compounds are in accord with the above arguments. It is also interesting that tetracyanoethylene shows better complexing properties than chloranil (Table 1): this is not surprising owing, other things being equal, to the higher electron affinity of the former (2·2 eV) with respect to the latter acceptor (1·7 eV) (Briegleb, 1964).

In conclusion it can be pointed out that in phenyl-hydrazones the possibility of obtaining a CT inter-action is firstly related to the absence of a discrete amount of strain on the hydrazono group that, consequently, may exist in a planar structure that allows conjugation in the group. Mesomeric and inductive effects of the substituents can only contribute to the amount and to the stability of the complex.

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Crystal Structure and Photochemistry of Four α-Cycloalkyl-*p*-chloroacetophenones

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Abstract

The photochemical fragmentation or cyclization reactions of α-cycloalkylacetophenones have been studied by crystal-structure analyses of four chloro derivatives with varying cycloalkyl-ring sizes, and by correlation of crystal- and molecular-structure parameters with photochemical behaviour. Crystal data are: $T = 295$ K, Mo $K\alpha_1$, $\lambda = 0.70930$ Å, or Cu $K\alpha_1$, $\lambda = 1.54056$ Å; α-cyclobutyl-4-chloroacetophenone [1-(4-chlorophenyl)-2-cyclobutylethanone], $C_{12}H_{13}ClO$, $M_r = 208.69$, monoclinic, $C2/c$, $a = 26.403$ (9), $b = 10.903$ (4), $c = 7.800$ (2) Å, $\beta = 103.94$ (3)°, $V = 2179.3$ (12) Å³, $Z = 8$, $D_x = 1.272$ g cm⁻³, $\mu =$

3·1 cm⁻¹, $F(000) = 880$, $R = 0.035$ for 727 observed reflections; α-cyclopentyl-3,4-dichloroacetophenone [2-cyclopentyl-1-(3,4-dichlorophenyl)ethanone], $C_{13}H_{14}Cl_2O$, $M_r = 257.16$, monoclinic, $P2_1/a$, $a = 13.206$ (2), $b = 7.859$ (1), $c = 24.815$ (2) Å, $\beta = 105.05$ (1)°, $V = 2487.1$ (6) Å³, $Z = 8$ (two molecules per asymmetric unit), $D_x = 1.373$ g cm⁻³, $\mu = 45.8$ cm⁻¹, $F(000) = 1072$, $R = 0.051$ for 1393 observed reflections; α-cycloheptyl-4-chloroacetophenone [1-(4-chlorophenyl)-2-cycloheptylethanone], $C_{15}H_{19}ClO$, $M_r = 250.77$, monoclinic, $P2_1/a$, $a = 8.085$ (3), $b = 10.961$ (3), $c = 15.280$ (5) Å, $\beta = 92.18$ (3)°, $V = 1353.1$ (7) Å³, $Z = 4$, $D_x = 1.231$ g cm⁻³, $\mu = 2.6$ cm⁻¹, $F(000) = 536$, $R = 0.044$ for 1204 observed reflections; α-cyclooctyl-4-chloroacetophenone [1-(4-chlorophenyl)-2-cyclooctylethanone], $C_{16}H_{21}ClO$, $M_r = 264.79$, triclinic, $P\bar{1}$, $a = 7.1095$ (6), $b = 7.9433$ (10), $c = 13.2683$ (13) Å, $\alpha = 75.315$ (8), $\beta = 86.169$ (9), $\gamma = 79.520$ (12)°, $V = 712.6$ (2) Å³, $Z = 2$, $D_x = 1.234$ g cm⁻³, $\mu = 2.5$ cm⁻¹, $F(000) = 284$, $R = 0.039$ for 1714 observed reflections. The cycloalkyl rings have the usual non-planar conformations, with the acetophenone moieties equatorial in all four molecules. All the compounds undergo photochemical reaction in solution and in the solid state, each molecule having an equatorial γ-H atom which is suitably oriented for abstraction by carbonyl O, *via* a boat-like six-atom geometry. The H···O abstraction distances vary from 3·1 Å in the cyclobutyl derivative to 2·7 Å for the larger cycloalkyl rings. The photoproduct ratios are relatively insensitive to reaction medium, but the amounts of cyclization (relative to cleavage) products increase with increasing cycloalkyl-ring size, the cyclization products have *cis* ring junctions for the smaller and *trans* ring junctions for the larger cycloalkyl rings, and the amount of cyclization product with OH *trans* to the adjacent ring-junction H atom increases for the larger rings in the solid state. These photochemical results can be correlated with changing angles between biradical *p* orbitals and with related ring torsion angles, with the detailed geometry of the biradicals, and with the greater steric stability of the *trans*-OH photoproducts.
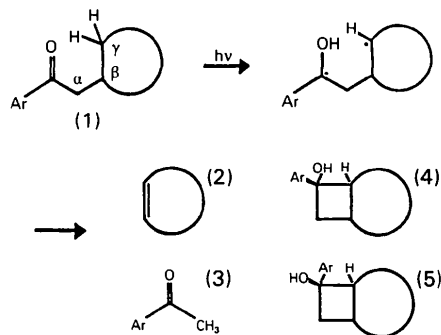

Fig. 1. The Norrish type II reaction.

Introduction

The Norrish type II reaction involves photochemical fragmentation or cyclization of γ-H-bearing alkyl or aryl ketones (Wagner, 1971). The photoreaction of molecules of general structure (1) in solution or in the solid state is believed to occur *via* abstraction of a favourably oriented γ-H atom to give a 1,4-biradical, which either undergoes cleavage of the α–β bond to yield the corresponding cycloalkene (2) and acetophenone (3), or cyclizes to form a mixture of two cyclobutanols (4) or (5) (Fig. 1). NMR data indicate that the two cyclobutanols differ in the configuration of the OH group, which is either *cis* (4) or *trans* (5) with respect to the H atom on the adjacent ring-junction C atom. A further point concerns the configuration of the ring junction itself, which again could be *cis* or *trans*, although only one configuration is found in each pair of cyclobutanol photoproducts. For the cyclobutyl and cyclopentyl compounds, the ring junctions of the cyclization photoproducts are certainly *cis*, since *trans* ring junctions would result in impossibly high strain energies for these small rings. A recent crystal-structure analysis of the *cis*-OH cyclobutanol photoproduct from the cyclooctyl compound has conclusively proved a *trans* ring junction (Ariel & Trotter, 1987), which leaves in doubt the ring-junction configuration of the cyclohexyl and (especially) cycloheptyl photoproducts (see *Discussion* below).

Despite the large amount of work on the Norrish type II reaction (Scaiano, 1982), little is known about the details of the abstraction geometry, or about the factors governing the partitioning of the products (Lewis & Hilliard, 1970). H abstraction probably involves a *p*-like radical *n* orbital on the O atom, generated by *n*–π* excitation of the carbonyl group. Parameters describing the abstraction geometry (Fig. 2) are the O···H_γ distance (*d*), the angle between the O···H_γ vector and the carbonyl-group plane (τ), and the C=O···H angle (Δ); ideal values for these parameters derived for other photochemical reactions are ≤ 2·72 Å, 0°, and 90°, respectively (Table 1) (Scheffer & Dzakpasu, 1978; Trotter, 1983). It has been suggested that cleavage can occur most efficiently when the two radical *p* orbitals are parallel to the central bond being cleaved (Fig. 3) (Wagner & Kemppainen, 1968; Wagner, Kelso, Kemppainen, McGrath, Schott & Zepp, 1972), with cyclization being presumed to dominate in the absence of this orbital arrangement. Of interest in attempts to rationalize the amounts of the various photoproducts are the angles (Table 1) between the radical *p* orbitals (θ_{pp}), and between each *p* orbital and the central bond broken during cleavage ($\theta_{C=O}$ and θ_γ). We define the direction of a radical *p* orbital as perpendicular to the plane containing the radical C atom and all non-H atoms bonded to it, as measured for the parent reactant. As far as the amount

of orbital overlap is concerned, the θ angles can also be expressed as their supplements, i.e. $\theta_{pp} \equiv 180° - \theta_{pp'}$, etc. However, the two directions of each p orbital are different (a fact which is reflected in the stereochemistry of the photoproducts), and we define the positive direction of each radical p orbital as the si face of the sp^2-hydridized C atom [$C_{carbonyl}$, C(7), and C_γ, C(10)], i.e. toward the viewer in Figs. 1 and 2 (Hanson, 1966), and the directions of the orbitals of the $C_\alpha-C_\beta$ [C(8)—C(9)] bond, which is broken in the cleavage reaction, as from each C atom towards the centre of the bond.

Since much of the conformational freedom in molecules of type (1) is about the central bonds, the torsion angles about these bonds are of importance:
$\varphi_1 = C_{carbonyl}-C_\alpha-C_\beta-C_\gamma$, $\varphi_2 = O=C_{carbonyl}-C_\alpha-C_\beta$, $\varphi_3 = O=C_{carbonyl}-C_{Ar}-C_{Ar}$ (or, alternatively, the angle between the aromatic and carbonyl planes), and $\psi = C_{ring}-C_\beta-C_\gamma-C_{ring}$ (Fig. 2). A normal staggered arrangement for the $C_\alpha-C_\beta$ bond, minimization of $O\cdots H_\alpha$ repulsions, and coplanarity of the carbonyl and

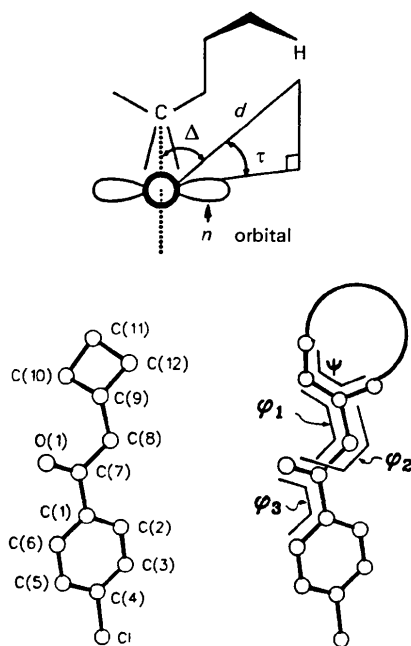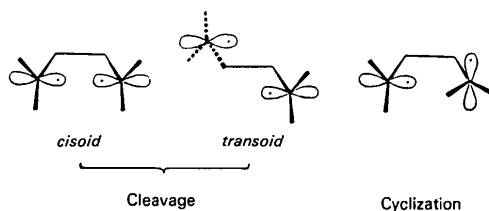Table 1. *Relevant parameters in the Norrish type* II *reaction* (*see Figs.* 2 *and* 3)

Parameter	Definition	Ideal value
d	$O\cdots H_\gamma$ distance	≤ 2.72 Å
τ	Angle between $O\cdots H_\gamma$ and carbonyl plane	0°
Δ	$C=O\cdots H_\gamma$	90
φ_1	C(7)—C(8)—C(9)—C(10)	±60, 180
φ_2	O(1)—C(7)—C(8)—C(9)	0
φ_3	C(6)—C(1)—C(7)—O(1)	0
ψ	C(8 + n)—C(9)—C(10)—C(11)	0*
$\theta_{C=O}$	Angle between $C_\alpha-C_\beta$ bond and radical p orbital on $C_{carbonyl}$	0*
θ_γ	Angle between $C_\alpha-C_\beta$ bond and radical p orbital on C_γ	0*
θ_{pp}	Angle between radical p orbitals	0*

* For cleavage reaction.

aromatic groups suggest ideal values of ±60 or 180° for φ_1, and 0° for φ_2 and φ_3. In addition, cleavage to form a cycloalkene would be favoured by $\psi = 0°$ (or possibly 180° for a less stable *trans*-cycloalkene) (Table 1).

The present study is part of an effort to gain some insight into the structural aspects of the Norrish type II reaction, and, if possible, to derive structure–reactivity relationships for reactions occurring in the solid state. The systems under study are the substituted α-cycloalkylacetophenones (Fig. 4). Crystal-structure analyses of five cyclohexyl derivatives (Fig. 4, $n = 6$, $Y = H$, $X = Cl$, CH_3, CH_3O, CO_2H, CN) indicate that all five compounds crystallize in a common conformation in which the $XC_6H_4COCH_2$— side-chain is equatorial with respect to the chair-shaped cyclohexane ring (Ariel & Trotter, 1985). The equatorial γ-H atom is suitably oriented for abstraction *via* a boat-like six-atom transition state; the abstraction parameters are very similar in all five molecules, with $d \sim 2.60$ Å, $\tau \sim 45°$, $\Delta \sim 90°$ (Table 1). Photochemical behaviour is also very similar for all five derivatives. In solution, cyclobutanols are the major products of photolysis, with cyclobutanol:cleavage ratios of about 75:25, and *cis:trans*-OH cyclobutanol ratios of about 35:65; photolysis in the solid state produces somewhat lesser amounts of cyclobutanols (cyclobutanol:cleavage about 50:50) (Ariel, Ramamurthy, Scheffer & Trotter,

Fig. 2. Definition of relevant H-abstraction parameters and torsion angles.

cisoid   transoid   Cleavage   Cyclization

Fig. 3. Orbital arrangements favouring cleavage and cyclization.
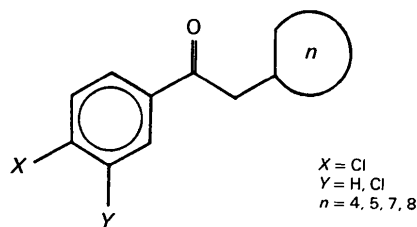

$X = Cl$
$Y = H, Cl$
$n = 4, 5, 7, 8$

Fig. 4. α-Cycloalkylacetophenones (n = number of C atoms in cycloalkyl ring).

Table 2. *Data-collection and refinement parameters for four α-cycloalkyl-p-chloroacetophenones*

	Cl-4R	Cl$_2$-5R	Cl-7R	Cl-8R
Crystal habit	{100} plates	{001} plates	{100} plates	{100}, {010}, {001} blocks
Dimensions (cut fragments) (mm)	0·01 × 0·35 × 0·40	0·25 × 0·20 × 0·20	0·05 × 0·20 × 0·25	0·40 × 0·25 × 0·02
Radiation	Mo $K\alpha_1$	Cu $K\alpha_1$	Mo $K\alpha_1$	Mo $K\alpha_1$
Reflexions for cell:				
Number	25	25	25	25
θ range (°)	12–17	25–40	10–17	14–21
Intensity measurements				
θ_{max} (°)	25·0	75·0	27·5	27·5
ω scan, $(a + b\tan\theta)$, a (°)	1·10	1·20	0·60	0·68
b (°)	0·35	0·14	0·35	0·35
Scan speeds (° min^{-1})	0·9–6·7	1·4–10·0	1·1–10·0	1·2–10·0
h	0→31	−8→0*	−10→10	−8→9
k	0→12	0→9	0→14	0→10
l	−9→8	−22→22	0→19	−16→16
Transmission factors	—	0·26–0·38	—	—
Total unique reflections	1953	3135	3100	3261
Reflections with $I \geq 3\sigma(I)$	727	1393	1204	1714
%	37·2	44·4	38·8	52·6
Structure refinements				
Number of parameters refined†	127	289	154 (214)	163 (247)
Data/parameter ratio†	5·7	4·8	7·8 (5·6)	10·5 (6·9)
Δ/σ mean	0·008	0·002	0·010	0·001
maximum	0·13	0·019	0·074	0·004
$\Delta\rho$ (e Å^{-3})	±0·17	±0·25	±0·17	+0·17/−0·25
R $|I \cdot 3\sigma(I)|$	0·035	0·051	0·044	0·039
wR	0·038	0·061	0·045	0·043
S (goodness of fit)	1·34	2·28	1·72	1·58
R (all data)	0·156	0·132	0·184	0·101
Extinction, g	—	—	4·1 (7) × 10^4	—

* Data for $h = -14$ to -9 were inadvertently lost during data processing, but are mainly weak reflections.
† Numbers in parentheses include refined H parameters.

1983). Hence variation in phenyl substituents (X) does not appear to influence greatly the molecular conformations and geometries or the photochemical behaviour.

The present paper investigates the effects of changes in the cycloalkyl-ring size (n, Fig. 4) on molecular conformation, geometry and packing, and examines consequent changes in photochemical behaviour in the solid state and in solution. Crystal structures are determined for four compounds with $X = $ Cl, $Y = $ H or Cl, and $n = $ four-, five-, seven-, or eight-membered cycloalkyl rings (Fig. 4): α-cyclobutyl-4-chloroacetophenone (Cl-4R, $Y = $ H, $n = 4$), α-cyclopentyl-3,4-dichloroacetophenone (Cl$_2$-5R, $Y = $ Cl, $n = 5$), α-cycloheptyl-4-chloroacetophenone (Cl-7R, $Y = $ H, $n = 7$) and α-cyclooctyl-4-chloroacetophenone (Cl-8R, $Y = $ H, $n = 8$).

Experimental

The general procedures and parameters of data collection are summarized in Table 2. Intensities were measured at 295 K with a CAD-4F diffractometer, ω–2θ scan (extended 25% on each side for background measurement), horizontal aperture $(2·0 + \tan\theta)$ mm, vertical aperture 4 mm. Mo $K\alpha$ (graphite monochromator) or Cu $K\alpha$ (nickel-filtered) radiations were used (Table 2). Intensity checks indicated a gradual decrease in intensity of 40% for compound Cl-4R during data collection (probably due to slow volatilization of the crystal), and data were scaled accordingly; no significant variations were found for the other three

compounds. Absorption corrections were applied for the Cu $K\alpha$ data for Cl$_2$-5R. The crystals generally do not scatter well, probably as a result of small crystal size, some disorder in the structures, and maximum θ values which are quite high for these organic crystals; reflections with $I \geq 3\sigma(I)$ represent about 37–53% of the total numbers of reflections measured, for data/parameter ratios of 5–10 (Table 2) $[\sigma^2(I) = S + 4(B_1 + B_2) + (0·04I)^2$, where $S = $ scan, B_1 and B_2 = background counts].

The structures were determined by direct methods with use of *MULTAN*80;* for Cl-7R and Cl-8R, this involved renormalization of the data on the basis of a Cl position from the Patterson map, and on the basis of an incorrectly positioned molecular fragment, respectively. Refinement was by full-matrix least-squares methods on F, with $w = 1/\sigma^2(F)$ giving uniform values of $\sum w\Delta F^2$; H atoms were placed in calculated positions for Cl-4R and Cl$_2$-5R, and were refined (except for possibly disordered sites) for Cl-7R and Cl-8R. Scattering factors were from *International Tables for X-ray Crystallography* (1974). Details of the refinements are in Table 2. The thermal parameters for some of the outer atoms of the five- and seven-membered cycloalkyl rings are rather high, and suggest some possible disorder at these sites (described more fully below).

* Programs used include locally written programs and locally modified versions of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964); *FORDAP* (A. Zalkin, unpublished); *ORTEP*II (Johnson, 1976).

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

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cl-4R (Cl x, y, z × 10^5)				
Cl	6407 (4)	15281 (13)	61194 (16)	86
O(1)	3075 (1)	63 (3)	5942 (4)	69
C(1)	2363 (1)	1150 (3)	6501 (5)	45
C(2)	2167 (1)	2156 (4)	7227 (5)	51
C(3)	1642 (2)	2289 (4)	7111 (5)	57
C(4)	1305 (1)	1402 (4)	6264 (5)	55
C(5)	1485 (1)	405 (4)	5500 (5)	58
C(6)	2013 (2)	288 (3)	5632 (5)	52
C(7)	2933 (1)	957 (4)	6631 (5)	48
C(8)	3320 (1)	1878 (3)	7616 (5)	49
C(9)	3883 (1)	1607 (4)	7682 (5)	52
C(10)	4143 (1)	535 (4)	8814 (5)	60
C(11)	4617 (2)	1341 (4)	9555 (6)	79
C(12)	4297 (1)	2452 (4)	8807 (6)	72
Cl$_2$-5R (Cl x, y, z × 10^5)				
Cl(1)	51543 (19)	17444 (34)	70017 (8)	88
Cl(2)	69742 (18)	37322 (30)	66638 (9)	86
Cl(1')	17891 (19)	81853 (32)	19649 (8)	85
Cl(2')	−3481 (18)	61377 (31)	16100 (9)	88
C(1)	4239 (9)	1673 (9)	5343 (3)	42
C(2)	4289 (6)	1439 (9)	5899 (3)	48
C(3)	5108 (7)	2032 (10)	6307 (3)	50
C(4)	5934 (7)	2926 (10)	6168 (3)	54
C(5)	5874 (6)	3159 (10)	5612 (4)	55
C(6)	5043 (7)	2579 (10)	5202 (3)	52
C(7)	3347 (7)	980 (10)	4912 (3)	50
C(8)	3210 (6)	1386 (9)	4309 (3)	52
C(9)	2237 (7)	718 (10)	3903 (3)	59
C(10)	1210 (7)	1489 (10)	3971 (3)	62
C(11)	546 (7)	1827 (13)	3399 (4)	87
C(12)	1241 (11)	1871 (24)	3035 (5)	188
C(13)	2222 (8)	1090 (12)	3290 (3)	82
O(1)	2706 (4)	66 (7)	5056 (2)	62
C(1')	1097 (6)	8340 (10)	309 (3)	44
C(2')	1589 (6)	8566 (9)	869 (3)	49
C(3')	1163 (7)	7909 (10)	1272 (3)	50
C(4')	233 (8)	7045 (11)	1121 (3)	55
C(5')	−279 (6)	6794 (11)	567 (4)	63
C(6')	153 (7)	7429 (10)	163 (3)	53
C(7')	1586 (7)	9087 (11)	−123 (3)	50
C(8')	1111 (6)	8688 (9)	−726 (3)	55
C(9')	1699 (7)	9350 (10)	−1131 (3)	57
C(10')	2783 (7)	8536 (11)	−1058 (3)	66
C(11')	2871 (9)	8141 (13)	−1639 (5)	98
C(12')	1837 (12)	8266 (20)	−2006 (5)	154
C(13')	1117 (8)	9036 (12)	−1747 (3)	80
O(1')	2352 (5)	9985 (7)	29 (2)	62
Cl-7R				
Cl	7927 (2)	9029 (1)	2081 (1)	85
O(1)	5413 (5)	7684 (3)	6078 (2)	74
C(1)	6664 (6)	8717 (5)	4923 (3)	48
C(2)	7576 (7)	9691 (6)	4625 (3)	59
C(3)	7951 (7)	9801 (6)	3752 (4)	61
C(4)	7422 (7)	8923 (5)	3174 (3)	56
C(5)	6503 (7)	7946 (5)	3446 (3)	57
C(6)	6128 (7)	7851 (5)	4312 (3)	53
C(7)	6257 (6)	8550 (5)	5870 (3)	51
C(8)	6914 (9)	9472 (6)	6522 (3)	58
C(9)	6599 (7)	9220 (5)	7487 (3)	52
C(10)	7732 (10)	8203 (6)	7830 (4)	70
C(11)	7358 (13)	7713 (8)	8737 (4)	87
C(12)	7958 (11)	8461 (8)	9500 (4)	130
C(13)	7707 (8)	9752 (7)	9546 (4)	99
C(14)	6393 (10)	10337 (7)	8974 (4)	89
C(15)	6803 (9)	10403 (5)	8001 (3)	65
Cl-8R (Cl x, y, z × 10^5)				
Cl	−14663 (9)	54140 (9)	−22303 (5)	74
O(1)	5996 (2)	1719 (2)	821 (1)	74
C(1)	2890 (3)	2336 (2)	162 (1)	41
C(2)	1084 (3)	1910 (3)	198 (2)	50
C(3)	−260 (3)	2856 (3)	−537 (2)	54
C(4)	221 (3)	4228 (3)	−1299 (1)	48
C(5)	1996 (3)	4696 (3)	−1350 (2)	53
C(6)	3326 (3)	3751 (3)	−620 (2)	48
C(7)	4405 (3)	1341 (3)	926 (1)	48
C(8)	3941 (3)	−151 (3)	1808 (2)	47

Table 3 (cont.)

	x	y	z	U_{eq}
C(9)	5536 (3)	−935 (3)	2598 (2)	43
C(10)	5753 (3)	371 (3)	3238 (2)	54
C(11)	7798 (4)	575 (3)	3394 (3)	71
C(12)	9235 (3)	−1101 (3)	3755 (2)	64
C(13)	8858 (4)	−2295 (4)	4803 (2)	70
C(14)	7136 (4)	−3215 (3)	4918 (2)	58
C(15)	6710 (3)	−3884 (3)	3993 (2)	50
C(16)	5141 (3)	−2714 (3)	3267 (2)	48

Discussion

Final positional parameters are in Table 3.* The aromatic rings in all four compounds (Fig. 5) show small, but not structurally significant deviations from exact planarity, χ^2 values being 14·5 for Cl-4R, 1·8 and 2·2 for the two independent molecules of Cl$_2$-5R, 3·3 for Cl-7R, and 15·0 for Cl-8R, with maximum displacements of C atoms from mean planes of 0·009 (4) and 0·004 (2) Å for the most non-planar rings (in Cl-4R and Cl-8R), respectively. The Cl atoms are only slightly displaced from the aromatic planes, by 0·033 (1), 0·020–0·037 (3) (on the same side of the plane), 0·040 (2) and 0·017 (1) Å, for the four compounds. Bond lengths and angles in the aromatic rings (Table 4) are close to expected values, with mean C—C = 1·379, 1·380, 1·379 and 1·378 Å, mean C—C—C = 120°, and C—Cl distances of 1·735 (4), 1·710–1·748 (8) [mean 1·725 (8)], 1·738 (5) and 1·746 (2) Å.

The four-membered cyclobutyl ring has the usual folded conformation, with bond torsion angles of ±14·0 (3)° (Fig. 5 and Table 5). C—C bond lengths in the ring are 1·512–1·534 (5), mean 1·524 Å, and C—C—C bond angles are 88·3–89·7 (3), mean 89·2°. The five-membered cyclopentyl rings of the two independent molecules of Cl$_2$-5R both exhibit some disorder of the outer atoms, C(11)–C(13), indicated by the large apparent r.m.s. thermal displacements along **b** of ~0·6 Å for C(12) and ~0·3 Å for C(11) and C(13) (in both molecules), and by apparently short C—C distances of 1·415–1·446 (14) Å. Split-atom models were not tested, since correlations between parameters would probably preclude accurate determination of atomic positions, and since the disorder does not obscure structural details in other regions of the molecules. The detailed conformations of the rings have thus not been established, but bond lengths and angles (Table 4) are generally close to expected values [1·534 (11) Å for C(9)—C(10), mean of 1·520 Å for adjacent bonds, and apparently foreshortened distances in the disordered region].

* Lists of anisotropic thermal parameters, H positions, torsion angles and structure factors, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44423 (72 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The seven-membered cycloheptyl ring in Cl-7R appears to have a conformation between a chair [with mirror plane through C(9) and the midpoint of C(12)–C(13)] and a twist-chair [with a C_2 axis through C(12) and the midpoint of C(9)–C(15)] (Fig. 5 and Table 5). The ring is probably disordered over these two conformations, although the disorder is less severe than in Cl$_2$-5R, with r.m.s. thermal displacements of up to about 0·4 Å for C(12) and C(13), and an apparently foreshortened C(12)–C(13) length of 1·432 Å (mean of bond lengths remote from the disordered region = 1·528 Å). The disorder was left untreated for reasons similar to those given for Cl$_2$-5R. Although the twist-chair is the minimum-energy conformer for the cycloheptyl ring (Hendrickson, 1967), the presence of the disorder is not unexpected, since the transformation from twist-chair to chair requires only small rotations about the ring bonds, with an energy barrier of <9 kJ mol^{-1} (Hendrickson, 1961; Bixon & Lifson, 1967). Bond angles in the cycloheptyl ring are opened significantly from tetrahedral geometry (although the values may be affected by the disorder), with an average [excluding angles at C(12) and C(13)] of 115·1°, which is close to predicted values (Hen-

drickson, 1967; Bixon & Lifson, 1967). The opening of the bond angles has been attributed partly to a relief of transannular H···H interactions, and some contacts below the van der Waals distance are expected for both chair and twist-chair conformations (Hendrickson, 1961). No exceptionally short H···H contacts are found in Cl-7R, although this may be partly due to the displacement of H positions normally found by X-ray methods [mean C(sp^3)–H = 1·00 Å for Cl-7R].

The eight-membered cyclooctyl ring (Fig. 5) has a boat-chair conformation with an approximate mirror plane through C(12) and C(16). This is the expected conformation for the ring (Hendrickson, 1964, 1967; Bixon & Lifson, 1967), being favoured over other possible conformations by about 6 kJ mol^{-1}, and the measured ring torsion angles are close to theoretical values (Table 5). Bond lengths in the ring are close to normal values, mean 1·523 Å, and bond angles are again larger than the tetrahedral angle, with values 113·3–118·3 (2), mean 116·6°.

The non-planarity of the cycloalkyl-ring systems permits the designation of ring substituents as axial and equatorial (or pseudo-axial and pseudo-equatorial). In all four molecules the acetophenone moieties are

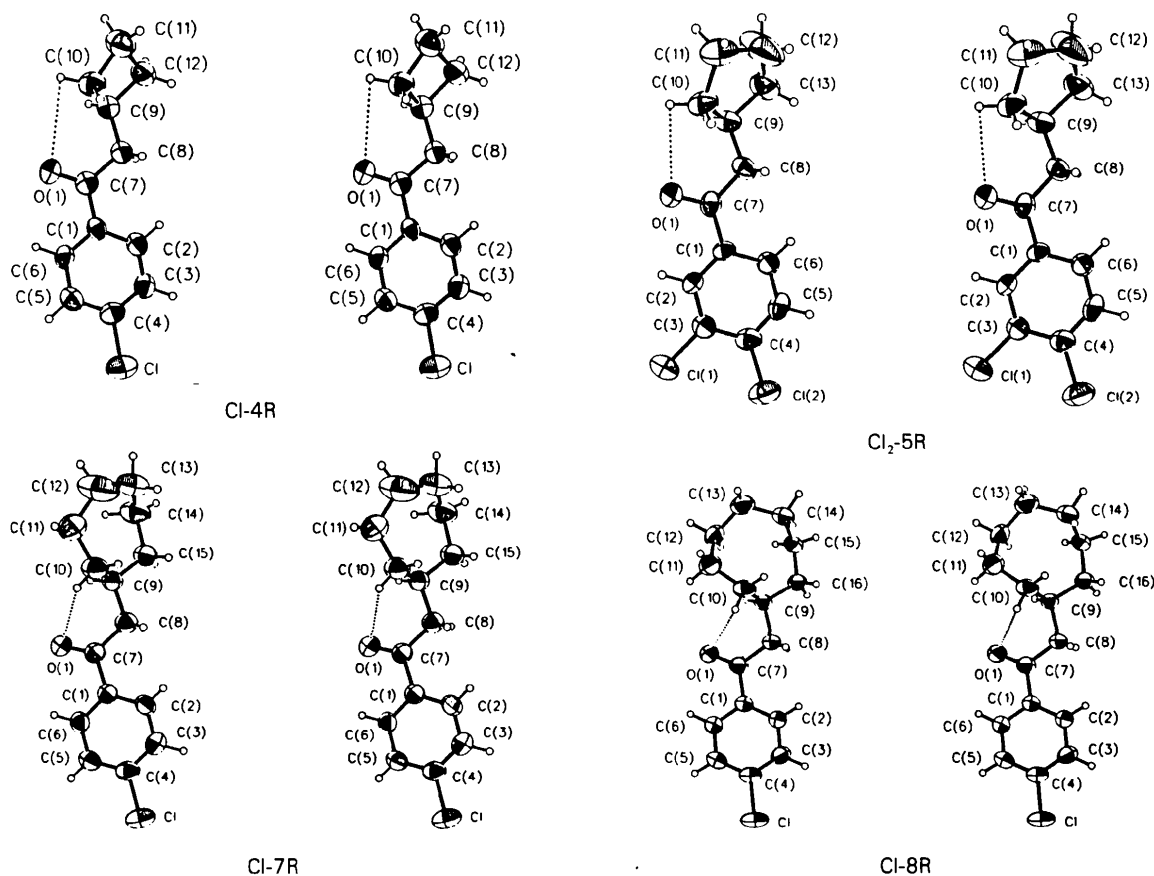Fig. 5. Stereoviews of the molecules of Cl-4R, Cl$_2$-5R (unprimed molecule only), Cl-7R, and Cl-8R. For Cl-4R, the molecule shown is the enantiomorph of that listed in Table 3; the crystals are racemic. Dotted lines indicate H-abstraction pathways.

Table 4. *Bond lengths* (Å) *and angles* (°), *with standard deviations in parentheses*

Cl-4R

Cl–C(4)	1·735 (4)	C(7)–C(8)	1·505 (5)
C(1)–C(2)	1·391 (5)	C(7)–O(1)	1·214 (4)
C(1)–C(6)	1·376 (4)	C(8)–C(9)	1·505 (5)
C(1)–C(7)	1·500 (5)	C(9)–C(10)	1·525 (5)
C(2)–C(3)	1·375 (5)	C(9)–C(12)	1·534 (5)
C(3)–C(4)	1·371 (5)	C(10)–C(11)	1·525 (5)
C(4)–C(5)	1·378 (5)	C(11)–C(12)	1·512 (5)
C(5)–C(6)	1·380 (5)		

C(2)–C(1)–C(6)	117·9 (3)	C(1)–C(7)–C(8)	119·2 (4)
C(2)–C(1)–C(7)	123·4 (4)	C(1)–C(7)–O(1)	119·6 (4)
C(6)–C(1)–C(7)	118·8 (4)	C(8)–C(7)–O(1)	121·2 (3)
C(1)–C(2)–C(3)	121·7 (4)	C(7)–C(8)–C(9)	115·4 (3)
C(2)–C(3)–C(4)	119·0 (4)	C(8)–C(9)–C(10)	118·2 (3)
Cl–C(4)–C(3)	120·2 (3)	C(8)–C(9)–C(12)	117·6 (3)
Cl–C(4)–C(5)	118·8 (3)	C(10)–C(9)–C(12)	88·3 (3)
C(3)–C(4)–C(5)	120·9 (4)	C(9)–C(10)–C(11)	89·5 (3)
C(4)–C(5)–C(6)	119·2 (4)	C(10)–C(11)–C(12)	89·1 (3)
C(1)–C(6)–C(5)	121·4 (3)	C(9)–C(12)–C(11)	89·7 (3)

Cl₂-5R

Cl(1)–C(3)	1·724 (8)	C(11)–C(12)	1·446 (14)
Cl(2)–C(4)	1·710 (8)	C(12)–C(13)	1·425 (14)
Cl(1')–C(3')	1·717 (8)	C(1')–C(2')	1·384 (9)
Cl(2')–C(4')	1·748 (8)	C(1')–C(6')	1·402 (10)
C(1)–C(2)	1·377 (9)	C(1')–C(7')	1·507 (10)
C(1)–C(6)	1·396 (10)	C(2')–C(3')	1·369 (10)
C(1)–C(7)	1·474 (10)	C(3')–C(4')	1·368 (10)
C(2)–C(3)	1·359 (9)	C(4')–C(5')	1·379 (10)
C(3)–C(4)	1·414 (10)	C(5')–C(6')	1·369 (10)
C(4)–C(5)	1·374 (10)	C(7')–C(8')	1·499 (9)
C(5)–C(6)	1·367 (10)	C(7')–O(1')	1·210 (8)
C(7)–C(8)	1·494 (10)	C(8')–C(9')	1·513 (10)
C(7)–O(1)	1·232 (8)	C(9')–C(10')	1·534 (11)
C(8)–C(9)	1·506 (10)	C(9')–C(13')	1·541 (10)
C(9)–C(10)	1·534 (10)	C(10')–C(11')	1·509 (12)
C(9)–C(13)	1·543 (10)	C(11')–C(12')	1·435 (13)
C(10)–C(11)	1·485 (10)	C(12')–C(13')	1·415 (14)

C(2)–C(1)–C(6)	118·5 (7)	C(2')–C(1')–C(6')	118·6 (7)
C(2)–C(1)–C(7)	119·9 (8)	C(2')–C(1')–C(7')	119·2 (8)
C(6)–C(1)–C(7)	121·5 (7)	C(6')–C(1')–C(7')	122·2 (7)
C(1)–C(2)–C(3)	121·5 (7)	C(1')–C(2')–C(3')	120·7 (8)
Cl(1)–C(3)–C(2)	121·0 (7)	Cl(1')–C(3')–C(2')	120·1 (7)
Cl(1)–C(3)–C(4)	118·7 (6)	Cl(1')–C(3')–C(4')	120·1 (7)
C(2)–C(3)–C(4)	120·3 (7)	C(2')–C(3')–C(4')	119·7 (7)
Cl(2)–C(4)–C(3)	122·3 (6)	Cl(2')–C(4')–C(3')	122·5 (7)
Cl(2)–C(4)–C(5)	120·0 (7)	Cl(2')–C(4')–C(5')	116·3 (8)
C(3)–C(4)–C(5)	117·7 (7)	C(3')–C(4')–C(5')	121·2 (7)
C(4)–C(5)–C(6)	121·9 (8)	C(4')–C(5')–C(6')	119·1 (8)
C(1)–C(6)–C(5)	120·0 (7)	C(1')–C(6')–C(5')	120·6 (7)
C(1)–C(7)–C(8)	120·9 (8)	C(1')–C(7')–C(8')	118·9 (7)
C(1)–C(7)–O(1)	119·0 (7)	C(1')–C(7')–O(1')	118·9 (7)
C(8)–C(7)–O(1)	120·1 (8)	C(8')–C(7')–O(1')	122·2 (7)
C(7)–C(8)–C(9)	117·2 (7)	C(7')–C(8')–C(9')	116·0 (7)
C(8)–C(9)–C(10)	114·4 (6)	C(8')–C(9')–C(10')	113·7 (6)
C(8)–C(9)–C(13)	112·6 (7)	C(8')–C(9')–C(13')	113·1 (7)
C(10)–C(9)–C(13)	104·4 (6)	C(10')–C(9')–C(13')	105·1 (7)
C(9)–C(10)–C(11)	106·6 (7)	C(9')–C(10')–C(11')	105·9 (7)
C(10)–C(11)–C(12)	106·7 (9)	C(10')–C(11')–C(12')	107·2 (9)
C(11)–C(12)–C(13)	111·3 (9)	C(11')–C(12')–C(13')	112·4 (9)
C(9)–C(13)–C(12)	107·3 (8)	C(9')–C(13')–C(12')	107·4 (9)

Cl-7R

C(1)–C(2)	1·384 (7)	C(7)–O(1)	1·218 (5)
C(1)–C(6)	1·390 (6)	C(8)–C(9)	1·531 (7)
C(1)–C(7)	1·507 (6)	C(9)–C(10)	1·523 (7)
C(2)–C(3)	1·384 (7)	C(9)–C(15)	1·521 (7)
C(3)–C(4)	1·365 (7)	C(10)–C(11)	1·527 (8)
C(4)–C(5)	1·376 (7)	C(11)–C(12)	1·491 (9)
C(4)–Cl	1·738 (5)	C(12)–C(13)	1·432 (9)
C(5)–C(6)	1·373 (7)	C(13)–C(14)	1·494 (9)
C(7)–C(8)	1·503 (7)	C(14)–C(15)	1·538 (8)

C(2)–C(1)–C(6)	117·5 (5)	C(8)–C(7)–O(1)	122·6 (5)
C(2)–C(1)–C(7)	123·3 (5)	C(7)–C(8)–C(9)	116·7 (5)
C(6)–C(1)–C(7)	119·2 (5)	C(8)–C(9)–C(10)	110·1 (5)
C(1)–C(2)–C(3)	121·6 (5)	C(8)–C(9)–C(15)	108·9 (4)
C(2)–C(3)–C(4)	119·1 (6)	C(10)–C(9)–C(15)	113·2 (5)
C(3)–C(4)–Cl	119·7 (5)	C(9)–C(10)–C(11)	115·6 (6)
C(5)–C(4)–Cl	119·4 (4)	C(10)–C(11)–C(12)	116·5 (7)
C(4)–C(5)–C(6)	119·5 (5)	C(11)–C(12)–C(13)	122·6 (6)
C(1)–C(6)–C(5)	121·4 (6)	C(12)–C(13)–C(14)	119·6 (6)
		C(13)–C(14)–C(15)	114·2 (6)

Table 4 (*cont.*)

C(1)–C(7)–C(8)	118·0 (5)	C(9)–C(15)–C(14)	115·8 (5)
C(1)–C(7)–O(1)	119·4 (5)		

Cl-8R

C(1)–C(2)	1·381 (3)	C(8)–C(9)	1·530 (3)
C(1)–C(6)	1·389 (3)	C(9)–C(10)	1·532 (3)
C(1)–C(7)	1·497 (3)	C(9)–C(16)	1·529 (3)
C(2)–C(3)	1·385 (3)	C(10)–C(11)	1·525 (3)
C(3)–C(4)	1·363 (3)	C(11)–C(12)	1·514 (3)
C(4)–C(5)	1·372 (3)	C(12)–C(13)	1·510 (4)
C(4)–Cl	1·746 (2)	C(13)–C(14)	1·517 (4)
C(5)–C(6)	1·375 (3)	C(14)–C(15)	1·523 (3)
C(7)–C(8)	1·507 (3)	C(15)–C(16)	1·533 (3)
C(7)–O(1)	1·213 (2)		

C(2)–C(1)–C(6)	118·6 (2)	C(8)–C(7)–O(1)	120·6 (2)
C(2)–C(1)–C(7)	123·1 (2)	C(7)–C(8)–C(9)	114·4 (2)
C(6)–C(1)–C(7)	118·3 (2)	C(8)–C(9)–C(10)	110·8 (2)
C(1)–C(2)–C(3)	120·9 (2)	C(8)–C(9)–C(16)	109·1 (2)
C(2)–C(3)–C(4)	119·0 (2)	C(10)–C(9)–C(16)	113·3 (2)
C(3)–C(4)–C(5)	121·5 (2)	C(9)–C(10)–C(11)	115·9 (2)
C(3)–C(4)–Cl	119·1 (2)	C(10)–C(11)–C(12)	117·3 (2)
C(5)–C(4)–Cl	119·4 (2)	C(11)–C(12)–C(13)	117·2 (3)
C(4)–C(5)–C(6)	119·3 (2)	C(12)–C(13)–C(14)	117·8 (2)
C(1)–C(6)–C(5)	120·7 (2)	C(13)–C(14)–C(15)	116·7 (2)
C(1)–C(6)–C(7)	119·4 (2)	C(14)–C(15)–C(16)	116·3 (2)
C(1)–C(7)–O(1)	120·0 (2)	C(9)–C(16)–C(15)	118·3 (2)

Table 5. *Cycloalkyl-ring bond torsion angles* (°)

	Cl-4R		Cl₂-5R Unprimed	Primed
'9-10	-13·9 (3)	9-10	15 (1)	12 (1)
10-11	14·1 (3)	10-11	-20 (1)	-15 (1)
11-12	-14·0 (3)	11-12	18 (2)	12 (2)
12-9	14·1 (3)	12-13	-8 (2)	-4 (2)
		13-9	-4 (1)	-5 (1)

Cl-7R

		Theoretical*	
	Measured	Chair	Twist-chair
9-10	67 (1)	64	72
10-11	-79 (1)	-83	-88
11-12	47 (1)	66	39
12-13	19 (1)	0	39
13-14	-72 (1)	-66	-88
14-15	77 (1)	84	72
15-9	-62 (1)	-64	-54

Cl-8R

	Measured	Theoretical boat-chair*
9-10	101·6 (2)	102·2
10-11	-48·7 (4)	-44·7
11-12	-61·9 (4)	-65·0
12-13	67·1 (4)	65·0
13-14	38·5 (4)	44·7
14-15	-99·3 (3)	-102·2
15-16	68·7 (3)	65·0
16-9	-65·8 (3)	-65·0

* Hendrickson (1967).

equatorial with respect to the cycloalkyl rings, presumably because these positions are sterically more favourable than the axial sites. The conformations of the central parts of the molecules (Table 6) are all very similar to each other, and to the conformations of the α-cyclopentyl- and α-cyclohexyl-4-chloroaceto-phenones which have been studied previously (Cl-5R and Cl-6R; Ariel & Trotter, 1985, 1986). The φ_1 and φ_2 torsion angles are within about 10° of their expected values of 60 and 0°, respectively, and the carbonyl groups are nearly coplanar with the aromatic rings (rotations of up to 7°). As a result of the increasing size and flexibility of the cycloalkyl rings ($n = 4, 5, 6, 7, 8$),

Table 6. *Molecular conformations, H-abstraction and biradical geometries, and photoproduct ratios for chloro-substituted α-cycloalkylacetophenones*

	Cl-4R	Cl-5R*	Cl₂-5R		Cl-6R†	Cl-7R	Cl-8R
			Unprimed	Primed			
Molecular conformation (°, Figs. 2 and 5)							
φ_1	71	71	66	65	71	74	70
φ_2	0	0	3	5	7	5	7
Carbonyl-ring angle	2	5	7	7	4	3	3
ψ	14	30	15	12	55	67	102
H abstraction							
Ring conformation	Twist-boat	Boat	Twist-boat		Boat	Boat	Boat
d (Å)	3·10	2·76	2·88	2·91	2·60	2·71	2·71
τ (°)	23	31	27	28	42	42	46
Δ (°)	101	96	101	99	90	82	77
Biradical geometry (°, Fig. 3 and Table 1)							
$\theta_{C=O}$	90	90	94	95	95	94	96
θ_y	51	69	53	51	88	99	131
θ_{pp}	57	66	60	62	74	79	88
% Cyclization							
Benzene	10	8	10		65	36	70
CH₃CN	12	8	14		69	35	73
Solid state	8	8	10		55	31	96
% cis-OH cyclobutanol							
Benzene	‡	38	40		34	32	30
CH₃CN	‡	40	32		49	41	44
Solid state	‡	34	43		47	23	4

* Ariel & Trotter (1986).
† Ariel & Trotter (1985).
‡ Not determined because of overlapping gas-chromatogram peaks.

the C(8+n)—C(9)—C(10)—C(11) intra-annular torsion angles, ψ, increase in the series from 14 to 102°.

The molecular packings differ considerably in the four compounds studied in the present paper,* but one common feature is the arrangement of parallel aromatic rings around centres of symmetry, with interplanar spacings of 3·44–3·66 Å, but with different degrees of overlap of ring atoms in the four structures. In Cl₂-5R there are two intermolecular Cl···Cl contacts of 3·421 (3) and 3·692 (3) Å, which may indicate possible enhanced interactions, but all other distances in the four compounds correspond to van der Waals forces. In Cl₂-5R the two independent molecules, which have similar geometries and dimensions, are related very approximately by the relationship: $x + x' \sim 0.7$, $y + y' = 1$, $z - z' = 0.5$.

All compounds in Table 6 undergo the Norrish type II reaction upon irradiation in solution and in the solid state (Omkaram, 1986; Omkaram & Scheffer, 1987). In all the molecules there is an equatorial H atom on C(10) which is suitably oriented for abstraction by carbonyl O. The six-membered rings formed during the abstraction process can be described as distorted boats or twist-boats, with O(1) and C(9) at the prow and stern (Fig. 5), as previously found for cyclohexyl derivatives (Ariel *et al.*, 1983). The H-abstraction distances vary from 3·1 Å in the cyclobutyl derivative

* For packing diagrams, see deposition footnote.

to a uniform value of 2·7 Å for the larger cycloalkyl rings (n = 6–8). The near planarity and smaller intra-annular bond angles of the cyclobutyl and cyclopentyl rings require the γ-H atoms to be more remote from the O atom. Consequently compounds Cl-4R, Cl-5R, and Cl₂-5R have H_γ···O distances (3·1, 2·8, 2·9 Å) which are slightly longer than the previously suggested upper limit of 2·72 Å, but this does not appear to preclude photochemical reaction. As the cycloalkyl-ring size increases, the rings become nonplanar, and the H_γ···O distances decrease, the conformational flexibility of the larger rings allowing the H to ride up on the van der Waals surface of the O atom, with τ increasing from 23 to 46° in the series (Table 6). A suggested $\cos^2\tau$ dependence for abstraction (Wagner, 1976) would reduce the relative reactivity by a factor of only 1·2–2. The Δ angles differ by only about 10° from the ideal 90° value. Since the cyclobutyl ring is not far from planar, the axial H on C(10) is also not much less favourable for abstraction, d, τ, and Δ being 3·28 Å, 39°, and 78°, respectively. For the cyclopentyl ring the corresponding axial H values are 3·1 Å, 43° and 75° (almost identical values for the two molecules in the asymmetric unit), but distances in the cycloheptyl and cyclooctyl derivatives are >4·0 Å; the cyclooctyl compound has a δ-H on C(11) with d = 2·98 Å, but no products of δ-H abstraction are found.

The cyclization:cleavage ratio (expressed in Table 6 as % cyclization) is relatively insensitive to reaction medium, which is somewhat surprising, as the crystal lattice is expected to provide more severe restrictions on molecular motion than solution media, and so favour products which can be formed with a minimum of molecular motion. It is possible that photolysis is occurring not in the bulk of the crystal but in defects; however, it is unlikely that the molecular environment in a defect would be equivalent to that of solution media, and so produce near-identical product ratios. The amount of cyclization does increase markedly with increasing cycloalkyl-ring size, from about 10% cyclization for cyclobutyl and cyclopentyl rings to about 70% for the cyclooctyl compound (and nearly 100% for the cyclooctyl compound in the solid state) (Table 6). The % cyclization for the cyclohexyl and cycloheptyl compounds varies somewhat from a uniform increase with increasing ring size.

Cleavage had been thought to predominate when the radical p orbitals were parallel to the central C_α–C_β bond being broken, *i.e.* when $\theta_{C=O}$ and θ_y (Table 1) were 0°. Geometrical constraints in the present molecules, in particular the C(7)—C(8)—C(9) and C(8)—C(9)—C(10) bond angles (mean 115° for the four molecules studied), limit the range of the θ values to 25–90° (or the supplement of these angles; see previous angle definitions). $\theta_{C=O}$ is uniformly near 90° (Table 6), so that this orbital is almost perfectly misaligned for cleavage; θ_y varies from about 50° for the cyclobutyl

and cyclopentyl rings to about 90° for the cyclohexyl and cycloheptyl rings, and to about 130° (supplement 50°) for the cyclooctyl ring. Thus the cyclobutyl and cyclooctyl derivatives have very similar degrees of overlap of the C_γ radical p orbital with the C_α–C_β bond, but show opposite photochemical behaviour. However, although the degree of overlap is similar, the type of product which would be formed is not, as cleavage of the cyclooctyl compound would most readily produce the more-sterically hindered *trans*-cyclooctene. The same point also emerges from an examination of the cycloalkyl-ring torsion angles, ψ, which vary from 14° for the cyclobutyl ring to 102° for the cyclooctyl ring (Table 6); this angle must be close to 0° in the *cis*-cycloalkene photoproducts produced in a cleavage reaction. Thus, cleavage will be favoured when θ_p and ψ approach 0°; the cyclobutyl and cyclopentyl rings require relatively small motions to achieve this geometry, but the cyclohexyl, cycloheptyl, and cyclooctyl rings would have to undergo greater rotational motions about the C(9)—C(10) bonds to achieve geometries favourable for cleavage. The reaction medium, whether solution or solid, may hinder the motions required for cleavage, particularly the larger motions required for the larger cycloalkyl rings. This explanation is consistent with the decreased amount of cleavage products for the larger rings, particularly for the cyclooctyl derivative in the solid state.

The reason for the observed trend may lie not just in the ability of the reactants to assume geometries favourable for cleavage, but may depend on the ease of product formation. Cyclization involves formation of products with fused four-membered and *n*-membered rings ($n = 4$–8), with reduction of non-bonded C(7)··· C(10) distances in the reactants of about 3·2 Å (3·27, 3·24, 3·17, 3·19, 3·20, 3·14 Å for the six compounds in Table 6) to bonded distances of about 1·5 Å. The decreased amount of cyclization products for the smaller cycloalkyl rings may just reflect the higher strain energy involved in fusing two small rings. Although the strain energy in a polycyclic molecule is roughly equal to the sum of the strain of the component rings (Ferguson, 1973), detailed comparison [see Table V of Chang, McNally, Shary-Tehrany, Hickey & Boyd (1970)] suggests that the additional strain energy in forming the cyclobutyl relative to the cyclooctyl photoproduct is about 30 kJ mol⁻¹.

The final piece of photochemical information concerns the partitioning of the cyclization products between the cyclobutanol isomers with *cis*- and *trans*-OH groups [(4) and (5) in Fig. 1]. The *cis:trans*-OH ratios (expressed as % *cis* in Table 6) are somewhat more dependent on the medium than the cyclization:cleavage ratios, a dependence which also increases with cycloalkyl-ring size. The proportion of *cis*-OH isomer generally increases slightly in the more polar acetonitrile solvent, as expected (Wagner, 1967), but

the most marked difference in product ratio is found for the larger cycloalkyl rings, where the amount of *trans*-OH isomer increases (to nearly 100% for the cyclooctyl compound in the solid state).

On the basis of the observed geometries of the cycloalkylacetophenones (Fig. 5), probable structures can be derived for the biradical intermediates in the photoreactions; examples are shown in Fig. 6, for Cl₂-5R and Cl-8R. Cyclobutanol cyclization products with *cis*-fused ring junctions, and with *cis*- and *trans*-OH configurations (relative to the adjacent ring-junction H atom) would be formed by overlap of lobe a (Fig. 6) with lobes b and b', respectively. Cyclobutanols with *trans*-fused ring junctions would be formed by overlap of lobe a' with lobes b and b'.

For the cyclobutyl and cyclopentyl compounds, only *cis* ring-junction cyclization products are possible, and the geometries of the biradicals (Fig. 6) and the values of θ_{pp} and θ_p (both ~60°) (Table 6) suggest that the *cis*-OH isomer should be more readily formed than the *trans*-OH (since lobe a is much closer to lobe b than it is to lobe b'). As the cycloalkyl-ring size increases, lobe a moves further from lobe b (and from lobe b') (Fig. 6) θ_{pp} and θ_p increase (to about 90 and 130°, respectively, for the cyclooctyl compound), so that cyclization to form *trans* ring-junction photoproducts becomes more favourable, lobe a' then being in closer proximity to lobes a and b. This is exactly the observed behaviour. Many efforts to obtain crystals of the photoproducts have been unsuccessful, but very recently a crystalline sample of the minor cyclooctyl cyclization product has been prepared; crystal-structure analysis has shown this molecule to have a *trans*-fused ring junction, with a *cis*-OH configuration (Ariel & Trotter, 1987). The *trans*-fused ring junction is in accord with the proximity of lobe a' to lobes b and b' (Fig. 6) and with the related θ_p angle (131°). The major photoproduct is the
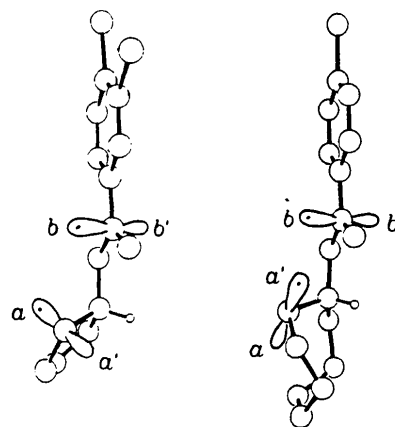

Fig. 6. Biradical intermediates for Cl₂-5R (left) and Cl-8R. Unprimed lobes a and b are on the *si* faces and primed lobes a' and b' on the *re* faces of the sp^2-hybridized radical C atoms (Hanson, 1966).

trans-OH isomer (Table 6), and this must involve reorientation of the acetophenone grouping to allow interaction of lobes *a'* and *b'*. The reason for the preponderance of *trans*-OH isomer, and for the increasing amounts of *trans*-OH with increasing cycloalkyl-ring size, may lie in the detailed geometries of the photoproducts. The crystal-structure study of the minor cyclooctyl photoproduct indicates that the four-membered cyclobutanol ring is folded, and that the *cis*-OH isomer contains a bulky axial 4-chlorophenyl substituent, while this substituent would be equatorial in the *trans*-OH isomer. Thus steric effects would favour the formation of the *trans*-OH isomer, and this product would become more favourable as the (fused) cycloalkyl ring becomes more bulky. These rationalizations are in accord with the observed product ratios (Table 6). No information is available on the ring-junction configurations for the cyclohexyl and cycloheptyl cyclization products; with θ_y angles of 88 and 99°, respectively (Table 6), either a *cis* or *trans* ring junction is feasible. The cyclohexyl and cycloheptyl compounds do follow the trend of increasing *trans*-OH product with increasing cycloalkyl-ring size.

Thus, the correlation of structural and photochemical data for the α-cycloalkyl-*p*-chloroacetophenones indicates that the photoproduct ratios are relatively insensitive to reaction medium, so that intramolecular rather than crystal-packing forces govern the course of the photoreactions. The increase in cyclization with increasing cycloalkyl-ring size correlates well with the changing angles between biradical *p* orbitals and with related ring torsion angles. The formation of cyclobutanol cyclization photoproducts with *trans*-fused ring junctions for the cyclooctyl compound is in accord with the orientations of the biradical *p* orbitals, and the preponderance of *trans*-OH cyclobutanol photoproduct for the whole series can be related to the greater steric stability of this isomer, particularly for the larger cycloalkyl rings.

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