parameter[a]	this study	Cruickshank[12]	Einspahr[14]	Meresse[13b]
$1—1^1$	1·401	1·416	1·399	1·403
$1—2$	1·359	1·357	1·334	1·357
$2—3$	1·416	1·420	1·414	1·408
$3—3^1$	1·421	1·405	1·425	1·424
α	120·4	120·5	120·8	119·7
β	120·9	120·3	119·7	122·3
γ	118·7	119·2	118·7	117·8
δ	122·6	121·5	122·7	124·1

[a] Bond lengths are averages only when correcting non-substituted atoms; [b] average for both molecules reported.

EXPERIMENTAL

The given melting points are uncorrected. The purity of compounds and reaction mixture composition was determined by thin layer chromatography (Silufol UV 256, Kavalier, Czechoslovakia), benzene–chloroform 4 : 1. ^{1}H-NMR spectra were carried out using Varian XL-100 spectrometer, infrared spectra were measured using Perkin-Elmer 325 spectrometer and mass spectra on AEI-MS 902. Samples for analysis were dried in vacuo (oil pump) at room temperature for 8 h.

TABLE VI
Intramolecular Contacts

	Ketone I		
Contact		molecule E	molecule F
O(1)	H(C9)	2·41 Å	2·28 Å
O(1)	H(C10)	2·37	2·28
C(2)	C(13)	3·142	3·098
C(11)	C(22)	3·117	3·098
C(9)	H(C23)3	2·78	3·15
C(10)	H(C23)3	2·80	3·08
C(14)	H(C1)3	2·99	2·96
C(15)	H(C1)3	2·91	3·11
C(11)	H(C23)1	2·69	3·01
C(11)	H(C23)3	2·83	2·84
C(13)	H(C1)1	2·82	2·56
C(13)	H(C1)3	2·92	2·99
C(12)	H(C9)	2·57	2·58
C(12)	H(C15)	2·61	2·55
C(12)	H(C23)3	2·82	2·92
C(12)	H(C1)3	2·76	2·91

	Acetate IX				
O(1)	H(C1)2	2·41 Å	C(2)	H(C23)3	2·69 Å
C(12)	H(C15)	2·50	C(10)	H(C23)2	2·69
O(1)	H(C15)	2·49	C(11)	H(C23)2	2·56
C(24)	H(C15)	2·63	H(C1)2	H(C23)3	2·41
O(2)	H(C15)	2·69	H(C9)	H(C12)	2·02
C(9)	H(C12)	2·53	H(C15)	H(C12)	2·04
C(15)	H(C12)	2·63			

Bis(2-methyl-1-naphthyl) Ketone (*I*)

To a solution of Grignard reagent, prepared by heating 3·3 g (0·14 mol) of magnesium activated by iodine with 28·1 g (0·14 mol) 1-bromo-2-methylnaphthalene[15] in 160 ml of ether over a period of 3 h, 21·5 g (0·105 mol) of 2-methyl-1-naphthoyl chloride in 80 ml of ether was added during 45 min. After boiling for 2 h the mixture was decomposed by 250 ml of a saturated solution of ammonium chloride and 15 ml of concentrated hydrochloric acid. The precipitate was filtered off, the water layer was extracted with 3 . 80 ml of ether and the combined ether extracts after drying over magnesium sulfate evaporated *in vacuo* to give 37 g of an oil. Upon addition of an equal volume of ether 12 g of the crude product precipitated after standing overnight. Two crystallizations from ethanol yielded 9·1 g (25·8)% of ketone *I*, m.p. 106—108°C. For $C_{23}H_{18}O$ (310·4) calculated: 89·00% C, 5·85% HM found: 88·73% C, 5·88% H. A substance, which separated during decomposition of the reaction mixture, (0·4 g) melting 271—273°C, was identified as a diketone. For $C_{23}H_{28}O_2$ (480·6) calculated: 87·47% C, 5·87% H; found: 87·56% C, 5·83% H. IR spectrum: (CO) 1 642 and 1 687 cm^{-1}. ^{1}H-NMR spectrum: (ppm) 1·62; 1·96; 2·54; (singlet).

Bis(2-methyl-1-naphthyl) Ketimine (*III*)

To 2·84 g (0·12 mol) of magnesium activated with iodine a solution of 16·0 g 1-bromo-2-methyl-naphthalene in 15 ml of ether was added. After the reaction having started, further 1-bromo-

TABLE VII
Crystallographic data

Compound		Ketone *I*	Acetate *IX*
Formula		$C_{23}H_{18}O$	$C_{25}H_{22}O_2$
F.w.		310·40	354·45
Temperature		20°C	−160°C
Systematic		h01, 1 = 2n + 1	h01, h + 1 = 2n + 1
Absences		0k0, k = 2n + 1	0k0, k − 2n + 1
Space group		P2$_1$/c	P2$_1$/n
	a	21·115 (3) Å	12·083 (2) Å
	b	8·5405 (6)	7·993 (2)
	c	21·875 (4)	19·199 (8)
	β	120·72 (1)°	97·44 (2)
	V	3 391·2 Å^3	1 847·8 Å^3
	Z	8	4
F(000)		1 312	752
	D$_c$	1·216 g cm^{-3}	1·250 g cm^{-3} ^{a}
	D$_0$^{b}	1·218	1·244

^{a} Based on unit cell volume of 1 884·36 Å^3 at 20°C, as calculated by INDEX of the CAD-4 system using 15 reflections. ^{b} Measured by floatation in aqueous KI at 20°C.

-2-methylnaphthalene, (together 38·8 g, 0·18 mol) in 60 ml of ether was added. After boiling for 3 h and addition of a solution of 26 g 2-methyl-naphthonitrile (m.p. 87—89°C, prepared from 1-bromo-2-methylnaphthalene and cuprous cyanide in pyridine[16]) in 70 ml of ether was added. After boiling over a period of 2·5 h and 12 h standing at room temperature the mixture was cooled to −5°C and decomposed by 100 g of ice and 150 ml of a saturated solution of ammonium chloride. The ether layer was separated, the water layer washed with 2 . 50 ml of ether and the combined ether extracts dried with sodium sulfate. On evaporation 80 ml of an oil were obtained, which was dissolved in an equal volume of ether. A saturated ethereal solution of hydrochloric acid (25 ml) was then added, the precipitate centrifuged and decanted 2 . 100 ml of ether and 100 ml of hot acetone. The crystals (18·8 g) were dissolved in 300 ml of hot ethanol and precipitated by adding light petroleum. After 24 h, 7·5 g (27%) of yellow bis(2-methyl-1-naphthyl) ketimine hydrochloride, m.p. 183—185°C was filtered off. For $C_{23}H_{20}ClN$ (345·5) calculated: 79·91% C, 5·78% H, 4·05% N; found: 79·75% C, 5·72% H, 3·92% N.

The N-acetyl derivative of bis(2-methyl-1-naphthyl) ketimine was obtained by treating with acetic anhydride in a yield of 32·8%, m.p. 173—175°C (ethanol). For $C_{25}H_{21}NO$ (351·0) calculated: 85·47% C, 5·98% H, 3·98% N; found: 85·75% C, 6·11% H, 3·74% N.

N-Acetyl-bis(2-methyl-1-naphthyl)methylamine

To a stirred suspension of 1·24 (32·4 mmol) of lithium aluminium hydride in 60 ml of ether a suspension of 2 g (5·7 mmol) of ketimine hydrochloride in 50 ml of ether was added dropwise. After refluxing 10 h the mixture was decomposed according to Mičovič and Mihajlovič, the obtained precipitate was filtered off and washed 2 . 30 ml of ether, the filtrate was combined with the ethereal layer of the liquid residue and dried over potassium carbonate. After evaporation of the solvent 0·5 g of remaining material was mixed with 15 ml of acetic anhydride. After standing at room temperature for 12 h the mixture was poured into 150 ml of water and the oil which separated was extracted with ether. After evaporation of the dried ether solution 0·45 g of a solid was obtained, which was crystallized from methanol, yielding 0·2 g of N-acetyl-bis(2-methyl-1-naphthyl)methylamine, m.p. 154—157°C, which was pure according to thin layer chromatography. For $C_{25}H_{23}NO$ (353·0) calculated: 84·99% C, 6·51% H, 3·96% N; found: 84·77% C, 6·30% H, 3·71% N.

Reaction of 2-Methyl-l-naphthyllithium with Carbon Dioxide

A) A solution of 2-methyl-1-naphthyllithium, prepared[4] refluxing 1·5 g (0·2 g at) of lithium and 22·1 g (0·1 mol) 1-bromo-2-methylnaphthalene in 50 ml of ether during a period of 1 h (containing 83·4% of the reagent according to Gilman titration[17]) was filtered under nitrogen pressure into a suspension of 100 g of dry ice in 150 ml of ether. The mixture was made alkaline by addition of a 5% sodium hydroxide solution, the water layer separated and acidified with 1M-HCl. On crystallization of the separated solid (18·8 g) from diluted acetic acid (1 : 1) 13·2 g (89%) of 2-methyl-1-naphthoic acid, m.p. 123—126°C were obtained. The ketone could not be obtained nor detected.

B) Gaseous carbon dioxide was passed into a stirred solution of 2-methyl-1-naphthyllithium, obtained from 11·05 g (0·05 mol) of 1-bromo-2-methylnaphthalene and 0·76 g (0·1 g at) of lithium in 40 ml of ether at room temperature during 30 min. The mixture after being treated as at procedure *A* afforded 3·9 g (41·9%) of acid. From the etheral solution 5·2 g of a liquid was isolated after drying and evaporation. After standing over a period of 12 h 0·6 g of crystals, m.p. 83—86°C,

TABLE VIII

Atomic Fractional Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) of Ketone I

The temperature factor is expressed as: $\exp(-2\pi^2[U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$.

Standard deviation for last digit in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O (1)	8 898 (1)	−3 640 (2)	4 462 (1)	110 (2)	53 (1)	67 (1)	6 (1)	54 (1)	− 8 (1)
C (1)	7 430 (2)	−1 631 (4)	4 738 (2)	59 (2)	66 (2)	88 (3)	4 (2)	36 (2)	− 6 (2)
C (2)	8 018 (2)	−2 574 (4)	5 345 (2)	64 (2)	49 (2)	73 (2)	−14 (2)	43 (2)	−16 (2)
C (3)	7 893 (2)	−2 999 (4)	5 897 (2)	76 (2)	68 (2)	92 (3)	−16 (2)	55 (2)	−18 (2)
C (4)	8 375 (2)	−3 892 (4)	6 450 (2)	101 (3)	83 (3)	80 (3)	−34 (2)	65 (2)	−19 (2)
C (5)	9 029 (2)	−4 467 (4)	6 494 (1)	82 (2)	60 (2)	49 (2)	−24 (2)	29 (2)	− 9 (2)
C (6)	9 536 (2)	−5 444 (4)	7 061 (2)	100 (3)	87 (3)	57 (2)	−30 (2)	34 (2)	− 7 (2)
C (7)	10 150 (2)	−5 960 (4)	7 092 (2)	93 (3)	73 (3)	58 (2)	−11 (2)	8 (2)	7 (2)
C (8)	10 308 (2)	−5 559 (4)	6 558 (2)	70 (2)	69 (2)	64 (2)	− 3 (2)	17 (2)	− 5 (2)
C (9)	9 830 (2)	−4 646 (4)	6 004 (1)	63 (2)	58 (2)	53 (2)	− 2 (2)	20 (2)	− 5 (2)
C (10)	9 171 (2)	−4 073 (3)	5 946 (1)	57 (2)	44 (2)	52 (2)	−15 (2)	29 (2)	−13 (1)
C (11)	8 656 (1)	−3 091 (3)	5 379 (1)	56 (2)	43 (2)	53 (2)	−11 (1)	30 (1)	−11 (1)
C (12)	8 803 (1)	−2 633 (3)	4 802 (1)	56 (2)	48 (2)	48 (2)	− 3 (1)	27 (1)	− 9 (1)
C (13)	8 827 (1)	−934 (3)	4 647 (1)	65 (2)	44 (2)	58 (2)	3 (1)	35 (2)	4 (1)
C (14)	8 404 (2)	−384 (4)	3 926 (1)	85 (2)	54 (2)	60 (2)	1 (2)	38 (2)	− 1 (2)
C (15)	7 942 (2)	−1 348 (4)	3 341 (2)	101 (3)	68 (2)	57 (2)	3 (2)	35 (2)	2 (2)
C (16)	7 522 (2)	−722 (5)	2 668 (2)	114 (3)	95 (3)	65 (2)	6 (2)	38 (2)	3 (2)
C (17)	7 550 (2)	868 (5)	2 545 (2)	114 (3)	106 (3)	77 (3)	28 (3)	51 (2)	28 (2)
C (18)	7 984 (2)	1 816 (5)	3 090 (2)	78 (2)	81 (3)	92 (3)	14 (2)	65 (3)	24 (2)
C (19)	8 415 (2)	1 247 (4)	3 790 (2)	94 (3)	59 (2)	83 (2)	7 (2)	55 (2)	12 (2)
C (20)	8 868 (2)	2 243 (4)	4 361 (2)	81 (2)	45 (2)	109 (3)	8 (2)	69 (2)	2 (2)
C (21)	9 274 (2)	1 692 (4)	5 026 (2)	60 (2)	55 (2)	88 (3)	−17 (2)	52 (2)	−18 (2)
C (22)	9 258 (2)	93 (4)	5 191 (2)	69 (2)	52 (2)	67 (2)	−10 (2)	38 (2)	−14 (2)
C (23)	9 735 (2)	−359 (4)	5 959 (2)	69 (2)	66 (2)	67 (2)	−18 (2)	27 (2)	−22 (2)

TABLE VIII
(Continued)

				Molecule F					
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O (1)	4 708 (1)	8 592 (3)	5 689 (1)	62 (1)	70 (2)	85 (2)	−16 (1)	15 (1)	− 1 (1)
C (1)	3 181 (2)	6 180 (5)	5 834 (2)	95 (3)	101 (3)	121 (3)	−27 (3)	74 (3)	−31 (3)
C (2)	2 972 (2)	7 087 (4)	5 174 (2)	58 (2)	70 (2)	100 (3)	−10 (2)	40 (2)	−37 (2)
C (3)	2 207 (2)	7 293 (5)	4 589 (2)	61 (2)	88 (3)	142 (4)	−12 (2)	50 (2)	−52 (2)
C (4)	1 964 (2)	8 096 (5)	4 079 (2)	54 (2)	81 (3)	135 (4)	10 (2)	12 (2)	−50 (3)
C (5)	2 454 (2)	8 799 (4)	3 898 (2)	68 (2)	66 (2)	92 (3)	14 (2)	12 (2)	−35 (2)
C (6)	2 195 (2)	9 600 (5)	3 245 (2)	106 (3)	74 (3)	94 (3)	30 (2)	− 9 (2)	−29 (2)
C (7)	2 671 (3)	10 280 (5)	3 089 (2)	169 (5)	65 (3)	76 (3)	32 (3)	12 (3)	5 (2)
C (8)	3 429 (2)	10 158 (5)	3 560 (2)	126 (4)	76 (3)	79 (3)	21 (3)	32 (3)	4 (2)
C (9)	3 695 (2)	9 371 (4)	4 186 (2)	85 (3)	68 (2)	70 (2)	13 (2)	26 (2)	− 2 (2)
C(10)	3 219 (2)	8 651 (4)	4 379 (2)	57 (2)	57 (2)	67 (2)	10 (2)	13 (2)	−19 (2)
C(11)	3 466 (2)	7 754 (4)	5 013 (2)	48 (2)	56 (2)	75 (2)	− 3 (2)	23 (2)	−23 (2)
C(12)	4 280 (2)	7 488 (4)	5 494 (2)	53 (2)	62 (2)	57 (2)	− 4 (2)	23 (2)	− 8 (2)
C(13)	4 551 (1)	5 845 (4)	5 723 (1)	45 (2)	62 (2)	63 (2)	− 3 (2)	30 (1)	5 (2)
C(14)	5 056 (2)	5 541 (4)	6 464 (2)	54 (2)	74 (2)	64 (2)	− 3 (2)	34 (2)	3 (2)
C(15)	5 319 (2)	6 717 (4)	6 996 (2)	65 (2)	91 (3)	62 (2)	0 (2)	28 (2)	5 (2)
C(16)	5 778 (2)	6 348 (5)	7 697 (2)	83 (3)	114 (4)	69 (2)	7 (3)	34 (2)	4 (2)
C(17)	6 006 (2)	4 808 (5)	7 904 (2)	89 (3)	128 (4)	70 (2)	0 (3)	30 (2)	20 (3)
C(18)	5 769 (2)	3 644 (5)	7 408 (2)	91 (3)	94 (3)	81 (3)	3 (2)	42 (2)	18 (2)
C(19)	5 284 (2)	3 979 (4)	6 683 (2)	66 (2)	77 (2)	76 (2)	4 (2)	42 (2)	14 (2)
C(20)	5 013 (2)	2 782 (4)	6 165 (2)	91 (3)	63 (2)	99 (3)	4 (2)	56 (2)	8 (2)
C(21)	4 556 (2)	3 105 (4)	5 471 (2)	77 (2)	67 (2)	85 (3)	− 6 (2)	49 (2)	−14 (2)
C(22)	4 313 (2)	4 649 (4)	5 228 (2)	52 (2)	62 (2)	73 (2)	− 4 (2)	37 (2)	− 9 (2)
C(23)	3 834 (2)	4 883 (2)	4 441 (2)	58 (2)	76 (2)	68 (2)	− 7 (2)	30 (2)	−16 (2)

could be obtained, probably 2,2′-dimethyl-1,1′-binaphthyl. Mislow and coworkers[18] describe 64—67°C for this compound.

Reaction of Lithium 2-Methyl-1-naphthoate with 2-Methyl-1-naphthyllithium

To a suspension of 7·3 g (3·9 mmol) of lithium 2-methyl-1-naphthoate (m.p. 245—247°C, prepared[5] from 0·38 g (0·05 at) lithium and 8 g (0·045 mmol) of acid in 80 ml of methanol (89·1%) in 60 ml of ether a solution of 2-methyl-1-napthyllithium, prepared from 11·05 g (0·05 mol) 1-bromo-2-methylnaphthalene and 0·76 g (0·1 at) of lithium was added. The stirred solution was refluxed 2 h and decomposed by adding 30 ml of water and 30 ml of 0·1M-HCl. The separated ether layer was made alkaline with a 5% sodium hydroxide solution, the water layer acidified with 0·1M-HCl, the ether layer washed with water and dried over sodium sulfate. The acid (2·75 g) was isolated from the water layer. The ether layer furnished 6·8 g of an oil after evaporation of the solvent, from which 2·2 g of 2-methylnaphthalene was isolated. The remaining material was shown to be a mixture according thin layer chromatography in which no ketone was present.

Reaction of 2-Methyl-1-naphthyllithium with Carbon Monoxide

Carbon monoxide was passed into a stirred solution of 2-methyl-1-naphthyllithium obtained upon reaction of 1-bromo-2-methylnaphthalene (22·1 g, 0·1 mol) and 1·5 g (0·2 at) of lithium in 60 ml of ether after cooling to −70°C and diluting with 20 ml of ether during 2 h at −70 − −80°C. The mixture was decomposed adding 40 ml of ethanol and 50 ml of 4M-HCl. The ether layer was separated and extracted with 3 . 50 ml of a saturated potassium carbonate solution, 3 . 50 ml of a 5% sodium hydroxide solution, with water and dried with sodium sulfate. After ether having been destilled off an oil was obtained setting into crystals after standing 48 h in the refrigerator, affording 0·55 g of orange crystals upon two crystallizations from ethanol, m.p. 161—162°C. This substance was shown to be 2,2′-dimethyl-1,1′-binaphthoyl according infrared, ^{1}H-NMR and mass spectra. Mass spectrum: (only fragments determining the structure are given; m/e, relative intensity (%), fragment): 115, 77, $(C_{10}H_6CH_3—C_2H_2)^{·+}$; 141, 85, $(C_{10}H_6CH_3)^{·+}$; 169, 100, $(C_{10}H_6CH_3CO)^{·+}$; 337, 63, M.[+] IR spectrum: 3030 ms, 3010 ms, 2920 w, 1695 vs, 1615 vw, 1595 ms, 1560 vw, 1510 s, 1445 w, 1420 ms, 1370 w, 1330 vw, 1175 s, 1155 vw, 1140 w, 1065 ms, 1020 ms, 960 vw, 870 s, 865 ms, 810 s, $\nu(C—H_{Ar})$ 3010—3030 cm^{-1}, $\nu(C=O)$ = 1695 cm^{-1}. ^{1}H-NMR spectrum: CH$_3$ 2·38, Ar—H 7·16—7·86 ppm. For $C_{24}H_{18}O_2$ (338·0) calculated: 85·21% C, 5·31% H; found: 85·34% C, 5·33% H. The mother liquor was steam distilled. From 800 ml of the destillate 3·2 g of a mixture of 2-methylnaphthalene and 1-bromo-2-methylnaphthalene was isolated. The residue was free from ketone according thin layer chromatography.

Bis(2-methyl-1-naphthyl) Ketone (II)

An ether solution of (S)-(+)-2-methyl-1-butyl-magnesium chloride was prepared refluxing 0·29 g (11·8 mmol) of magnesium with 1·2 g (11·2 mmol) of (S)-(+)-1-chloro-2-methylbutane in 15 ml of ether over a period of 5 h. A suspension of 3·10 g (10 mmol) of ketone I in 30 ml of ether was added dropwise to this solution. The mixture was refluxed 12·5 h, decomposed adding 15 ml of a saturated ammonium chloride solution, the separated water layer was extracted with 2·5 ml portions of ether, the combined organic layer successively washed with 10 ml 5% sulfuric acid, 15 ml 2% sodium hydrogen carbonate solution, 10 ml of water and then dried over sodium sulfate. On evaporation 1·6 g of the starting ketone, m.p. 103—105°C was recovered. The oily residue (0·9 g) according thin layer chromatography a mixture, did not contain any alcohol as product of reduction. On column chromatography (35 g silicagel, benzene) 0·1 g of ketone I was obtained

TABLE IX

Atomic Fractional Coordinates ($\times 10^5$) and Thermal Parameters ($\times 10^4$) of Acetate IX

The temperature factor is expressed as: $\exp(-2\pi^2 U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*])$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O (1)	87 929 (7)	80 413 (12	59 074 (4)	211 (4)	233 (5)	178 (3)	− 50 (5)	6 (4)	−17 (3)
O (2)	102 633 (9)	78 778 (15)	52 563 (5)	279 (5)	382 (6)	358 (6)	− 63 (5)	76 (4)	− 8 (5)
C (1)	72 365 (13)	104 403 (20)	54 961 (8)	350 (8)	269 (7)	347 (7)	61 (6)	18 (6)	−94 (6)
C (2)	71 897 (11)	93 344 (17)	48 524 (7)	214 (6)	211 (6)	256 (6)	1 (5)	41 (5)	− 7 (5)
C (3)	66 579 (11)	100 351 (18)	42 354 (7)	234 (7)	201 (6)	349 (7)	48 (5)	47 (5)	57 (6)
C (4)	64 999 (11)	91 632 (19)	36 244 (7)	210 (6)	300 (7)	256 (6)	32 (5)	15 (5)	98 (5)
C (5)	68 637 (10)	74 860 (18)	35 906 (6)	154 (5)	275 (7)	191 (6)	− 16 (5)	27 (4)	40 (5)
C (6)	66 757 (11)	65 351 (19)	29 689 (6)	181 (6)	376 (8)	178 (6)	− 30 (6)	25 (5)	28 (5)
C (7)	69 788 (11)	48 950 (19)	29 457 (7)	212 (6)	356 (8)	193 (6)	− 75 (6)	49 (5)	−62 (5)
C (8)	74 903 (11)	41 300 (17)	35 520 (7)	249 (6)	225 (7)	247 (6)	− 23 (5)	76 (5)	−29 (5)
C (9)	76 973 (10)	50 187 (17)	41 615 (6)	202 (6)	218 (6)	189 (6)	4 (5)	40 (5)	20 (5)
C (10)	74 023 (10)	67 374 (16)	42 032 (6)	158 (5)	204 (6)	182 (6)	14 (5)	39 (4)	17 (5)
C (11)	75 760 (10)	77 011 (17)	48 333 (6)	165 (5)	213 (6)	185 (6)	5 (5)	24 (4)	21 (5)
C (12)	81 911 (10)	68 279 (16)	54 542 (6)	179 (5)	203 (6)	159 (6)	7 (5)	10 (4)	−18 (5)
C (13)	75 440 (10)	57 156 (16)	59 225 (6)	178 (5)	196 (6)	158 (6)	8 (5)	26 (4)	−29 (5)
C (14)	82 156 (10)	46 967 (16)	64 145 (6)	197 (6)	195 (6)	163 (6)	− 20 (5)	27 (4)	−29 (5)
C (15)	93 988 (10)	46 810 (17)	64 548 (7)	195 (6)	226 (6)	206 (6)	− 13 (5)	21 (5)	5 (5)
C (16)	100 068 (11)	37 878 (19)	69 634 (7)	209 (6)	263 (7)	263 (6)	7 (5)	5 (5)	19 (5)
C (17)	94 827 (12)	28 512 (19)	74 611 (7)	286 (7)	298 (8)	245 (6)	22 (6)	− 11 (5)	64 (6)
C (18)	83 497 (12)	27 682 (19)	74 207 (7)	295 (7)	282 (7)	230 (6)	6 (6)	57 (5)	68 (5)
C (19)	76 973 (11)	36 673 (17)	68 987 (6)	230 (6)	214 (6)	213 (6)	− 16 (5)	46 (5)	− 6 (5)
C (20)	65 235 (11)	35 542 (18)	68 480 (7)	250 (7)	264 (7)	247 (6)	− 51 (5)	74 (5)	7 (5)
C (21)	59 087 (11)	44 912 (18)	63 654 (7)	178 (6)	293 (7)	252 (6)	− 39 (5)	55 (5)	−51 (5)
C (22)	63 889 (10)	56 271 (17)	59 088 (6)	186 (6)	234 (6)	185 (6)	− 12 (5)	23 (5)	−46 (5)
C (23)	55 656 (11)	67 006 (19)	54 705 (7)	167 (6)	310 (7)	287 (7)	12 (5)	19 (5)	7 (5)
C (24)	98 097 (11)	85 029 (18)	57 261 (7)	212 (6)	260 (7)	228 (6)	− 30 (5)	11 (5)	46 (5)
C (25)	102 867 (12)	98 503 (20)	61 985 (7)	302 (7)	334 (8)	278 (7)	−105 (6)	−39 (5)	12 (6)

and 0·4 g of a substance, melting at 207—209°C after two crystallizations from benzene-ethanol. This substance was identified as ketone *II* based on infrared, UV and ^{1}H-NMR spectra. For $C_{23}H_{18}O$ (310·4) calculated: 89·00% C 5·85% H; found: 88·91% C, 6·07% H. The spectral data are summarized in Table I.

Bis(2-methyl-1-naphthyl)methanol (*VI* and *VII*)

To a suspension of 0·21 g (5·5 mmol) of lithium aluminium hydride in 40 ml of ether a solution of 1·55 g (5 mmol) of ketone *I* in 30 ml of ether was added dropwise over a period of 30 min. The mixture was refluxed 10 h and decomposed by addition of 10 ml of water and 20 ml of 20% sulfuric acid. The ether layer was separated, the water layer extracted with two 50 ml portions of ether. The combined extracts were washed with water to neutrality and dried over sodium sulfate. On evaporation *in vacuo* 1·3 g (88·6%) of alcohol *VI*, m.p. 58—60°C was obtained. For $C_{23}H_{20}O$ (312·4) calculated: 88·43% C, 6·43% H; found: 88·73% C, 6·68% H. *A)* Alcohol *IV* was allowed to stand in a closed flask and its melting point was checked every 3rd day. After 6 weeks isomerisation to alcohol *VII* (m.p. 105—108°C) occured. This experiment was repeated several times with the equal result. *B)* Alcohol *VII* was dissolved in 15 ml of boiling methanol, gradually chilled and allowed to stand for 12 h. After evaporation of the solvent 0·5 g of a voluminous substance, m.p. 56—58°C was obtained. The product was shown to be alcohol *VI*. This experiment was twice repeated with equal result.

[1-^{2}H]Bis(2-methyl-1-naphthyl)methanol

To a suspension of 0·42 g (11 mmol) of lithium aluminium deuteride in 30 ml of ether a solution of 1·55 g (5 mmol) of ketone *I* in 40 ml of ether was added dropwise. The mixture was stirred and refluxed over a period of 16 h and after further standing for 12 h at room temperature decomposed using 20 ml of water and 40 ml of 20% sulfuric acid. The ether layer was separated, the water layer extracted with 3 . 20 ml of ether, the combined ether portions washed with water to neutrality and dried over sodium sulfate. After evaporation of the solvent 1·2 g (81%) of alcohol *VI*, labelled with deuterium, m.p. 58—60°C was obtained.

Acetate *VIII* of the Bis(2-methyl-1-naphthyl)methanol (*VI*)

To a solution of 0·5 g (1·61 mmol) of alcohol *VI* in 3 ml of pyridine 2·0 g (2·74 mmol) of acetyl chloride was added under cooling. The solidified mixture was heated 10 min to reflux and allowed to stand at room temperature 30 min. After addition of 20 ml of benzene and heating 1 h the mixture was poured into 100 ml of water. The separated oil was 3 times extracted with 25 ml portions of benzene and the solvent evaporated *in vacuo*. The residue was dissolved in boiling benzene and the filtered solution purified by column chromatography on silicagel. On elution with benzene a substance was obtained which set into crystals after drying *in vacuo* over a period of 16 h. The yield of acetate was 0·35 g (51·5%), m.p. 105—107°C. For $C_{25}H_{22}O_2$ (354·4) calculated: 84·72% C, 6·25% H; found: 84·39% C, 6·93% H.

Acetate *IX* of the bis(2-methyl-1-naphthyl)methanol (*VII*)

A solution of 0·20 g (2 mmol) of acetic anhydride in 5 ml of pyridine was dropwise added to 0·62 g (2 mmol) of alcohol *VII*. After heating for 3 h the mixture was chilled and poured into 200 ml of water. The mixture was extracted with 3 . 20 ml of ether and after washing with 20 ml of 10% hydrochloric acid dried over magnesium sulfate. No starting alcohol was present in the solution

TABLE X

Hydrogen Atom Parameters of ketone *I* Positional Parameters ($\times 10^3$) and Isotropic Temperature Factors

* Parameters were not refined by least-squares calculations.

	Molecule E				Molecule F			
	x	y	z	B (Å²)	x	y	z	B (Å²)
H(C1)1*	760	− 35	480	6·7	345	520	587	8·6
H(C1)2*	695	−158	473	6·7	278	573	588	8·6
H(C1)3*	734	−190	426	6·7	357	666	629	8·6
H(C3)	743(2)	−256 (4)	587 (2)	7·5 (8)	187 (2)	681 (4)	486 (2)	10·0 (10)
H(C4)	826 (1)	−419 (4)	681 (1)	6·8 (7)	143 (2)	821 (4)	373 (2)	9·5 (10)
H(C6)	934 (2)	−555 (4)	740 (2)	8·8 (9)	159 (2)	956 (5)	295 (2)	11·8 (12)
H(C7)	1 050 (1)	−664 (4)	746 (2)	7·7 (8)	248 (2)	1 088 (5)	265 (2)	13·3 (13)
H(C8)	1 078 (2)	−598 (1)	659 (1)	7·6 (8)	377 (2)	1 059 (4)	345 (2)	9·4 (10)
H(C9)	992 (1)	−437 (3)	560 (1)	6·0 (7)	425 (2)	931 (4)	453 (2)	7·8 (8)
H(C15)	791 (1)	−248 (3)	343 (1)	5·4 (7)	513 (2)	781 (4)	683 (2)	7·9 (9)
H(C16)	721 (2)	−145 (4)	232 (1)	7·2 (8)	594 (2)	725 (4)	806 (2)	9·7 (10)
H(C17)	723 (2)	124 (4)	205 (2)	9·7 (10)	635 (2)	454 (4)	840 (2)	9·5 (10)
H(C18)	804(2)	302 (4)	303 (2)	8·6 (9)	592 (2)	250 (4)	756 (2)	9·8 (10)
H(C20)	885 (1)	334 (4)	426 (1)	6·6 (7)	513 (2)	171 (4)	631 (2)	8·2 (9)
H(C21)	961 (1)	233 (3)	543 (1)	6·7 (8)	441 (1)	228 (3)	512 (1)	5·3 (7)
H(C23)1*	935	− 53	615	6·7	330	494	425	6·4
H(C23)2*	1 009	43	629	6·7	390	385	420	6·4
H(C23)3*	1 000	−141	606	6·7	399	574	423	6·4

according thin layer chromatography. After the solvent having been destilled off, 0·8 g of a residue was obtained which, after two crystallization from ethanol, afforded 0·45 g (63·4%) of acetate *IX*, melting at 120—121°C. For $C_{25}H_{22}O_2$ (354·4) calculated: 84·72% C, 6·25% H; found: 84·74% C, 6·61% H.

Oxidation of Alcohol *VI*

To a solution of 0·5 g (1·7 mmol) of alcohol *VI* in 30 ml of ether a mixture of 0·74 g (0·6 mmol) of potassium bichromate, 5 ml of concentrated sulfuric acid and 50 ml of water was added dropwise. Further 5 ml of acid in 20 ml of water was added after 2 h. After stirring the mixture over a period of 3 h at room temperature the ether layer was separated and the water layer extracted with 2 . 30 ml of ether. The combined organic portions were washed with a saturated sodium hydrogencarbonate solution, water and finally dried over sodium sulfate. After evaporation of the solvent 0·45 g of a product melting at 107—109°C was obtained which was proved to be ketone *I* using thin layer chromatography.

Oxidation of Alcohol *VII*

This experiment was performed starting from the same quantities as in the former oxidation, the reaction proceeded more slowly. After stirring over a period of 7 h and the usual work-up 0·4 g of a substance melting 105—107°C was isolated, which was by thin layer chromatography identified as ketone *I*.

Reduction of Ketone *I* with Lithium Aluminium Hydride and (—)-Quinine

To a suspension of 0·21 g (5·5 mmol) of lithium aluminium hydride in 50 ml of ether 1·78 g (5·5 mmol) of quinine was added. After refluxing the stirred mixture over a period of 20 min a solution of 1·55 g (5 mmol) of ketone *I* in 30 ml of ether was added. The stirred solution was, refluxed for 10 h, decomposed with 10 ml of water and 20 ml of 20% sulfuric acid. The ether layer was separated, the water layer extracted with 2 . 15 ml of ether, the combined ether portions washed 3× with diluted sulfuric acid and dried with sodium sulfate. On evaporation 0·8 g of a semicrystalline substance was obtained. The presence of starting ketone *I* and a product the R_F of which corresponds to alcohols *VI* and *VII* were proved. The substance was dissolved in benzene and separated by column chromatography on 60 g of Al_2O_3. On evaporating the individual fractions subsequently 0·4 g of starting ketone *I* was obtained, then 0·2 g of an oil, containing starting material and product and finally 0·1 g of crystals melting at 70—72°C, exhibiting R_F corresponding to those of both alcohols; $[\alpha]_D = 0$ (c 3·6, chloroform).

X-Ray Measurements of Ketone *I* and Acetate *IX*

Crystals of ketone *I* were grown in a diffusion cell from acetone–water while crystals of acetate *IX* were grown from ethanol by solvent evaporation. The data crystals chosen were parallelopiped shaped with similar dimensions, 0·14 × 0·17 × 0·54 mm and 0·17 × 0·21 × 0·57 mm for ketone *I* and acetate *IX*, respectively. All X-ray measurements were made with a Nonius CAD-4 automatic diffractometer using Ni-filtered CuKα radiation ($\lambda = 1·54178$ Å). The intensity data were collected with $\Theta - 2\Theta$ scans allowing a maximum scan time of 60 s with 2/3 of that time spent scanning the peak and 1/6 on each the left and right background. Ketone *I* measurements were made at 20°C. The space group was determined to be $P2_1/c$ and the intensities of all independent reflections with $\Theta \leqq 65°$ were collected. Of the 5740 reflections, 2066 could not be

distinguished from the background on the basis that the net count was less than $2T^{1/2}$, where T is the total count. These reflections were not used in the least-squares refinement. The acetate *IX* measurements were made at $-160°C$. The space group was determined as $P2_1/n$ and all 3788 unique intensity data with $\Theta \leqq 75°$ were collected. Of these, 498 were considered indistinguishable from the background, having net counts less then $2T^{1/2}$. They were assigned an intensity of $1.4\ T^{1/2}$ for the purpose of least-squares refinement. The least-squares cell parameters of each compound were determined from averages of $+2\Theta$ and -2Θ values of 36 reflections measured with $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å). The crystallographic data are shown in Table VII. The data were corrected for background radiation, Lorentz and polarization effects and were scaled in accordance with the intensity variations of a monitor reflection which was measured after every 30 reflections. No absorption corrections were made due to the relatively low linear absorption coefficients, 5.73 and 6.32 cm^{-1} for ketone *I* and acetate *IX*, respectively. Each structure amplitude was assigned a weight given by $W_F = 1/\sigma_F^2$ where σ_F is the standard deviation of the amplitude and is given by $\sigma_F = 1/2\{[\sigma^2 + (0.05\ P)^2]/(Lp)\ P\}^{1/2}$ in which $\sigma = T^{1/2}\ V$, V scan speed, $P = [Pk - 2(R + L)]\ V$, Pk peak count, R right background count, L left background count, Lp Lorentz polarization factor.

TABLE XI

Hydrogen Atom Parameters of Acetate *IX* Positional Parameters (($\times 10^3$)) and Isotropic Temperature Factors

Molecule	x	a	z	B (Å^2)
H(C1)1	796 (1)	1 108 (2)	554 (1)	3.8 (4)
H(C1)2	717 (1)	979 (2)	593 (1)	2.9 (4)
H(C1)3	661 (1)	1 116 (2)	544 (1)	3.3 (4)
H(C3)	639 (1)	1 119 (2)	425 (1)	2.6 (3)
H(C4)	613 (1)	967 (2)	322 (1)	2.6 (3)
H(C6)	628 (1)	713 (2)	252 (1)	3.0 (4)
H(C7)	683 (1)	425 (2)	254 (1)	3.0 (4)
H(C8)	772 (1)	293 (2)	354 (1)	2.5 (3)
H(C9)	806 (1)	446 (2)	457 (1)	1.9 (3)
H(C15)	979 (1)	533 (2)	609 (1)	1.8 (3)
H(C16)	1 081 (1)	376 (2)	695 (1)	2.5 (3)
H(C17)	990 (1)	222 (2)	782 (1)	2.4 (3)
H(C18)	795 (1)	207 (2)	774 (1)	1.6 (3)
H(C20)	617 (1)	281 (2)	718 (1)	2.3 (5)
H(C21)	512 (1)	439 (2)	633 (1)	2.0 (3)
H(C23)1	481 (1)	632 (2)	556 (1)	2.8 (3)
H(C23)2	562 (1)	654 (2)	495 (1)	2.6 (3)
H(C23)3	566 (1)	791 (2)	561 (1)	2.6 (3)
H(C12)	877 (1)	612 (2)	526 (1)	1.2 (3)
H(C25)1	1 107 (2)	987 (3)	618 (1)	4.9 (5)
H(C25)2	1 001 (2)	981 (3)	666 (1)	5.4 (5)
H(C25)3	1 006 (2)	1 096 (3)	603 (1)	6.1 (6)

Structure Determinations and Refinements

Both structures were solved by direct phasing techniques using the program Multan[19]. The structures were refined by block-diagonal least-squares methods, using 9×9 blocks for anisotropic atoms and 4×4 blocks for isotropic atoms, minimizing the quantity $\sum W_F(|kFo| - |Fc|)^2$. Difference-Fourier maps were calculated after a few cycles of isotropic and subsequent anisotropic refinement when $R = (\sum ||kFo| - Fc||)/\sum |kFo|$ of both structures had dropped to 0·1. They showed reasonable positions for all expected hydrogen atoms. Each hydrogen atom was assigned a temperature factor $1e^2$ larger than that of the carbon atom to which it was bonded. The positional and thermal parameters of the methyl hydrogen atoms of ketone *I* were kept fixed while all other hydrogen atom parameters were added as variables in subsequent refinement cycles. Least-squares refinement was continued for both structures until all parameter shifts of the carbon and oxygen atoms were no larger than one half of their standard deviations and all shifts in hydrogen parameters were less than 0·75. The final values for R were 0·057 for ketone *I* (3 674 observed data) and 0·048 for acetate *IX* (all 3 788 data). An analysis of the structure factors at the end of refinement showed that average values of $W_F(|kFo| - |Fc|)^2$ were independent of Fo and sin Θ/λ, validating the weighting scheme employed in the refinement. A final difference Fourier synthesis for each structure showed peaks ranging from 0·14 to $-0·11$ and 0·26 to $-0·29$ e/Å³ for ketone *I* and acetate *IX* respectively. The final atomic parameters are given in Tables VIII—XI.

The atomic scattering factors for C and O were taken from International Tables for X-Ray Crystallography[20]. The scattering factors for the hydrogen atoms were taken from Stewart, Davidson and Simpson[21]. The structure-factor least-squares and Fourier calculations were made with the programs by Ahmed[22,23] and the stereoscopic drawings were made with Johnsons' ORTEP program[24].

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