parameters, d, τ and $\varDelta$ (Evans & Trotter, 1988a)* of 2·98 Å, 44° and 75°, respectively, in a boat-like reaction geometry, while *endo* H is slightly less favourably situated, at 3·13 Å, 26° and 100°, in a chair-like geometry.

α-Norbornyl-4-chloroacetophenone undergoes the Norrish type II reaction upon irradiation in solution and in the solid state (Omkaram, 1986), giving cyclization products with a four-membered ring formed by $C(7)\cdots C(10)$ bonding, and *p*-chloroacetophenone and norbornene *via* $C(8)-C(9)$ bond cleavage. The cyclization-to-cleavage ratio is again relatively insensitive to reaction medium (Evans & Trotter, 1988a,b), with cyclization of $13\pm1\%$ in benzene and acetonitrile solutions and in the solid state. Thus the photoreaction seems to be governed by intra- rather than intermolecular forces, and cleavage is the predominant process. The biradical *p*-orbital angles (Evans & Trotter, 1988a)* are $\theta_{C=O}=94$, $\theta_p=40$, $\theta_{pp}=64°$. The θ_p angle is not far from the range of 51–69° found in cyclobutyl- and cyclopentylacetophenones, and the product ratios are very similar, so that cleavage does again seem to be favoured by lower values of θ_p. The ψ

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* $d = O\cdots H$ abstraction distance, τ = angle between the $O\cdots H$ vector and the carbonyl plane, $\varDelta = C=O\cdots H$; the biradical p orbitals are taken at right angles to the carbonyl (C=O) and $C(9)-C(10)-C(11)$ (γ) planes, and the angles quoted are between these orbitals and the $C(8)-C(9)$ bond.

torsion angle of close to 0° also favours cleavage, and the strain involved in fusing an additional four-membered ring to the norbornyl nucleus makes cyclization less likely. No data are available on the cyclization product ratios, since the products are only formed in small amounts.

The molecules are oriented in the unit cell with their long axes along **c**, with the directions of the long axes alternating along **b**.* Nearest neighbours pack around centres of symmetry with the aromatic rings separated by 3·62 Å.

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* For packing diagram, see deposition footnote.

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Structure of α-Cycloheptyl-4-methylacetophenone*

BY STEPHEN V. EVANS AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Abstract. $C_{16}H_{22}O$, $M_r = 230\cdot35$, monoclinic, $P2_1/a$, $a = 16\cdot287$ (4), $b = 5\cdot5518$ (7), $c = 15\cdot533$ (3) Å, $\beta = 99\cdot95$ (1)°, $V = 1383\cdot4$ (5) Å^3, $Z = 4$, $D_x = 1\cdot106$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0\cdot70930$ Å, $\mu = 0\cdot6$ cm^{-1}, $F(000) = 504$, $T = 295$ K, $R = 0\cdot042$ for 1227 reflections. The molecular conformation and geometry are similar to those of related molecules, with the acetophenone grouping occupying an equatorial site on the twist-chair cycloheptyl ring. Parameters are favourable for photochemical hydrogen abstraction, $d = 2\cdot68$ Å, $\tau = 49°$, $\varDelta = 76°$, and photoproduct ratios fit the previously established correlations with angles between biradical p orbitals.

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* 2-Cycloheptyl-1-(4-methylphenyl)ethanone.

Introduction. Previous studies of series of α-cycloalkyl-4-chloro- and -4-carboxyacetophenones have led to useful correlations between molecular structure parameters and photoproduct ratios (Evans & Trotter, 1988a,b). The present paper describes the structure and photochemistry of a 4-methyl derivative (Me-7R).

Experimental. Colourless {100} plates, cut crystal with dimensions $0\cdot20 \times 0\cdot25 \times 0\cdot35$ mm, Enraf–Nonius CAD-4F diffractometer, monochromatized Mo $K\alpha$ radiation, lattice parameters from 25 reflections with $\theta = 11–21°$. Intensities for $\theta \le 25°$, $hkl -18$ to 18, 0 to 6, 0 to 18, $\omega–2\theta$ scan, ω-scan width $(0\cdot85 + 0\cdot35\tan\theta)°$ at $1\cdot5–10°$ min^{-1}, extended 25% on each side for background measurement, three stan-

dard reflections (no decay), Lp but no absorption corrections, 2418 reflections measured, 1227 with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04I)^2$, S = scan, B_1 and B_2 = background counts. Structure determined by direct methods, refined by full-matrix least squares on F, H atoms from a difference map, $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs (Evans & Trotter, 1988*a*), final $R = 0.042$, $wR = 0.048$ for 1227 reflections, $S = 1.78$, 154 parameters [non-H atoms, plus 88 H-atom parameters; H atoms behaved fairly well in the refinement, but with rather large thermal parameters for the cycloheptyl H atoms, and somewhat unreasonable bond angles involving H atoms at C(14)], $R = 0.104$ for all 2418 reflections, $\Delta/\sigma = 0.009$ (mean), 0.177 (maxium), maximum final difference density ± 0.2 e Å^{-3}.

Discussion. Final positional parameters are in Table 1, and other data have been deposited.* The molecular structure (Fig. 1) is quite similar to that of the chloro derivative (Evans & Trotter, 1988*a*). Aromatic C–C bond lengths and angles (Table 2) vary from 1.370 to 1.395 (4) Å (mean 1.381 Å) and 116.8 to 122.6 (3)° (mean 120.1°), respectively. The aromatic ring is not rigorously planar within experimental error ($\chi^2 = 12.9$), but no atom deviates more than 0.006 (3) Å from the least-squares plane. The methyl C atom lies 0.037 (4) Å off the plane and the carbonyl group is rotated out of the plane of the aromatic ring by 7°. The φ_1 and φ_2 torsion angles (Evans & Trotter, 1988*a*) of 70 and 12° are not far from expected values of 60 and 0°, respectively (Table 3).

The acetophenone moiety is substituted at an equatorial position with respect to the cycloheptyl ring, which has an approximate twist-chair conformation, with the characteristic C_2 axis passing through C(11) and the midpoint of the C(14)–C(15) bond (Fig. 1). This is a different twist-chair from that of the chloro derivative (Evans & Trotter, 1988*a*), in that the acetophenone substituent occupies a different equatorial position on the ring, but one with comparable steric hindrance (Hendrickson, 1967). Measured intraannular torsion angles compare fairly well with those predicted for a twist-chair (Table 2), with the exception of those about C(11) and C(12), which differ from the predicted values by up to 18°. This may indicate a possible disorder over two conformations (as in the

* Lists of anisotropic thermal parameters, H-atom positions and isotropic thermal parameters, bond lengths and angles involving H atoms, torsion angles, structure factors, and a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44944 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional (fractional* $\times 10^4$*) and equivalent isotropic thermal parameters* ($U \times 10^3$ Å^2*), with standard deviations in parentheses*

$U_{eq} = \frac{1}{3} \times$ trace of diagonalized U tensor.

	x	y	z	U_{eq}
C(1)	6235 (1)	219 (4)	211 (1)	53
C(2)	5916 (2)	2247 (5)	−252 (2)	64
C(3)	6022 (2)	2577 (5)	−1103 (2)	71
C(4)	6454 (1)	977 (5)	−1529 (2)	63
C(5)	6775 (2)	−1044 (5)	−1064 (2)	67
C(6)	6669 (1)	−1429 (5)	−219 (2)	61
C(7)	6135 (1)	−243 (4)	1129 (2)	57
C(8)	5773 (2)	1723 (5)	1626 (2)	62
C(9)	5841 (1)	1292 (5)	2601 (2)	61
C(10)	6746 (2)	1473 (7)	3058 (2)	80
C(11)	6981 (3)	26 (10)	3891 (2)	116
C(12)	6470 (4)	307 (9)	4585 (3)	122
C(13)	5953 (3)	2505 (10)	4602 (2)	123
C(14)	5183 (3)	2720 (11)	3924 (2)	110
C(15)	5286 (2)	3067 (6)	2978 (2)	78
C(16)	6586 (3)	1422 (9)	−2448 (2)	91
O(1)	6335 (1)	−2188 (3)	1471 (1)	79

Table 2. *Bond lengths (Å), bond angles (°) and seven-membered-ring torsion angles (°), with standard deviations in parentheses*

C(1)–C(2)	1.389 (3)	C(7)–O(1)	1.223 (3)
C(1)–C(6)	1.395 (3)	C(8)–C(9)	1.518 (3)
C(1)–C(7)	1.485 (3)	C(9)–C(10)	1.525 (4)
C(2)–C(3)	1.374 (4)	C(9)–C(15)	1.521 (4)
C(3)–C(4)	1.372 (4)	C(10)–C(11)	1.515 (5)
C(4)–C(5)	1.387 (3)	C(11)–C(12)	1.480 (5)
C(4)–C(16)	1.500 (4)	C(12)–C(13)	1.485 (5)
C(5)–C(6)	1.370 (4)	C(13)–C(14)	1.497 (6)
C(7)–C(8)	1.513 (3)	C(14)–C(15)	1.521 (5)

C(2)–C(1)–C(6)	117.3 (2)	C(8)–C(7)–O(1)	120.9 (2)
C(2)–C(1)–C(7)	123.0 (2)	C(7)–C(8)–C(9)	115.3 (2)
C(6)–C(1)–C(7)	119.7 (2)	C(8)–C(9)–C(10)	110.6 (2)
C(1)–C(2)–C(3)	120.6 (3)	C(8)–C(9)–C(15)	109.6 (2)
C(2)–C(3)–C(4)	122.6 (3)	C(10)–C(9)–C(15)	111.6 (3)
C(3)–C(4)–C(5)	116.8 (2)	C(9)–C(10)–C(11)	116.3 (3)
C(3)–C(4)–C(16)	121.5 (3)	C(10)–C(11)–C(12)	118.4 (3)
C(5)–C(4)–C(16)	121.7 (3)	C(11)–C(12)–C(13)	119.4 (4)
C(4)–C(5)–C(6)	121.8 (3)	C(12)–C(13)–C(14)	117.5 (4)
C(1)–C(6)–C(5)	121.0 (3)	C(13)–C(14)–C(15)	118.1 (4)
C(1)–C(7)–C(8)	118.8 (2)	C(9)–C(15)–C(14)	117.5 (3)
C(1)–C(7)–O(1)	120.3 (2)		

Intraannular torsion angles

Bond	This work	Twist-chair*
9–10	85.2	88.1
10–11	−52.0	−39.1
11–12	−21.1	−39.1
12–13	73.2	88.1
13–14	−68.4	−72.3
14–15	52.1	54.3
15–9	−64.7	−72.3

* Hendrickson (1967).

chloro derivative), but the successful refinement of most of the H atoms, and thermal parameters at C(11) to C(14) which are not unreasonably large, indicate that disorder is not severe, and that the major conformer is the twist-chair.

As in the chloro derivative, the valence angles of the cycloheptyl ring are opened significantly from tetra-

Table 3. *Molecular conformations, hydrogen abstraction and biradical geometries, and photoproduct ratios for substituted α-cycloalkylacetophenones*

	Me-6R*	Cl-7R†	Me-7R‡
Molecular conformation (°)			
φ_1 = C(7)–C(8)–C(9)–C(10)	69	75	70
φ_2 = O(1)–C(7)–C(8)–C(9)	14	5	12
Carbonyl/ring	13	3	7
ψ = C(8 + n)–C(9)–C(10)–C(11)	56	67	85
Hydrogen-abstraction parameters			
Ring conformation	Boat	Boat	Boat
d(Å)	2·60	2·71	2·68
τ(°)	50	42	49
Δ(°)	88	82	76
Biradical p-orbital angles (°)¶			
$\theta_{C=O}$	101	94	100
$\theta\gamma$	87	99	116
θ_{pp}	76	80	81
% Cyclization§			
Benzene	58	36	37
Acetonitrile	63	35	41
Solid state	49	31	45
% cis-Cyclobutanol§			'
Benzene	30	32	13
Acetonitrile	42	41	31
Solid state	38	23	16

* Ariel & Trotter (1985).
† Evans & Trotter (1988a).
‡ Present study; σ = 0·2–0·3° for molecular conformation angles.
¶ For definitions, see Evans & Trotter (1988a).
§ Omkaram (1986).

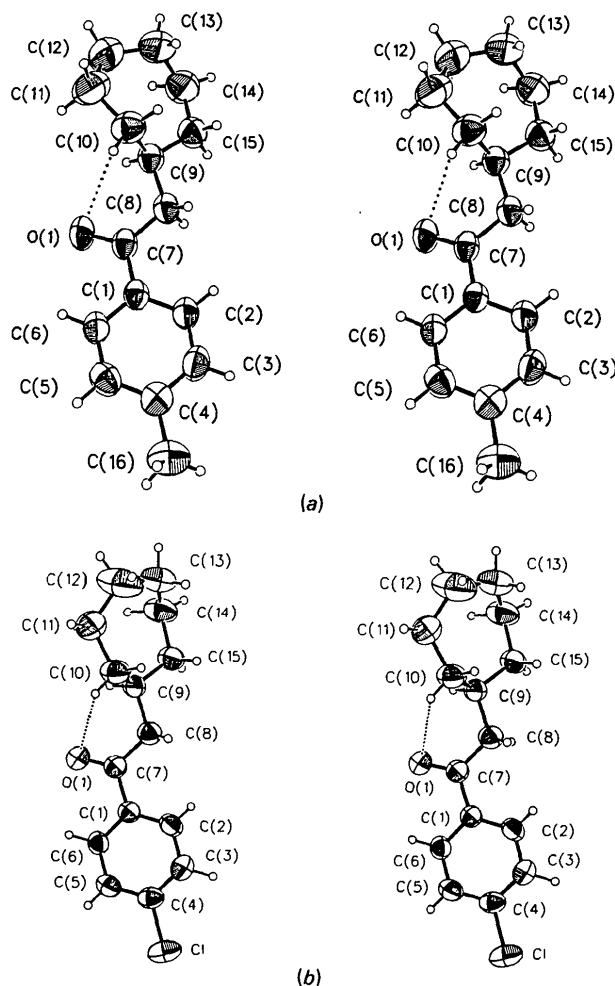
Fig. 1. (a) Stereoview of the α-cycloheptyl-4-methylacetophenone molecule, 50% probability ellipsoids, with (b) the chloro derivative (Evans & Trotter, 1988a) for comparison.

hedral geometry [the mean value, excluding C(12) and C(13), is 116·4°], but the transannular H···H contacts are generally longer than predicted. The H(12a)··· H(14b) contact is somewhat short at 1·70 (6) Å, but this may be an artifact of the higher thermal motion of the outer atoms of the ring, and inaccuracy in positioning the H atoms at C(14), as noted above.

The long axes of the molecules* lie approximately along c, with the direction of the long axes alternating along a. Nearest neighbours pack about a centre of symmetry with their phenyl moieties separated by approximately 3·48 Å. Intermolecular distances correspond to normal van der Waals contacts.

The different equatorial position occupied by the acetophenone moiety has not greatly altered the abstraction geometry compared with the chloro compound. The equatorial H(10a) is in the most favourable abstraction position with d = 2·68 Å, τ = 49° and Δ = 76° (Table 3), and forms an approximate boat-shaped reaction geometry. H(10b) lies more than 4·0 Å from O(1). The angle between the radical p orbitals, θ_{pp} (Evans & Trotter, 1988a) is 81°, and the $\theta_{C=O}$ and θ_p angles are 100 and 116°, respectively, with an intraannular torsion angle, ψ, of 85° (Table 3).

The general photochemical behaviour of α-cycloheptyl-4-methylacetophenone is quite similar to that of the α-cycloalkyl-4-chloro- and -4-carboxyaceto-

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* For packing diagram, see deposition footnote.

phenones described previously (Evans & Trotter, 1988a,b). The photoproduct ratios (Omkaram, 1986) are again not very dependent on reaction medium, and the data for the present cycloheptyl compound (Table 3) are in accord with the previously noted trends of increasing cycloalkyl ring size corresponding to increasing amounts of cyclization products, especially the amount of trans-OH cyclobutanol photoproduct (the ring junction stereochemistry has not been established for the cycloheptyl derivatives). The various molecular parameters of Me-7R are quite similar to those of the related molecules (Table 3), and fit quite nicely with previous correlations between photochemical results and angles between biradical p orbitals (Evans & Trotter, 1988a).

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Structure of 11α-Hydroxycon-1,4,18-trienine-3-one

BY R. RADHAKRISHNAN AND M. A. VISWAMITRA

Department of Physics and ICMR Centre on Genetics and Cell Biology, Indian Institute of Science, Bangalore-12, India

AND K. K. BHUTANI AND M. ALI

Regional Research Laboratory, Jammu-1, India

Abstract. $C_{21}H_{27}NO_2$, $M_r = 325.5$, orthorhombic, $P2_12_12_1$, $a = 7.516$ (2), $b = 13.430$ (2), $c = 18.047$ (2) Å, $U = 1821.79$ Å^3, $Z = 4$, $D_x = 1.186$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1.5418$ Å, $\mu = 0.56$ mm^{-1}, $F(000) = 704$, $T = 293$ K, final $R = 0.04$ for 1892 reflections with $I \geq 3\sigma(I)$. Ring A is planar, and rings B and C adopt a chair conformation. Rings D and E are envelopes, with C(14) and C(17) displaced from their respective planes by 0.643 (3) and 0.482 (3) Å. The ring system A/B shows quasi-*trans* fusion, whilst ring systems B/C and C/D are *trans* fused about C(8)–C(9) and C(13)–C(14) respectively. The D/E junction shows *cis* fusion.

Introduction. Steroidal alkaloids are a class of compounds possessing a steroidal skeleton with nitrogen incorporated as part of the ring system or in the side chain. As part of our crystallographic studies on these compounds we report here the structure of 11α-hydroxycon-1,4,18-trienine-3-one, a compound having an N atom present in ring E (Fig. 1). The compound was isolated from the bark of the plant *Holarrhena antidysentrica* (Bhutani, Ali, Sharma, Vaid & 1988). The *Holarrhena* alkaloids are important in herbal medicine as anthelmintics and antidysentrics. Earlier we have reported the crystal structure of 11α-hydroxycon-1,4-dienine-3-one monohydrate (Radhakrishnan, Viswamitra, Bhutani & Ali, 1988).

Experimental. Crystals were grown from acetone solution by evaporation. The cell parameters were refined from accurately determined 2θ values of 25 reflections $(4.1 < \theta < 38.7°)$ on a CAD-4 diffractometer. Intensity data were collected with Ni-filtered

Cu $K\alpha$ radiation using a crystal of dimensions $0.76 \times 0.61 \times 1.38$ mm up to $(\sin\theta)/\lambda = 0.627$ Å^{-1} using ω–2θ scan. Lorentz, polarization and absorption corrections (North,, Phillips & Mathews, 1968) were applied; the transmission factor varied from 91.1 to 99.2%. 2460 reflections were measured for $0 \leq h \leq 9$, $0 \leq k \leq 16$, $0 \leq l \leq 22$ of which 1892 had $I \geq 3\sigma(I)$. Three strong reflections monitored periodically showed that the crystal was stable to X-rays.

The structure was solved by direct methods using *MULTAN*11/82 (Main *et al.*, 1982). An E map computed with the best set of phases (CFOM = 2.797) revealed the positions of 23 of the 24 non-H atoms. The position of the last atom was located using a weighted Fourier map. Successive difference Fourier maps revealed the positions of 24 H atoms, and two H atoms were fixed stereochemically. After the final cycle of refinement with anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms, the R value was 0.04 and $wR = 0.04$. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where
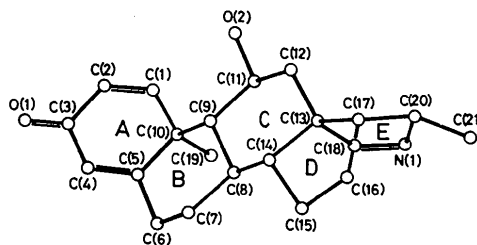

Fig. 1. Perspective view of 11α-hydroxycon-1,4,18-trienine-3-one showing the numbering scheme.