Cyclobutanol : Fragmentation Ratios for the Singlet and Triplet Excited States in the Type II Photochemistry of Some α-Alkylated Cyclohexanones [1]

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In the Type II photochemistry of the conformationally fixed cyclohexanones, *cis*-4-t-butyl-2-n-propylcyclohexanone (1), 17β-acetoxy-2α-n-propyl-5α-oestran-3-one (6), 2α-n-propyl-5α-cholestan-3-one (9), and 17α-acetoxy-4α-n-propyl-5α-oestran-3-one (12), there is in each case a higher cyclobutanol : fragmentation ratio than that usually found for open-chain ketones. The effect, which is probably a consequence of the fragmenting bond being held at an angle unfavourable for continuous overlap, is more marked in the triplet state reaction, where the ratio for (1) is 73 : 27. In both states the effect is in fact quite small, probably because the reactions are very exothermic. In the case of the 4α-n-propyl steroid (12), the cyclobutanol : fragmentation ratio is larger for both the singlet and the triplet states than in the other cases, as a result of the presence of the ring B residue adjacent to the propyl group. Type I products from the steroidal ketones were not detected, and the Type I product from *cis*-4-t-butyl-2-n-propylcyclohexanone (1) is very largely of the ester and not the aldehyde kind. 2-Cyclohexylcyclohexanone (14) gives a high cyclobutanol : fragmentation ratio in both the triplet (*ca.* 80 : 20) and singlet states (64 : 36).

PHOTOLYSIS of ketones having an accessible hydrogen atom on C-4 is well known [2,3] to give a fragmentation product and cyclobutanols. These products are now called [2] the Type II products, and both are known to be produced from both the singlet and the triplet excited states (Scheme 1). Recently, some interest has been shown in the proportion of these two products. One factor which has occasionally been cited [2,4-6] is the possibility that, in the fragmentation reaction, there is a need for continuous overlap of the orbitals involved. For example, the optimum condition for fragmentation in the triplet state reaction, in which there is a diradical intermediate, is expected to be one in which the 2,3-bond is parallel to the singly occupied orbitals on C-1 and -4. The requirement for cyclobutanol formation is not

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[6] A. Padwa, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, 1969, **91**, 456; R. R. Sauers, M. Gorodetsky, J. A. Whittle, and C. K. Hu, *ibid.*, 1971, **93**, 5520; F. D. Lewis, R. W. Johnson, and R. A. Ruden, *ibid.*, 1972, **94**, 4292; R. B. Gagosian, J. C. Dalton, and N. J. Turro, *ibid.*, 1970, **92**, 4752.

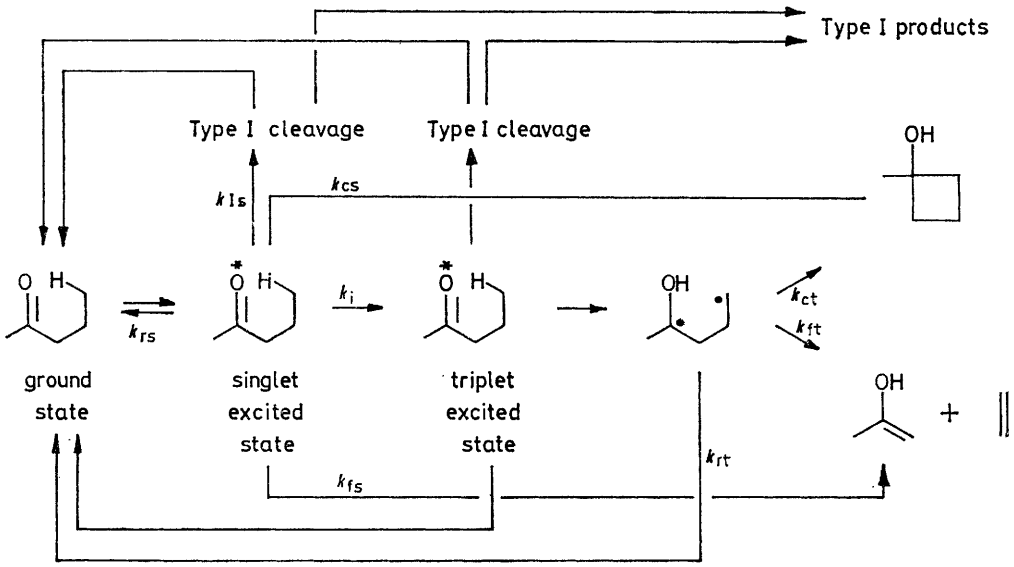
expected to be so dependent upon the orientation of this bond, and hence a high cyclobutanol : fragmentation ratio will be expected of ketones in which the 2,3-bond is held more or less rigidly in an orientation unfavourable for fragmentation.

Several ketones are known [5-7] to give an unusually high proportion of cyclobutanols, and in many of them the orientation of the 2,3-bond is unfavourable for fragmentation. None of these cases, however, is unambiguously explained by this effect; most of the examples were found by chance, and were not expressly designed to test the hypothesis. We now report higher than usual cyclobutanol : fragmentation ratios in some rather less ambiguous examples. We also report that this effect is small and that it is more in evidence for the triplet state reaction than for the singlet state reaction.

We have looked at the products from the photolysis of the cyclohexanones (1), (6), (9), (12), (14), and (20) in each of which the fragmenting bond is equatorial and therefore at an angle which should be unfavourable for fragmentation. The photolysis of ketone (1) has also been studied by Turro and Weiss,[8] but they did not observe the formation of cyclobutanols, largely because they used cyclohexane as a solvent. In this solvent (unlike t-butyl alcohol [9-11]) most of the reaction is from the singlet state, and in the singlet-state reaction cyclobutanols are very minor products (see later).

RESULTS

The direct photolysis of the ketones (1), (6), (9), (12), and (14) in t-butyl alcohol gave the products shown in Scheme 2. The cyclobutanols (2), (7), (10), (13), and (15) were generally isolated as mixtures of stereoisomers, some of which could be separated into pure compounds. In each case the cyclobutanol : fragmentation ratio (Table) was relatively high compared with the values for open-chain ketones recorded in the literature (usually $\leqslant 10 : 90$ [10-12] for the singlet state and $\leqslant 30 : 70$ [4,10-13] for the triplet state). When the triplet state reaction was quenched with piperylene the proportion of cyclobutanols fell to more normal values (Table), except for the ketones (12) and (14), where there was substantial cyclobutanol formation even in the singlet state.



SCHEME 1

To measure the yield of cyclobutanols from the triplet state is not easy. Photosensitisation of the triplet state of a saturated ketone is not well precedented (but see the following paper). We were therefore obliged to measure the absolute yields of the products in the direct and the quenched reactions It was necessary to do a Stern–Volmer plot, in order to exclude the small amount of singlet quenching,[14] and many runs had to be made before our figures were accurate enough Thus we have a reliable value (73 : 27) only for ketone (1) and a rough value (*ca.* 80 : 20) for ketone (14). For all five ketones, however, it is clear that the cyclobutanol : fragmentation ratio is higher in the triplet state than in the singlet state. It can easily be shown that the cyclobutanol : fragmentation ratio for the triplet state reaction is always higher than the ratio observed in the direct photolysis

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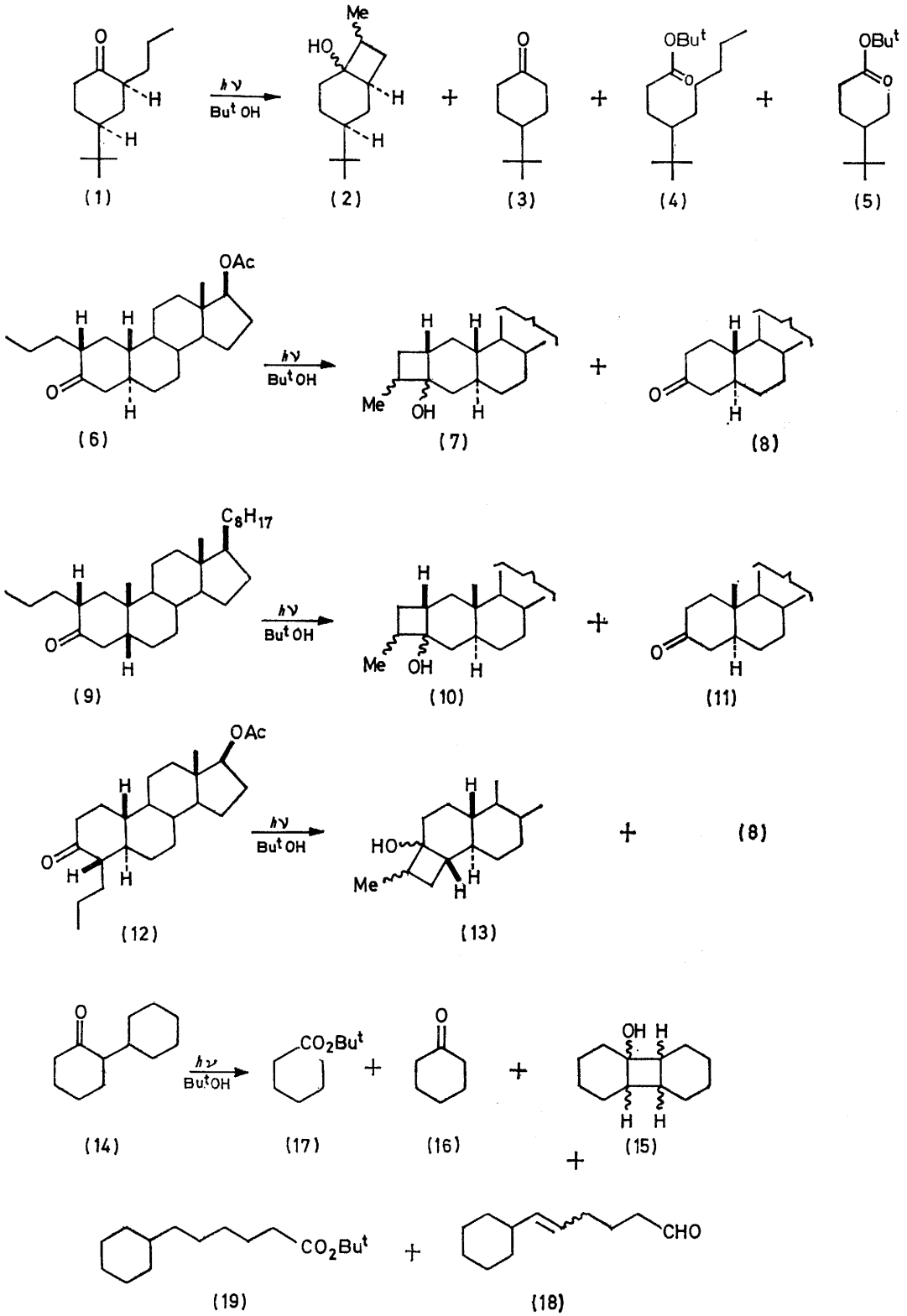
Me
HO
H
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(1)
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OH
(6)
(7)
(8)
C8H17
(9)
(10)
(11)
(12)
(13)
CO2But
OH
(14)
(17)
(16)
(15)
CHO
(19)
(18)

SCHEME 2

provided that this ratio is reduced on quenching, as it is in all our cases and in all reported cases.

DISCUSSION

We do not know all the rate constants of Scheme 1, so we cannot give a full account of the reactivity of the intermediates involved. We can however come to the following conclusions.

Starting material	Photolysis conditions	Products [a] of photolysis [b]: Cyclobutanols (%)	Fragmentation products (%)	Type I product (%)	Cyclobutanol : fragmentation ratios: Singlet state + triplet state	Singlet state alone	Triplet state alone
(1)	Direct in But^{t}OH,[c]	30 [d]	55 [e]	13	35 : 65		73 : 27 [i]
	quenched [f] in But^{t}OH	13 [g]	87	0 [h]		13 : 87	
(6)	Direct in But^{t}OH,	42	58	0	42 : 58		>42 : 58
	quenched [f] in But^{t}OH	24	76	0		24 : 76	
(9)	Direct in But^{t}OH,	30	70	0	30 : 70		>30 : 70
	quenched [f] in But^{t}OH	11	89	0		11 : 89	
(12)	Direct in But^{t}OH,	70	30	0	70 : 30		>70 : 30
	quenched [f] in But^{t}OH	46	54	0		46 : 54	
(14)	Direct in But^{t}OH,	26 [j]	6	67 [k]	82 : 18		
	quenched in neat piperylene	56 [l]	18 [m]	0		76 : 24	
	Pentane–piperylene mixture containing 10% But^{t}OH				72 : 28	64 : 36	~80 : 20 [n]

[a] Values are average of two or three runs and are reproducible to ±2 or 3%. Yields are expressed as percentages of detectabl products at 10—20% conversion. [b] Concentration was 0.08M for (1), 0.02M for the steroids, and 0.06M for (14). [c] Two unidentifie products with short g.l.c. retention times were also detected to the extent of *ca.* 1—2% each. [d] Four cyclobutanols, which we hav called A—D, could be detected (see Experimental section) very approximately in the ratios 5 : 15 : 60 : 20. [e] This includes the Typ I product (5) which is formed from the Type II product by secondary photolysis, usually to the extent of *ca.* 15% at 20% conversion [f] t-Butyl alchol was made 2.3M in piperylene. [g] The four cyclobutanols could now be detected very approximately in the ratio 20 : 60 : 15 : 5. [h] The amount of Type I reaction left unquenched was too small to measure. [i] For details of this measurement se Experimental section. As a result of an arithmetical error, this ratio was unfortunately reported in our preliminary communicatio to be 68 : 32; the difference is probably not even significant. [j] Two fractions by g.l.c., A and B, in the ratio of 16 : 10. [k] Two isomer of (18) and the ester (19) in the ratio 7 : 51 : 9 respectively. There was very little of the secondary photoproduct (17). [l] A and I were not in the ratio 41 : 15. [m] 26% Unidentified product was also present. [n] See the following paper for confirmation of a numbe in this region.

(i) The main effect of having a 2,3-bond oriented unfavourably for fragmentation is to make both Type II processes inefficient. The quantum yield for (1) is 0.05 (Turro and his co-workers [15] obtained a value of 0.1) in line with the usual range [16] for 2-alkylcyclohexanones (0.16—0.04).

(ii) The steroidal ketones (6), (9), (12), and (20) gave no Type I products in t-butyl alcohol. Photolysis of ketone (20) in cyclohexane did give hydrocarbon products, so evidently the diradical intermediate in the Type I reaction was being formed, but presumably it always reclosed in t-butyl alcohol to give the starting ketone.

(iii) The Type I product from ketone (1) was entirely of the ester kind, presumably for the reasons given by Turro and his co-workers.[15]

(iv) Although all of the ketones did give relatively high cyclobutanol : fragmentation ratios, the effect of having the 2,3-bond oriented unfavourably for fragmentation is small. The rate of cyclobutanol formation was increased by no more than a factor of ten relative to the rate of fragmentation. The effect is even smaller if comparison is made with 2-methylvalerophenone,[5] a ketone with the same degree of substitution at both C-2 and -4 as our ketones: here the ratio for the triplet state reaction is 43 : 57, which represents only an approximately 4-fold reduction for ketone (1) in the rate of fragmentation relative to cyclobutanol formation.

(v) The large effect is in the triplet-state reaction. For ketone (1) the cyclobutanol : fragmentation ratio in the triplet state is 73 : 27. The ratio in the singlet state remains small (13 : 87), presumably because it is so much more exothermic than the triplet state reaction.

(vi) Ketone (12) has quite a high cyclobutanol : fragmentation ratio (46 : 54) even in the singlet state. This is probably caused by a buttressing effect from the C-5·C-6 bond.

(vii) Ketone (20), has both the buttressing effect and because the hydrogen abstracted is primary,[10,17] a predominantly triplet state reaction. The result is that the cyclobutanol (21) is virtually the only photoproduct in t-butyl alcohol.

(viii) Ketone (14) is a special case. In the diradical intermediate (22) of the triplet state reaction, the fragmenting bond is unfavourably oriented with respect to *both* radical centres. Perhaps because this ketone is no conformationally rigid, this does not lead to a significant increase in the cyclobutanol : fragmentation ratio in the triplet state. Indeed, the 20% fragmentation may well have come from a conformation of the diradical [*e.g.* (23)], in which the bond joining the two rings is axial to at least one of the rings. The interesting feature in this ketone is that the singlet state reaction shows a high cyclobutanol : fragmentation ratio, namely 64 : 36. Whether or not there is a diradical intermediate, in the singlet-state reaction, there is unlikely to be time for conformational change after the light has been absorbed

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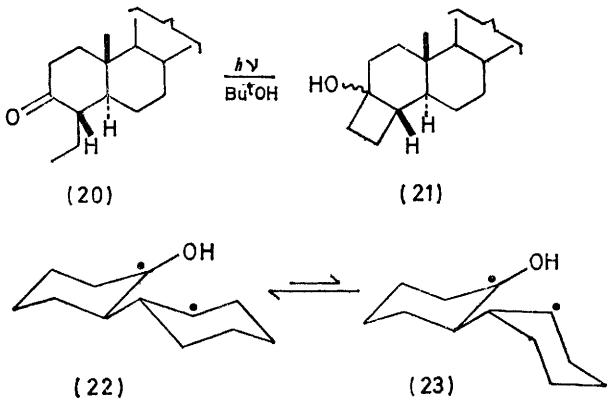
Since some, at least, of the reaction can have come from the minor conformation corresponding to (23), the cyclobutanol : fragmentation ratio in the singlet state reaction of a conformationally rigid analogue of (14) can be expected to be even higher than 64 : 36. This could be useful knowledge from the synthetic point of view. Type I reactions of cyclic ketones are triplet state reactions,[18]



(20) (21)

(22) (23)

and it is useful to be able to quench them when they are undesirable; thus if cyclobutanols are to be major products, it is preparatively convenient that the cyclobutanol : fragmentation ratio be high in the singlet state. Evidently an especially unfavourable orientation of the fragmenting bond, as in (14), *can* be made to raise the cyclobutanol : fragmentation ratio in the singlet state reaction.

Synthesis of the Ketones (1), (6), (9), *and* (12).—In planning to synthesise ketones (1), (6), (9), and (12), we immediately came up against the well known difficulty of achieving regioselective monoalkylation of the parent ketones. Although much work has been done in this field, our efforts along several established lines,[19-22] although not fruitless, were not encouraging. Only one, (12), of the ketones was readily made using Stork's reductive alkylation method [19] for achieving regioselective monoalkylation. The other three n-propyl ketones were eventually prepared most easily by modification of the procedure in ref. 23 for the allylation of cyclohexanone, followed by hydrogenation. In this procedure, the diallyl acetal of cyclohexanone is heated to give, by way of a Claisen type rearrangement of the enol ether, allylcyclohexanone, and allyl alcohol. Our modification was simply to combine the two steps: by heating the ketones (3), (8), and (11) with 2,2-dimethoxypropane, allyl alcohol, and toluene-*p*-sulphonic acid in toluene, and distilling off the acetone, methanol, and allyl alcohol, the allyl ketone was produced directly in acceptable yield. The method also works on cholestenone, to give 4-allylcholestenone in better yield than by the alkylation route.[24] In the case of 4-t-butylcyclohexanone (3), we observed that the product was initially rich in the *trans* (axially alkylated) isomer (71% *trans*: 29% *cis*); on equilibration, the usual [20] mixture (*ca.* 15% *trans*: *ca.* 85% *cis*) was produced. Alkylations of enolates are not usually very stereoselective,[25] but alkylations of enamines [20] like protonation of enamines [26] and of enol ethers [25] are much more stereoselective. Evidently the Claisen type rearrangement is also stereoselective, probably because it too is not very exothermic. Because our reaction conditions are potentially equilibrating conditions, the stereoselectivity we observe is not necessarily the optimum.

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EXPERIMENTAL

cis-4-*t-Butyl*-2-*n-propylcyclohexanone* (1).—A mixture of *cis*- and *trans*-2-allyl-4-t-butylcyclohexanones was prepared as described for 2-allylcholestanone below. When the mixture was sampled 15 min after the distillation reached the b.p. of toluene, g.l.c. revealed that the *cis* : *trans*-ratio was 29 : 71 but that reaction was incomplete. After longer boiling (9 h) the mixture was distilled *in vacuo* to give a *cis* : *trans*-mixture of the ketones [75% yield (*cf.* enamine alkylation [20] 39% yield in the ratio 65 : 35)], b.p. 119—123.5° at 11 Torr (lit.,[20] 'about' 120° at 10 Torr). Equilibration to a *cis* : *trans*-ratio of 85 : 15 (lit.,[20] 87 : 13) was achieved by boiling the mixture in aqueous methanol containing a few drops of pyrrolidine for 30 min. The mixture was separated on silica (Mallinckrodt silica R CC-7) eluting the *cis*-isomer with light petroleum (b.p. 60—80°)–benzene (from 60 : 40 to 50 : 50) and the *trans*-isomer with light petroleum benzene (from 40 : 60 to 30 : 70). Both isomers have $\nu_{max.}$ 3 070, 1 710, and 1 640 cm^{-1}. Hydrogenation of the *cis*-isomer in ethyl acetate over palladium on carbon gave pure cis-4-*t-butyl*-2-*n-propylcyclohexanone* (Found: C, 79.2; H, 12.3. $C_{13}H_{24}O$ requires C, 79.5; H, 12.3%), $\nu_{max.}$ 1 714 cm^{-1}.

2α-*Allyl*-17β-*hydroxy*-5α-*oestran*-3-*one*.—This *ketone*, prepared from 17β-hydroxyoestran-3-one [27] in 42% yield by the method described for 2-n-propylcholestanone below was purified on alumina (Woelm neutral; grade 11) eluting with benzene–ether (90 : 10), and had m.p. 127.5—132° (from acetone–cyclohexane) (Found: C,79.4; H, 10.0. $C_{21}H_{32}O_2$ requires C, 79.7; H, 10.2%), $\nu_{max.}$ (KBr) 3 080, 1 710, and 1 638 cm^{-1}, (Nujol) 3 280 cm^{-1}. Some of the 4α-allyloestran-3-one (see below) was eluted after the 2α-isomer.

17β-*Acetoxy*-2α-*n-propyl*-5α-*oestran*-3-*one* (6).—The 2α-allyloestranone was hydrogenated and acetylated, as for the 4α-isomer (below), to give 17β-*acetoxy*-2α-*n-propyloestranone*, m.p. 111.5—113.5° (from ether–hexane) (Found: C, 76.7; H, 10.2. $C_{23}H_{36}O_3$ requires C, 76.6; H, 10.1%), $\nu_{max.}$ (KBr) 1 735 and 1 713 cm^{-1}.

2α-*n-Propyl*-5α-*cholestan*-3-*one* (9).—Cholestanone [28] (5 g), 2,2-dimethoxypropane (4.75 ml), allyl alcohol (2.1 ml), and toluene-*p*-sulphonic acid in toluene (60 ml) were heated under a fractionating column (a spinning band column gave the best results) rapidly at first and then more slowly (*ca.* 5 h) as the temperature at the still head approached the b.p. of toluene. It was sometimes necessary to add more toluene. The cooled solution was washed with sodium hydrogen carbonate solution, dried, and evaporated. T.l.c. of the residual oil showed four spots, two major close-running spots less polar than cholestanone, and two minor spots corresponding to cholestanone and the dimethyl acetal of cholestanone. After heating under reflux in methanolic sodium methoxide (250 ml, 5%) for 3 h the product showed that the more polar of the major products had been removed. A difficult crystallisation from methanol–ether gave a sample of 2α-*allyl*-5α-*cholestan*-3-*one*, m.p. 52—58° (Found: C, 84.5; H, 11.85. $C_{30}H_{50}O$ requires C, 84.45; H, 11.8%), $\nu_{max.}$ (KBr) 3 065, 1 710, and 1 638 cm^{-1}. Hydrogenation in ethyl acetate (100 ml) over palladium on carbon (1 g, 5%) took 8 min. Chromatography over alumina (400 g; Woelm basic; grade III), eluting with light petroleum (b.p. 60—80°), gave firstly 2,2-dimethoxycholestane (1.15 g), m.p. 80—82° (lit.,[29] 81—82, 82—83°), τ ($CDCl_3$) 6.80, 6.85 (each 3 H, s), and secondly 2α-n-propylcholestanone (1.8 g, 32%), m.p. 85.5—87° (from methanol–ether, by allowing the ether to evaporate) (Found: C, 83.9; H, 12.2. $C_{30}H_{52}O$ requires C, 84.0; H, 12.2%), $\nu_{max.}$ (KBr) 1 710 cm^{-1}, *m/e* 428 (4%), 413 (3), 386 (100, *m** 348), and 316 (14).

4α-*Allyl*-17β-*hydroxyoestran*-3-*one*.— 19-Nortestosterone (2 g) in dioxan–ether (40 ml; 1 : 1) was added to a vigorously stirred solution of lithium (0.4 g) in liquid ammonia (200 ml) in a dry ice–acetone bath. A solution of allyl bromide (20 ml) in ether (80 ml) was then added, the mixture allowed to boil under reflux for 2 h, and the ammonia allowed to evaporate over 48 h. The residue, in methylene dichloride, was washed with water, stirred with dilute hydrochloric acid overnight, washed with water, dried, and the solvent evaporated off. The residue was chromatographed on neutral alumina (activity II; 150 g). Elution with benzene–ether (85 : 15) gave 4α-*allyl*-17β-*hydroxyoestran*-3-*one* (13 g, 56%), m.p. 126—128° (from acetone–cyclohexane) (Found: C, 79.9; H, 10.25. $C_{21}H_{32}O_2$ requires C, 79.7; H, 10.2%), $\nu_{max.}$ (KBr) 3 070, 1 700, and 1 643 cm^{-1}, $\nu_{max.}$ (Nujol) 3 515 cm^{-1}.

17β-*Acetoxy*-4α-*n-propyl*-5α-*oestran*-3-*one* (12).—The allyl ketone above was hydrogenated in ethyl acetate solution over palladium on carbon and the product kept overnight in acetic anhydride–pyridine (1 : 1) at room temperature to give 17β-*acetoxy*-4α-*n-propyl*-5α-*oestran*-3-*one*, m.p. 113.5—116° (from ether–hexane) (Found: C, 76.4; H, 10.1%), $\nu_{max.}$ (KBr) 1 732 and 1 711 cm^{-1}.

Preparative Photolyses.—The general procedure used conventional Pyrex Hanovia cyclindrical vessels, a 125 W medium pressure lamp, a stream of nitrogen, and a water-bath at 27°.

(a) cis-4-*t-Butyl*-2-*n-propylcyclohexanone* (1). The ketone (1.19 g) in t-butyl alcohol (90 ml) was irradiated for 3 days. Column chromatography (100 g; silica R CC7), eluting with light petroleum (b.p. 60—80°)–benzene mixtures graded from 65 : 35 to pure benzene, and collecting fractions (30 ml) automatically gave (i) an unknown mixture of compounds (7 mg), (ii) another mixture of compounds (23 mg), (iii) (fractions 44—46) (123 mg) one of the cyclobutanols, called A, $\nu_{max.}$ 3 470 cm^{-1}, (iv) (fractions 47—53) (129 mg) the cyclobutanol A mixed with starting material, (v) (fractions 54—57) (27 mg) starting material, (vi) (fractions 61—70) (38 mg) a second cyclobutanol, called B, $\nu_{max.}$ 3 540 cm^{-1}, (vii) (fractions 71—75) a mixture of B with 4-t-butylcyclohexanone, (viii) (fractions 76—90) (42 mg) 4-t-butylcyclohexanone, (ix) fractions 95—100) (119 mg) a third cyclobutanol, called C, $\nu_{max.}$ 3 460–3 540 cm^{-1}, (x) (fractions 107—117) (117 mg) a fourth cyclobutanol called D, 4-*t-butyl*-8-*methylbicyclo*-[4.2.0]*octan*-1-*ol*, m.p. 50—56° (Found: C, 79.3; H, 12.5. $C_{13}H_{24}O$ requires C, 79.5; H, 12.3%), $\nu_{max.}$ (Nujol) 3 345 cm^{-1}, τ 0.09 (3 H, d, *J* 6 Hz, CHMe), 9.21 (9 H, s, Bu^t), 7.7—9.0 (m), and (xi) (fractions 118—135) (534 mg) largely a mixture of esters (4) and (5). G.l.c. (Perkin-Elmer F11 5 ft × 1/8 in; 5% LAC on CQ column; 100°) was used to check the purity of all these fractions and also to separate the esters. The order of elution from the g.l.c. column was: (i) a trace of unknown compound, (ii) the ester (5), $\nu_{max.}$ 1 733 cm^{-1}, τ 9.16 (9 H, s, CBu^t), 8.62 (9 H, s, OBu^t), and an envelope between 9.1 and 7.6 with a peak at 9.04, which was also the only photoproduct from irradiation of 4-t-butylcyclohexanone in t-butyl alcohol, (iii) a trace of an unknown compound, (iv) 4-t-butylcyclohexanone, (v) the ester (4), $\nu_{max.}$ 1 729 cm^{-1}, τ 9.14 (3 H, s, CBu^t), 8.61 (9 H, s, OBu^t), and an envelope between 7.6 and 9.1, *m/e* 255 (*M* − Me), 215, 214 (*M* − C_4H_8), 213 (*M* − C_4H_9), 199 (*M* − C_5H_{11}), and 197 (*M* − C_4H_9O), the formulation as (4) involving the long established [30] preference for Type I fragmentation towards the more substituted side of the ketone group, (vi) the cyclobutanol A, (vii) unchanged starting material, (viii) the cyclobutanols B and C, coincident by g.l.c., but separable by t.l.c., and (ix) the cyclobutanol D. All four cyclobutanols A—D gave *m/e* 196 (M^+, *ca.* 5%), 178 (*M* − H_2O, *ca.* 5), 163 (*M* − H_2O − Me, *ca.* 10%), 155 (*M* − C_3H_5, *ca.* 10), and 154 (*M* − C_3H_6, 100), with minor variations in the relative peak heights, *e.g.* 194 is very weak in D and 20% in B and 178 is very weak in C. T.l.c. [silica gel; light petroleum (b.p. 60—80°)–ethyl acetate (92 : 8)] gave approximate R_F values of: starting material (1) 0.40, cyclobutanol A 0.37, cyclobutanol B 0.29, ketone (3) 0.22, cyclobutanol C 0.18, and cyclobutanol D 0.13. The esters (4) and (5) were not detected on t.l.c.

(b) 17β-*Acetoxy*-2α-*n-propyloestran*-3-*one* (6). The ketone (99 mg) in t-butyl alcohol (45 ml) was irradiated for 43 h. T.l.c. (silica gel; CH_2Cl_2–EtOAc, 9 : 1) gave two bands but the first appeared to be of two compounds, one of which was starting material (12 mg), and the second appeared to be of at least four closely similar compounds. Repeated t.l.c. of this band gave two distinct fractions: (11 mg), $\nu_{max.}$ 3 470 and 1 722 cm^{-1} and (15 mg), $\nu_{max.}$ 3 450 and 1 733 cm^{-1}. They did not crystallise. Both gave mass spectra with weak bands at *m/e* 360 and 342 and a base peak at 318 and were accordingly formulated as the cyclobutanols (7).

(c) 2α-*n-Propylcholestan*-3-*one* (9). The ketone (0.5 g) in t-butyl alcohol (45 ml) was irradiated for 24 h. Preparative t.l.c. [silica gel; light petroleum (b.p. 60—80°)–EtOAc, 8 : 1] gave five fractions (detected on a narrow portion of the plate using molybdophosphoric acid spray and heating at 100°). The fastest (22 mg) was not identified; the second

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(87 mg) was starting material; the third (49 mg) was cholestanone; and the fourth (29 mg) was recrystallised to give a mixture of the (3′-methylcyclobutano[2,3]cholestan-3-ols) (10), m.p. 117—125° (from methanol–ether) (Found: C, 84.2; H, 12.1. Calc. for $C_{30}H_{52}O$: C, 84.0; H, 12.2%), $\nu_{max.}$ (Nujol) 3 380 cm^{-1}, *m/e* 428, 410, 386, and 316. The fifth band (23 mg) was a mixture, repeated t.l.c. of which gave more cyclobutanols, m.p. 70—105° (Found: C, 83.6; H, 11.9%) $\nu_{max.}$ 3 310 cm^{-1}, *m/e* 428 410, 386, and 316. A run taken to complete conversion (65 h) gave a 22% yield of mixed cyclobutanols.

(d) 17β-*Acetoxy*-4α-*n-propyloestran*-3-*one* (12). The ketone (0.09 g) in t-butyl alcohol (35 ml) was irradiated for 25 h. T.l.c. (silica gel; CH_2Cl_2–EtOAc, 9 : 1) gave three bands, the fastest (4 mg) was starting material, the second (14 mg) was 17β-acetoxyoestran-3-one (8), and the third (44 mg) was a mixture of the 17β-acetoxy-2′,3,3′,4-tetrahydro-2′-methylcyclobutano[3,4]oestran-3-ols (13) m.p. 143—151° (from aqueous methanol) (Found: C, 76.8; H, 10.3. Calc. for $C_{23}H_{36}O_3$: C, 76.6; H, 10.1%), $\nu_{max.}$ (Nujol) 3 680, 3 610, 3 410, and 1 718 cm^{-1}, *m/e* 360, 342, 318, and 300.

(e) 2-*Cyclohexylcyclohexanone* (14). The ketone was prepared by hydrogenation [31] of 2-cyclohexenylcyclohexanone,[32] and purified by careful distillation, column chromatography on silica gel eluting with ether–light petroleum (b.p. 60—80°) mixtures, and further fractional distillation. This was necessary in order to get reproducible results and g.l.c. traces free of small interfering peaks. The products of photolysis were not all separable but were identified by g.l.c. comparison with authentic samples. (i) *t-Butyl* 6-*cyclohexylhexanoate* (19) was prepared by heating the acid [33] (195 mg) under reflux in ether (5 ml) with thionyl chloride (0.8 ml) for 40 min, followed by heating the crude acid chloride under reflux with t-butyl alcohol (0.8 ml) and dimethylaniline (0.7 ml) for 90 min. The *ester* was molecularly distilled (100° at 0.2 Torr) (Found: C, 75.3; H, 11.6. $C_{16}H_{30}O_2$ requires C, 75.7; H, 11.9%), *m/e* 239 (M^+—15, 2%), 199 (15), 198 (8), 119, 117 (8), 69 (25), 57 (100), and 55 (40%), τ (CCl_4) 7.6—8.1 (2 H, m) and 8.2—9.2 (28 H, m, including a sharp singlet at 8.6). (ii) Cyclopentylcyclohexane was a possible Type I product. It was prepared by the literature method [34] but there was no peak in the g.l.c. trace of the photolysis mixture corresponding to this product. (iii) The aldehydes (18) were identified in the following ways. (a) Aqueous acid did not affect them under conditions in which both the t-butyl esters and the cyclobutanols were easily decomposed. (b) They were photo-unstable. (c) The photolysis mixture was treated with neopentyl glycol and a trace of acid. Four new peaks were detected at long retention times on g.l.c., two of which were identical with authentic samples of the neopentyl glycol acetals of (18), which had been synthesised by a method already described.[35] Another of the peaks had a retention time identical with that of the product from treating cyclohexylcyclohexanone with neopentyl glycol and acid, and the fourth peak was very small. The peaks identified as the acetals of (18) were not produced when the photolysis mixture was treated with acid in the absence of neopentyl glycol. (d) Furthermore, the pinacol acetals were prepared both from the photolysis mixture, and by synthesis using the same procedure [35] as that used for the neopentyl glycol acetals. Again, the g.l.c. properties of the two products were identical, but we did not characterise them fully. (iv) The cyclobutanols, *tricyclo*-[6.4.0.$0^{2,7}$]*dodecan*-1-*ols* (15), were photostable. A crude mixture of them could be obtained by photolysing (14) until it disappeared. This mixture was separated into fractions (A) and (B) by preparative g.l.c., but could be separated into two crystalline fractions (A1) and (A2) by liquid chromatography on a Waters Associates machine with a column 100 mm × 3/8 in (o.d.) packed with silica SLC-3, eluting with 25% chloroform in heptane at 1 ml min^{-1}. Fraction (A1) had $\nu_{max.}$ 3 350 cm^{-1}, τ (CCl_4) 7.8—8.9 (m, changing shape after shaking with D_2O). Fraction (A2) (Found: C, 79.7; H, 11.4. Calc. for $C_{12}H_{20}O$: C, 79.9; H, 11.2%) was obtained pure enough for combustion analysis; $\nu_{max.}$ 3 350 cm^{-1}, τ (CCl_4) 7.8—8.9; *m/e* 180 (M^+, 1%), 137 (3), 98 (100), 85 (60), and 83 (90). The sample of (B) was not completely free of (A), as shown by reinjection onto g.l.c., but the spectra of this material were similar to those of (A). 2-Cyclohex-1-enylcyclohexanone is known [36] to give high yields of a cyclobutanol on irradiation. Hydrogenation of this cyclobutanol gave a mixture of 10% of cyclohexylcyclohexanone (14) and 90% of a cyclobutanol (possibly a mixture) having a retention time on g.l.c. identical to that of (B). Brief treatment of the photolysis mixture with aqueous acid followed by g.l.c. analysis of the products showed that both (A) and (B) were destroyed by this procedure, as we expected. Although none of the cyclobutanols was fully characterised, we are confident that the peaks (A) and (B) on the g.l.c. trace are indeed cyclobutanols. They also bore an obvious resemblance in their spectra and g.l.c. behaviour to the cyclobutanols from the photolysis of (1).

(f) 4α-*Ethyl*-5α-*cholestan*-3-*one* (20). (i) The ketone [22] (100 mg) in t-butyl alcohol (45 ml) was irradiated for 34 h. The only substantial product [t.l.c., light petroleum (b.p. 60—80°)–benzene (1 : 1)], apart from starting material and a trace of cholestanone, and the slowest running of six spots was 3,3′,4β,4′-*tetrahydrocyclobutano*[3,4]-5α-*cholestan*-3-*ol* (21) (41 mg) m.p. 143—145° (from aqueous methanol) (Found: C, 84.05; H, 11.5. $C_{29}H_{50}O$ requires C, 84.0; H, 12.15%), $\nu_{max.}$ (KBr) 3 345 cm^{-1}, *m/e* 414, 399, 396, and 386. (ii) The ketone (100 mg) in cyclohexane (120 ml) was irradiated for 40 h. Only starting material could be detected. After replacing Pyrex with Vycor, the starting material disappeared after irradiation for 2 h. The i.r. spectrum of the product showed only C–H absorption, and the mass spectrum had peaks at *m/e* 552, 550, and 470. The latter corresponds to starting material minus carbon monoxide plus cyclohexane.

Quantitative Photolyses.—The general procedure was to use Pyrex tubes, either sealed *in vacuo* after four freeze–pump thaw cycles. For most runs these were strapped to the Hanovia (quartz) immersion well. The cooling water entered the apparatus at 26.5° and left it at 30°. For the oestranes, the solvent was evaporated off, the residue dissolved in tetrahydrofuran, and injected onto the g.l.c. column (5 ft × 1/8 in; 2% QF1 on CQ; *t* 220°). For the cholestanes, the solvent was evaporated, the residue dissolved in tetrahydrofuran (0.1 ml), dimethyl sulphoxide

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(0.05 ml), hexamethyl-disilazane (0.1 ml), and trimethylchlorosilane (0.05 ml), and kept at room temperature for 1 h, before g.l.c. analysis on the column used for the oestranes. These silylation conditions gave negligible silylation of the ketones and complete silylation of both cyclobutanol fractions [see (c) above]. Silylation was necessary because of extensive decomposition of the cyclobutanols on the column. For the 4-t-butyl-2-n-propylcyclohexanone and cyclohexylcyclohexanone photolyses, the solution was injected directly into the column [described under (a) above]. Response ratios were determined by making up mixtures of the photolysis products in approximately the proportions found in the photolysis and treating them by the appropriate procedure outlined above. Response ratios (moles/area) were: (11) : (10), 1.66 : 1; (12) : (8) : [(7) or (13)], 0.99 : 1.0 : 1.44; (2) : (1) : (4) : (3), 1.07 : 1.08 : 1.0 : 1.28; (15) : (16) : (18) : (19), 1.075 : 1.0 : 1.0 (assumed) : 0.685. Relative retention times on the columns were: (9) : (11) : (10). 1.25 : 1.0 : 0.49 and 0.37; (6) : (8) : (7), 1.43 : 1.0 : 0.75 and 0.66; (12) : (8) : (13), 1.31 : 1.0 : 0.7; (D) : (B) + (C) : (1) : (A) : (4) : (3) : n-$C_{16}H_{34}$ (see below) : (5), 2.94 : 2.28 : 1.79 : 1.50 : 1.22 : 1.0 : 0.54 : 0.39, (15B) : (15A) : (19) : (18) (two isomers) : (16) : (9), 24 : 20.7 : 13.6 : 12.1 and 10.4 : 0.8 : 0.4.

The quantum yield measurement was made by the method of Wagner and Hammond [17] using hexan-2-one in light petroleum as secondary actinometer, and assuming a value of 0.327 for the quantum yield of disappearance of this ketone.[12] The measurement of singlet quenching on the ketone (1) was performed in the merry-go-round apparatus, using freshly distilled piperylene as the quencher and n-hexadecane as an internal standard. A total of 37 measurements gave a least squares plot with a slope of 0.04 ± 0.02 and an intercept of 1.18 ± 0.01. Because of analytical difficulties we could not make a good measurement for the ketone (14). We can only estimate that the Type II products were being produced from the singlet and triplet states to about the same extent. The cyclobutanol : fragmentation ratio of 80 : 20 is not actually much affected by this uncertainty; even if the single state were responsible for as much as 90% of the direct reaction, which is very unlikely, the ratio for the triplet-state reaction would still only be 91 : 9.

For the calculation of cyclobutanol : fragmentation ratios in the triplet state, we define the following quantities; $f_s = \Phi_{sc}/(\Phi_{sc} + \Phi_{sf})$, $f_t = \Phi_{tc}/(\Phi_{tc} + \Phi_{tf})$, $f_{s+t} = (\Phi_{sc} + \Phi_{tc})/(\Phi_{sc} + \Phi_{sf} + \Phi_{tc} + \Phi_{tf})$, and $n_f = \Phi_{tf}/(\Phi_{sf} + \Phi_{tf})$, where Φ_{sc} is the quantum yield of cyclobutanol formation from the singlet state, Φ_{tc} is the quantum yield of cyclobutanol formation from the triplet state, Φ_{sf} is the quantum yield for fragmentation from the singlet state, and Φ_{tf} is the quantum yield of fragmentation from the triplet state. The quantities f_s and f_{s+t} are the readily measured ones (being, for example, 0.13 and 0.35, respectively in the case of *cis*-4-t-butyl-2-n-propylcyclohexanone) and n_f is the less easily measured fraction of fragmentation coming from the triplet state (*i.e.* 0.15 in the case of the same ketone). These quantities are related by equation (1)

$$f_t = \frac{f_{s+t} - f_s + f_s n_f (1 - f_{s+t})}{f_{s+t} - f_s + n_f (1 - f_{s+t})} \quad (1)$$

From equation (1), f_t was calculated to be 0.73 for ketone (1). It is also a property of equation (1) that if $f_{s+t} > f_s$ then $f_t > f_{s+t}$, as mentioned in the text.

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