The Photochemical Transformation of Phenyl Cyclohexyl Ketone into Acetophenone; an Unusual Double Type-II Cleavage†

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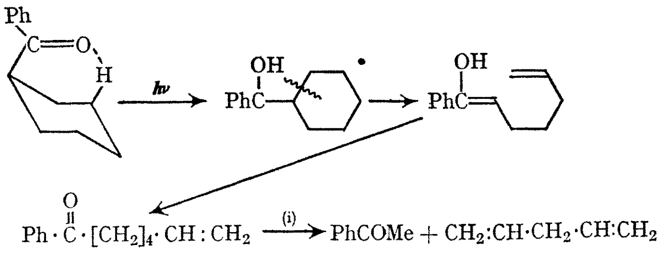
IRRADIATION of phenyl cyclohexyl ketone in propan-2-ol gives the diastereomeric acetophenone pinacols as the major product and the expected diastereomeric pinacols as a minor product. In benzene, acetophenone is the major product, together with small amounts of the pinacols of both ketones.

N.m.r. analysis permitted estimation of acetophenone and unchanged starting ketone present.‡ Carbon-14 labelling studies provided exact yields of the individual diastereomeric pincaols from both ketones§ (Table and Scheme). No 1,4-diene was found.¶ In view of its possible interactions as well as providing an allylic hydrogen source, this is not surprising.

Irradiation of phenyl cyclohexyl ketone[a]

Technique	Ketone (g.)	Solvent (c.c.)	Time (hr.)	Acetophenone (%)	Acetophenone pinacols (%)	Cyclohexyl phenyl ketone pinacols (%)	Starting ketone
N.m.r.	1·000	$\mathrm{Pr^iOH}$ (10)	48	(−)	(+)	N.A.	Fully reacted
N.m.r.	0·200	$\mathrm{Pr^iOH}$ (5)	18	(−)	(+)	N.A.	Present
N.m.r.	1·000	PhH (10)	96	23	R.A.	N.A.	25% present
N.m.r.	0·100	PhH (5)	36	24	N.A.	N.A.	26% present
^{14}C	0·100	$\mathrm{Pr^iOH}$ (5)	36		11·6[b]		
^{14}C	0·500	$\mathrm{Pr^iOH}$ (15)	24		17·9	7·6	
^{14}C	0·500	$\mathrm{Pr^iOH}$ (15)	96		51·3	15·2	
^{14}C	0·500	PhH (10)	48		6·6	11·9	
^{14}C	0·500	$\mathrm{Pr^iOH}$ [c] (10)	48		<0·5	<0·5	

[a] Pyrex reaction vessel, 3500 Å radiation, for further details see ref. 1. All yields based on starting ketone. N.A. signifies not available by this technique, see first footnote. Positive and negative signify presence and absence of the particular product. [b] Reverse isotope dilution with C^{14}-labelled acetophenone pinacols. [c] 50% aqueous, 0·2-N in KOH.



(i) Normal type-II Cleavage

A Fieser–Dreiding model of the starting ketone shows that the 3-cyclohexyl proton most closely approaches the carbonyl when both groups are axially situated; no other proton can approach the carbonyl as closely. The distance is almost exactly 1·5 times as large as the corresponding distance in the most favourable conformation of $\mathrm{Bu^nCOPh}$: this may represent an extreme case of type-II cleavage.

More than half the starting ketone may give acetophenone in $\mathrm{Pr^iOH}$, as indicated by a 51·3% total yield of diastereomeric acetophenone pinacols in one run. The absence of acetophenone itself in the $\mathrm{Pr^iOH}$ runs suggests that it is converted to pinacol as rapidly as it is formed. The yield of cyclohexyl phenyl ketone pinacols appears to be but little affected by the solvent.

The reaction is therefore considerably more complex that the simple reaction sequence presented. Essentially all of the intermediates are themselves capable of acting as hydrogen atom donors. The reaction pathway leading to the various pinacols *via* the conventional ketyls was not shown and may well interact with the sequence presented.

The ratio of (±)- to *meso*-acetophenone pinacol was between 1·05 and 1·10 for all quantitatively determined studies in $\mathrm{Pr^iOH}$, as found in an earlier analysis of the acetophenone system.[1] Since acetophenone was observed to yield its pinacol in alkaline media, the failure of the alkaline run (Table) indicates an involvement of base at some stage prior to acetophenone formation.

Attempts to photopinacolize phenyl cyclopropyl,[2] phenyl cyclobutyl,[3] and phenyl isobutyl[4] ketones have been un-

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† Closely related material has just appeared: A. Padwa and D. Eastman, *J. Amer. Chem. Soc.*, 1969, **91**, 462.

‡ The signals for the methyl groups of the acetophenone pinacols are masked by the cyclohexyl protons, which precludes satisfactory quantitative n.m.r. evaluation of the pinacols. Acetophenone yields were calculated by comparison, after normalization, of the C-CH_3 signal with the total aromatic area. Unchanged starting material was approximated by subtracting the acetophenone produced, from the separate, more deshielded, *o*-hydrogen phenyl ketone signals.

§ Phenyl cyclohexyl [^{14}C]ketone, was prepared by rhodium-catalyzed reduction of benzoic [^{14}C]acid, followed by conversion of the acid to the acid chloride ($SOCl_2$–benzene) which was used *in situ* with added $AlCl_3$ in a standard Friedel–Crafts reaction. The preparation and identification of the individual pinacols has been previously reported: *meso*- and (±)-acetophenone pinacol (ref. 1); *meso*- and (±)-1,2-dicyclohexyl-1,2-diphenylethanediol (J. H. Stocker, *J. Amer. Chem. Soc.*, 1966, **88**, 2878).

¶ G.l.c. ($AgNO_3$) (J. Shabatai, J. Herling, and E. Gil-Av, *J. Chromatog.*, 1963, **11**, 32). The column cleanly separated *cis*- and *trans*-penta-1,3-diene. No component with a shorter retention time than benzene itself was found.

successful. The last ketone is incapable of undergoing a type-II cleavage.

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[1] J. H. Stocker and D. H. Kern, *J. Org. Chem.*, 1966, **31**, 3755.
[2] D. C. Neckars, *Tetrahedron Letters*, 1965, 1889.
[3] D. C. Neckars, "Mechanistic Organic Photochemistry," Reinhold, New York, 1967, p. 173.
[4] N. D. Heindel, Ph.D. Thesis, University of Delaware, 1963, p. 111.