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## Approaches to the synthesis of triterpenes. V. An unusual acid-catalysed rearrangement of a $\beta,\gamma$ -unsaturated ketone<sup>1,2</sup>

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JOHN W. APSIMON, SATYANAND BADRIPERSAUD, MICHAEL L. POST, and ERIC J. GABE. Can. J. Chem. **56**, 2150 (1978).

The reaction of 2-keto-1 $\beta$ ,4 $\alpha\beta$ -dimethyl-1 $\alpha$ -[2-(3-keto-1,4,4-trimethylcyclohexyl)ethyl]-7-methoxy-1,2,3,4,4a,9-hexahydrophenanthrene **1a** and **b** with *p*-toluenesulphonic acid in boiling xylene yields the rearranged product, 1,10-dimethyl-2-[2-(3-keto-1,4,4-trimethylcyclohexyl)ethyl]-7-methoxy-3,4-dihydroanthracene (**3**). Crystals of **3** are monoclinic, space group  $P2_1/c$ ,  $Z = 4$ , with  $a = 7.2684(3)$ ,  $b = 30.942(2)$ ,  $c = 10.5544(7)$  Å,  $\beta = 98.24(1)^\circ$ . The structure was determined by direct methods from diffractometer data and refined by block-diagonal least-squares to an  $R$  of 0.043 for 1810 observed reflections. The molecule exhibits no unusual geometric features, although positional disorder is apparent in the cyclohexanone moiety.

A possible route for the formation of **3** from **1a** and **b** is presented.

JOHN W. APSIMON, SATYANAND BADRIPERSAUD, MICHAEL L. POST et ERIC J. GABE. Can. J. Chem. **56**, 2150 (1978).

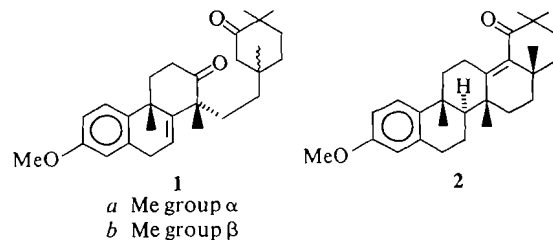
La réaction de l'oxo-2 diméthyl-1 $\beta$ ,4 $\alpha\beta$  [(oxo-3 triméthyl-1,4,4 cyclohexyl)-2 éthyl]-1 $\alpha$  méthoxy-7 hexahydro-1,2,3,4,4a,9 phénanthrène (**1a** et **b**) avec l'acide *p*-toluènesulfonique dans le xylène à l'ébullition conduit au diméthyl-1,10 [(oxo-3 triméthyl-1,4,4 cyclohexyl)-2 éthyl]-2 méthoxy-7 dihydro-3,4 anthracène (**3**), un produit de réarrangement. Les cristaux de **3** sont monocliniques, groupe d'espace  $P2_1/c$ ,  $Z = 4$  avec  $a = 7.2684(3)$ ,  $b = 30.942(2)$ ,  $c = 10.5544(7)$  Å,  $\beta = 98.24(1)^\circ$ . On a déterminé la structure par des méthodes directes à partir de données de diffraction de rayon X et on l'a affinée par la méthode des moindres carrés (blocs diagonaux) jusqu'à une valeur de  $R$  de 0.043 pour 1810 réflexions observées. La molécule ne présente aucune caractéristique géométrique inhabituelle quoique le désordre de position est apparent dans la portion de la cyclohexanone.

On présente une route possible permettant d'expliquer la formation de **3** à partir de **1a** et **b**.

[Traduit par le journal]

In the previous paper (1) we described the synthesis of the mixture of substituted reduced phenanthrenes **1a** and **b** and its conversion into the pentacyclic picenone **2** suitable as an intermediate in triterpene synthesis.

During our studies we noted that the reaction of a mixture of **1a** and **b** with *p*-toluenesulphonic acid in boiling xylene or benzene gave, after chromatography, a product whose physical properties did not correspond to those expected for a normal cyclisation product of **1a** and **b** although its molecular weight



( $M^+ 404$ ) corresponded to the loss of one molecule of water from **1a** or **1b** ( $M^+ 422$ ). Thus the mass spectrum of the cyclisation product showed a parent ion at  $m/e$  404.2717 corresponding to a molecular formula of  $C_{28}H_{36}O_2$  and a base peak at  $m/e$  237.1264 corresponding to a fragment of structure  $C_{17}H_{17}O$ . This loss of a fragment  $C_{11}H_{19}O$  (mol. wt. 167) suggested that the pendant trimethyl cyclo-

<sup>1</sup>Portions of this work are described in the Ph.D. thesis of S.B. (Carleton University, Ottawa, Ont., 1976). For Part IV see ref. 1.

<sup>2</sup>NRCC No. 16724.

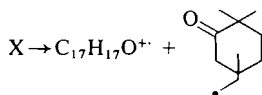
<sup>3</sup>To whom inquiries should be directed.

TABLE 1. Carbon-13 nuclear magnetic resonance data for 3

Carbon location*	Chemical shift ( $\delta$ )	Type of carbon	No. of carbon atoms	No. of protons	No. of oxygen atoms
18	215	C=O	1		1
7	156	O—C=	1		
1,2,1a,4a,5a,8a,10	125.6, 127.0, 128.6				
	129.9, 133.5, 135.9, 137.4	=C—	7		
5,6,8,9	106.7, 117.3, 118.9, 125.2	=C—H	4	4	
12	55.1	O—CH <sub>3</sub>	1	3	1
16,19	39.1, 44.1	—C—	2		
3,4,14,15,16,17,20,21	25.1, 28.7, 29.0	CH <sub>2</sub>	7	14	
	32.5, 36.5, 39.9, 49.8				
11,13	14.3 (2)	=C—CH <sub>3</sub>	2	6	
22,23,24	24.8, 25.4 (2)	—C—CH <sub>3</sub>	3	9	
		Total	C = 28	H = 36	O = 2

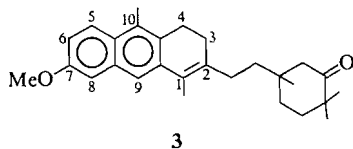
\*Carbon locations assigned as shown in Fig. 1.

hexanone ring had been lost together with its side chain:



This behaviour is reminiscent of that observed for species such as **1a** and **b** but not identical since in this latter case a McLafferty-type hydrogen rearrangement (1) is noted.

The 100 MHz proton magnetic resonance spectrum of the product 'X' indicated retention of the phenolic methyl ether system and the presence of two low field methyl groups, present as olefinic or aromatic substituents. The triplet for the olefinic proton appearing at  $\delta$  5.86 in the nmr spectrum of **11** was noted to be shifted downfield to  $\delta$  7.50 probably attributable to an isolated aromatic proton. The 25.15 MHz carbon-13 nmr spectrum indicated the presence of one carbonyl group (215.7 ppm) as well as eight  $sp^2$  fully substituted carbon atoms. Table 1 summarises the carbon  $^{13}C$  nmr spectrum. A single crystal X-ray structure determination was carried out on this material and revealed its structure to be the dihydroanthracene **3**. All of the spectroscopic properties (see Experimental) accord with this structure.



A view of the molecule as determined by X-ray diffraction is shown in Fig. 1 and final atomic coordinates and bond lengths and angles for the non-hydrogen atoms are presented in Tables 2 and 3. Full details concerning the H atoms and their bonding geometry have been placed in the Deposi-

tory of Unpublished Data.<sup>4</sup> The average of all C—H bond lengths is 0.97 Å while that for associated angles is 109° ( $sp^3$ ) and 119° ( $sp^2$ ). The geometric features of the molecule show no remarkable deviation from those expected. Thus, the aromatic portion of the anthracene moiety is close to planar ( $\pm 0.036$  Å) and the fused cyclohexene ring, with torsion angles C(1a)—C(1)—C(2)—C(3) and C(1)—C(1a)—C(4a)—C(4)  $< \pm 1^\circ$ , has a conformation best described as midway between a 'sofa' and a 'boat'. The extended dimethylene bridge, with torsion angles C(1)—C(2)—C(14)—C(15) and C(2)—C(14)—C(15)—C(16) of 95 and 176°, links to the trimethylcyclohexanone ring which is in 'chair' form. The intraring bond angle at the carbonyl group(s) approaches  $sp^2$  values. The crystal packing forces in the structure are of the van der Waals type with a majority of the closest intermolecular contacts occurring between the carbonyl O atom(s) and symmetry related H atoms of —CH<sub>2</sub>— and —CH<sub>3</sub> groups.

The formation of this species in acid can be explained by the stepwise transformation shown in Scheme 1; for a review of other acid-catalysed ketone rearrangements see ref. 2. It is interesting to note that in the initial rearrangement step it is the equatorial group that migrates rather than the methyl group, although it could be argued that other non-isolated reaction products could arise by an alternate route. We have been unable to detect other species of a similar nature to **3** although, as can be seen from the Experimental, **3** has been isolated in pure form in only about 25% yield. It is also interesting to note

<sup>4</sup>Tables of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom coordinates, and isotropic thermal parameters together with bond lengths and angles involving the hydrogen atoms are available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

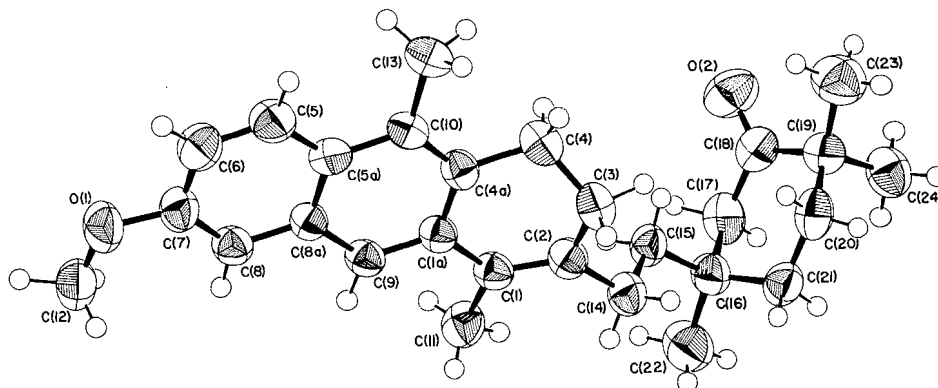


FIG. 1. Perspective view (3) of (3) as determined by X-ray analysis. Atom O(2) is shown in its major position (the minor site, O(2'), is on atom C(20)). Nonhydrogen atoms are represented by 50% probability thermal ellipsoids and hydrogen atoms by spheres of arbitrary radius.

TABLE 2. Final atomic coordinates ( $\times 10^4$ ) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
C(1)	5010(4)	384(1)	1473(3)	C(13)	7285(5)	-581(1)	5221(3)
C(1a)	4726(4)	-3(1)	2256(3)	C(14)	7136(5)	940(1)	720(3)
C(2)	6706(5)	554(1)	1495(3)	C(15)	7149(5)	1362(1)	1483(3)
C(3)	8344(5)	354(1)	2306(3)	C(16)	7691(4)	1773(1)	808(3)
C(4)	7863(4)	149(1)	3517(3)	C(17)	7657(5)	2154(1)	1737(4)
C(4a)	6124(4)	-124(1)	3283(3)	C(18)	9168(5)	2130(1)	2866(3)
C(5)	3844(5)	-1085(1)	4559(3)	C(19)	11144(5)	2063(1)	2602(3)
C(5a)	4203(4)	-718(1)	3830(3)	C(20)	11131(5)	1712(1)	1579(3)
C(6)	2247(5)	-1311(1)	4317(3)	C(21)	9683(5)	1747(1)	445(3)
C(7)	839(5)	-1180(1)	3341(3)	C(22)	6280(6)	1861(1)	-400(4)
C(8)	1113(4)	-837(1)	2601(3)	C(23)	12401(6)	1935(1)	3826(4)
C(8a)	2796(4)	-597(1)	2809(3)	C(24)	11818(5)	2491(1)	2100(4)
C(9)	3118(4)	-240(1)	2047(3)	O(1)	-739(3)	-1426(1)	3244(2)
C(10)	5856(4)	-465(1)	4067(3)	O(2)	8812(4)	2182(1)	3923(3)
C(11)	3314(5)	559(1)	633(3)	O(2')	12282(9)	1462(4)	1702(17)
C(12)	-2279(5)	-1306(1)	2355(4)				

that **3** now contains only one asymmetric centre and is racemic whereas **1a** and **b** was a mixture of diastereoisomers containing three such centres.

### Experimental

For general procedures and details of spectroscopic analyses see Part III of this series (4).

#### Acid-catalysed Rearrangement of 2-Keto-1 $\beta$ ,4 $\alpha\beta$ -dimethyl-1 $\alpha$ [2-(3-keto-1,4-trimethylcyclohexyl)ethyl]-7-methoxy-1,2,3,4,4a,9-hexahydrophenanthrene (**1a** + **b**)

The olefinic diketones **1a** and **b** (100 mg) were dissolved in 20 ml dry benzene under nitrogen. Solid *p*-toluenesulfonic acid (200 mg) was added and the mixture was refluxed for 7 h. Thin-layer chromatography indicated no loss of the starting material. An additional 200 mg of *p*-toluenesulfonic acid was added and reflux continued overnight. Thin-layer chromatography analysis showed, in addition to starting material, a new product of lesser polarity. After cooling the reaction mixture, water was added and the benzene layer separated. The aqueous layer was further extracted with ether ( $\times 3$ ). The combined organic layer was washed with saturated sodium bicarbonate solution, water, saturated sodium chloride solution and dried over magnesium sulphate (anhydrous). Evapor-

ation of the solvent gave an oil which was column chromatographed on silica gel. Elution with benzene gave 25 mg of the rearranged material (**3**) as an oil and further elution with 10% ether in benzene gave the starting diketones (60 mg).

The reaction was repeated under the above conditions except that the benzene was replaced by the higher boiling *p*-xylene. After column chromatography the product was obtained in higher yield (47%) as an oil. Although this material was homogeneous on thin layer chromatography, it was shown by nmr to be a mixture. Crystallization from methanol gave 24 mg of colorless crystals from 45 mg of the oil. The mother liquor appeared to be a mixture of compounds (nmr) which could not be resolved by column or thin-layer chromatography. Recrystallization of the crystalline material gave analytical sample of **3**: mp 117–120°C; uv max (95% C<sub>2</sub>H<sub>5</sub>OH): 308 (12 900), 295 (14 700), 257 (47 900); ir (Nujol): 1700 (C=O) and 1600 cm<sup>-1</sup> (aromatic, olefin); nmr (CDCl<sub>3</sub>)  $\delta$ : 1.00 (s, 3, CH<sub>3</sub>), 1.14 (s, 3, CH<sub>3</sub>), 1.16 (s, 3, CH<sub>3</sub>), 2.14 (s, 3, C—CH<sub>3</sub>), 2.58 (s, 3, =C—CH<sub>3</sub>), 3.93 (s, 3, O—CH<sub>3</sub>), and 7.00–8.00 (m, 4, ArH); nmr (C<sub>6</sub>D<sub>6</sub>)  $\delta$ : 0.82 (s, 3, CH<sub>3</sub>), 1.04 (s, 3, CH<sub>3</sub>), 1.08 (s, 3, CH<sub>3</sub>), 2.18 (s, 3, CH<sub>3</sub>), 2.42 (s, 3, CH<sub>3</sub>), 2.54 (s, 3, O—CH<sub>3</sub>), and 7.00–8.00 (m, 4, ArH); ms *m/e* (relative intensity): 404 (60), 202 (37), 237 (100); high resolution mass spectrum ion 404: mass calcd. for C<sub>28</sub>H<sub>36</sub>O<sub>2</sub><sup>+</sup>: 404.2715; measured 404.2717; ion *m/e* 237; mass calcd. for

TABLE 3. Bond distances and angles involving the nonhydrogen atoms

(a) Distances: estimated standard deviations  $\leq \pm 0.004 \text{ \AA}$  (except at O(2')  $\pm 0.01 \text{ \AA}$ )

Bond	Distance (Å)	Bond	Distance (Å)
C(1)—C(1a)	1.484	C(8a)—C(9)	1.404
C(1)—C(2)	1.338	C(9)—C(1a)	1.371
C(1)—C(11)	1.512	C(10)—C(13)	1.525
C(2)—C(3)	1.496	C(12)—O(1)	1.404
C(2)—C(14)	1.508	C(14)—C(15)	1.531
C(3)—C(4)	1.512	C(15)—C(16)	1.538
C(4)—C(4a)	1.510	C(16)—C(17)	1.536
C(4a)—C(10)	1.373	C(16)—C(21)	1.521
C(4a)—C(1a)	1.426	C(16)—C(22)	1.541
C(5a)—C(10)	1.426	C(17)—C(18)	1.502
C(5a)—C(8a)	1.426	C(18)—C(19)	1.516
C(5)—C(5a)	1.416	C(18)—O(2)	1.191
C(5)—C(6)	1.347	C(19)—C(20)	1.530
C(6)—C(7)	1.404	C(19)—C(23)	1.524
C(7)—C(8)	1.356	C(19)—C(24)	1.533
C(7)—O(1)	1.370	C(20)—C(21)	1.500
C(8)—C(8a)	1.422	C(20)—O(2')	1.13

(b) Angles: estimated standard deviations  $\leq \pm 0.3^\circ$  (except at O(2')  $\pm 0.8^\circ$ )

Bonds	Angle (deg)	Bonds	Angle (deg)
C(1a)—C(1)—C(2)	120.5	C(4a)—C(10)—C(5a)	120.4
C(1a)—C(1)—C(11)	116.7	C(4a)—C(10)—C(13)	121.5
C(11)—C(1)—C(2)	122.7	C(5a)—C(10)—C(13)	118.1
C(1)—C(1a)—C(4a)	119.6	C(7)—O(1)—C(12)	118.7
C(1)—C(1a)—C(9)	121.7	C(2)—C(14)—C(15)	112.1
C(4a)—C(1a)—C(9)	118.7	C(14)—C(15)—C(16)	116.4
C(1)—C(2)—C(3)	120.3	C(15)—C(16)—C(17)	108.1
C(1)—C(2)—C(14)	124.4	C(15)—C(16)—C(21)	112.4
C(3)—C(2)—C(14)	115.3	C(15)—C(16)—C(22)	110.2
C(2)—C(3)—C(4)	113.2	C(17)—C(16)—C(21)	107.6
C(3)—C(4)—C(4a)	112.8	C(17)—C(16)—C(22)	108.9
C(4)—C(4a)—C(1a)	117.8	C(21)—C(16)—C(22)	109.5
C(4)—C(4a)—C(10)	121.3	C(16)—C(17)—C(18)	113.2
C(1a)—C(4a)—C(10)	120.9	C(17)—C(18)—C(19)	117.7
C(5)—C(5a)—C(10)	124.1	C(17)—C(18)—O(2)	120.2
C(5)—C(5a)—C(8a)	117.0	C(19)—C(18)—O(2)	122.0
C(8a)—C(5a)—C(10)	118.9	C(18)—C(19)—C(20)	108.5
C(5a)—C(5)—C(6)	122.2	C(18)—C(19)—C(23)	110.4
C(5)—C(6)—C(7)	120.5	C(18)—C(19)—C(24)	107.6
C(6)—C(7)—C(8)	120.1	C(20)—C(19)—C(23)	110.9
C(6)—C(7)—O(1)	114.1	C(20)—C(19)—C(24)	109.9
C(8)—C(7)—O(1)	125.8	C(23)—C(19)—C(24)	109.6
C(7)—C(8)—C(8a)	120.6	C(19)—C(20)—C(21)	116.3
C(8)—C(8a)—C(5a)	119.5	C(19)—C(20)—O(2')	118.4
C(8)—C(8a)—C(9)	121.9	C(21)—C(20)—O(2')	125.6
C(5a)—C(8a)—C(9)	118.7	C(16)—C(21)—C(20)	113.3
C(8a)—C(9)—C(1a)	122.5		

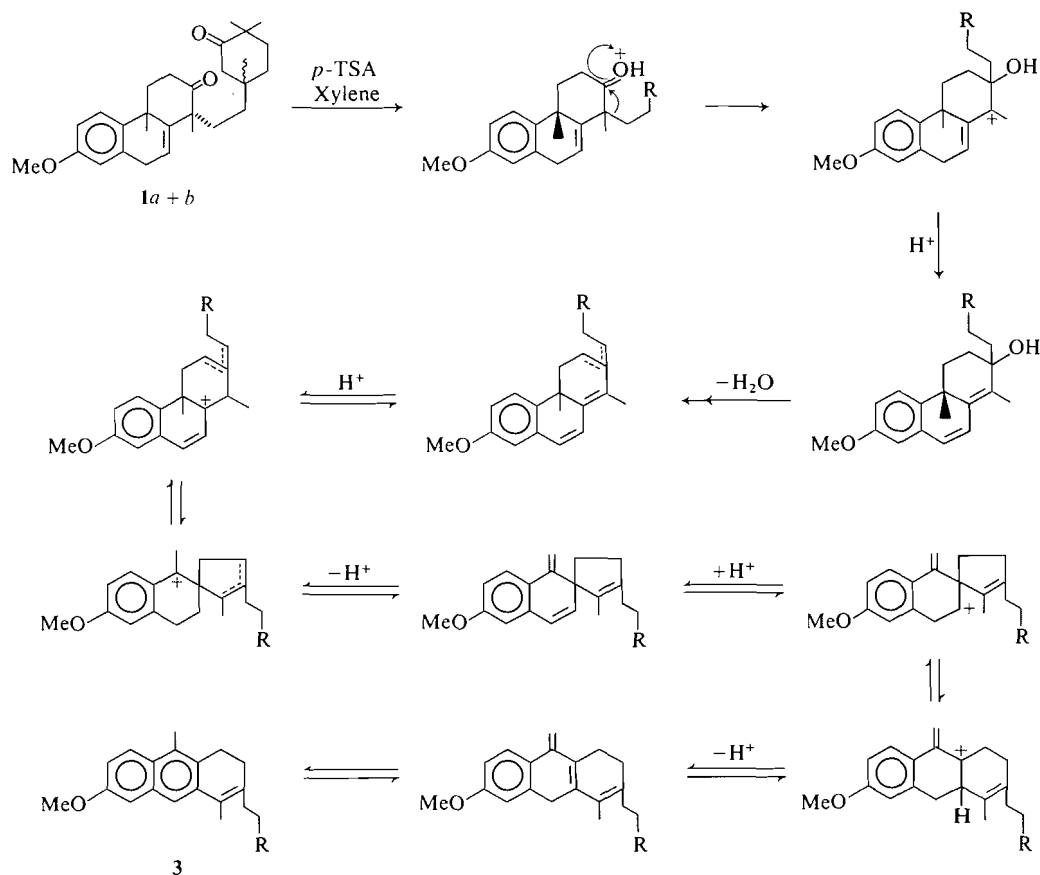
$\text{C}_{17}\text{H}_{17}\text{O}^+$ : 237.1279; measured: 237.1264. *Anal.* calcd. for  $\text{C}_{28}\text{H}_{36}\text{O}_2$ : C 83.12, H 8.97; found: C 82.95, H 9.12.

#### X-ray Analysis of 3

Crystallographic data for crystals of (3) are shown below. Preliminary work was carried out with Weissenberg and precession cameras and all intensity and cell data were measured on a Picker diffractometer using a locally written Fortran IV routine (5) on a PDP 8E computer. Accurate orientation and

cell parameters were derived with a least-squares treatment of 34 reflections (17 Friedel pairs) with  $2\theta > 80^\circ$ . The crystal data are as follows

$\text{C}_{28}\text{H}_{36}\text{O}_2$  fw = 404.57  
Monoclinic, space group  $P2_1/c$  from systematic absences  $h0l = 2n + 1, 0k0k = 2n + 1$ ;  $a = 7.2684(3)$ ,  $b = 30.942(2)$ ,  $c = 10.5544(7)$  Å,  $\beta = 98.24(1)^\circ$ ,  $V = 2349.2 \text{ \AA}^3$ ;  $\rho_c = 1.14$ ,  $\rho_m = 1.15 \text{ g cm}^{-3}$  (flotation in KCl solution);  $Z = 4$ . ( $F_{000} =$



SCHEME 1

880;  $\text{CuK}\alpha$ ,  $\lambda = 1.54056 \text{ \AA}$ , graphite monochromator;  $\mu = 5.46 \text{ cm}^{-1}$ ; crystal dimensions  $0.27 \times 0.29 \times 0.07 \text{ mm}$ . Data collection details:  $2\theta_{\text{max}} = 100^\circ$ , temperature  $23^\circ\text{C}$ ,  $\theta/2\theta$  scan at  $2^\circ \text{ min}^{-1}$  scan speed and background measurements of 21 s at each end of the scan; 2414 unique measured reflections of which 1810 were considered observed at the  $2\sigma$  level.)

The data collection scheme used was that described by Grant (6) for obtaining a set of controlled precision measurements. A maximum measuring time of 600 s per reflection was allowed and after a preliminary scan the routine decides:

(i) Whether the reflection is observed with  $I_{\text{net}} > 2\sigma(I_{\text{net}})$ . If not, no further measurement is made and the reflection is considered unobserved.

(ii) If it is above this level, can the reflection be measured to 3% statistical accuracy within the allotted time? If it can be so measured, the scan is repeated the required number of times.

(iii) If it cannot be measured to 3%, can the reflection be measured to at least 15% using the whole of the allotted time? If this precision can be achieved the routine spends the remaining time to do so. If not, no further time is spent on the reflection and it is again considered unobserved. The values 3% and 15% are input parameters to the routine. All unobserved reflections have  $I_{\text{net}}$  set to  $\frac{1}{3}\sigma(I_{\text{net}})$ .

Three reference measurements were taken after every 50 reflections and no drift was observed. The normal data reduction techniques were used to correct the intensity data to  $F_o$  and  $E$  values. No absorption corrections were made.

The structure was solved with MULTAN (7) after some initial difficulty. An  $E$ -map was computed with  $246|E| \geq 1.6$

which showed the 30 nonhydrogen atoms in the top 36 peaks. Refinement was carried out by block-diagonal least-squares methods, and following initial cycles a high thermal parameter on the carbonyl O atom together with evidence from a difference map, indicated positional disorder in the carbonyl group; the major and minor sites being related by a pseudo-mirror plane, defined approximately by the three methyl groups on the cyclohexanone ring. Refinement was continued with both sites included in the structural model. At an  $R^5$  of 15%, 32 of the hydrogen atoms were located in a difference map, the remainder being found at later stages, and following their inclusion with isotropic thermal parameters and anisotropic refinement of the nonhydrogen atoms, convergence was attained at an  $R$  of 0.043 for the observed data ( $R$  for all data = 0.063)<sup>4</sup> with  $R_w^5 = 0.043$ . The goodness of fit<sup>5</sup> values was 1.88. A final difference map showed no peaks  $> \pm 0.17 \text{ e}$ . The occupancies on the carbonyl sites were 0.85 and 0.21 (i.e., approximately 4:1) and no attempt was made to locate the partially occupied H atoms sites on C(18), any electron density owing to these atoms being compensated by high anisotropy on the adjacent O atom (nb, this also accounts for the sum of occupancies  $> 1.0$ ). Throughout refinement the function minimised was  $\sum w(|F_o| - |F_c|)^2$  with weights,  $w$ , based upon counting statistics. Scattering factor constants were taken from *International Tables for X-ray Crystallography* (8) and were

<sup>4</sup> $R = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $R_w = \{ \sum w(|F_o| - |F_c|)^2 / \sum w F_o^2 \}^{1/2}$ . Goodness of fit =  $\{ \sum w(|F_o| - |F_c|)^2 / (N_o - N_v) \}^{1/2}$  where  $N_o$  and  $N_v$  are the numbers of observations and variables.

employed in the analytical form:  $f_s = c + \sum_{i=1}^4 a_i \exp(-b_i s^2)$ .

All calculations were carried out on a PDP-8E computer using mostly locally written programs (9).

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