Tetrahedron Letters,Vol.27,No.39,pp 4675-4678,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

PHOTOCHEMISTRY OF LARGE RING 2-PHENYLCYCLOALKANONES AND 2,n-DIPHENYLCYCLOALKANONES

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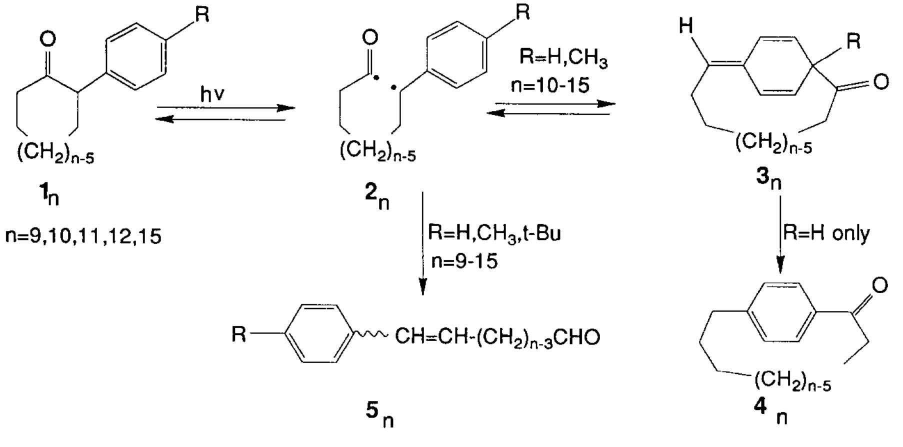
Summary. Photolysis of the title compounds (n=10,11,12,15) yields mainly cyclophanes. The product distribution depends on temperature and solvent.

Our recent kinetic studies of the biradicals generated by Type I cleavage of 2-phenylcycloalkanones[1] have yielded detailed information on the nature of intersystem crossing in biradicals and its relationship to biradical chain dynamics. We now report that the intermediate biradicals derived from ketones of ring sizes ⩾10 typically give rise to products which are unprecedented in the photochemistry of cyclic ketones.[2]

Scheme 1 summarizes the photochemistry of the large ring 2-phenylcycloalkanones.[3] (In the discussion below, R=H unless stated otherwise.)



Scheme 1

An Ar-purged 0.002M ketone solution was irradiated in quartz through a K_2CrO_4 filter with a 450W medium pressure Hg lamp. After removal of solvent at <50° the products were isolated by prep TLC. Irradiation of $\mathbf{1}_9$ in DMF gave exclusively $\mathbf{5}_9$. In DMF, formamide, or pyridine solvent, all other ketones $\mathbf{1}_n$ (n=10,11,12,15) produced 60-94% **4** plus 5-10% **5**.[3] However, irradiation of **1** in methanol or hexane solvent produced mainly **3** (by ^1H nmr[4]) plus some **4**. In all cases, **3** could be detected only in the crude photolyzate by nmr, since it converted to **4** on silica gel. At 280° in the GC, $\mathbf{3}_{12}$ decomposed to give 98% $\mathbf{1}_{12}$ and 2% $\mathbf{5}_{12}$. $\mathbf{3}_{12}$ was stable for 12 h at 25°C in hexane containing 1% AcOH, slowly converted to $\mathbf{4}_{12}$ over 12 h at 25° in neutral solution (methanol), and converted to $\mathbf{4}_{12}$ within minutes in basic media (hexane solution shaken with aqueous NaOH). In DMF solvent decarbonylation products are not formed at <15% photoconversion of $\mathbf{1}_{12}$, and constitute <2% of the products[5] at 85% conversion.

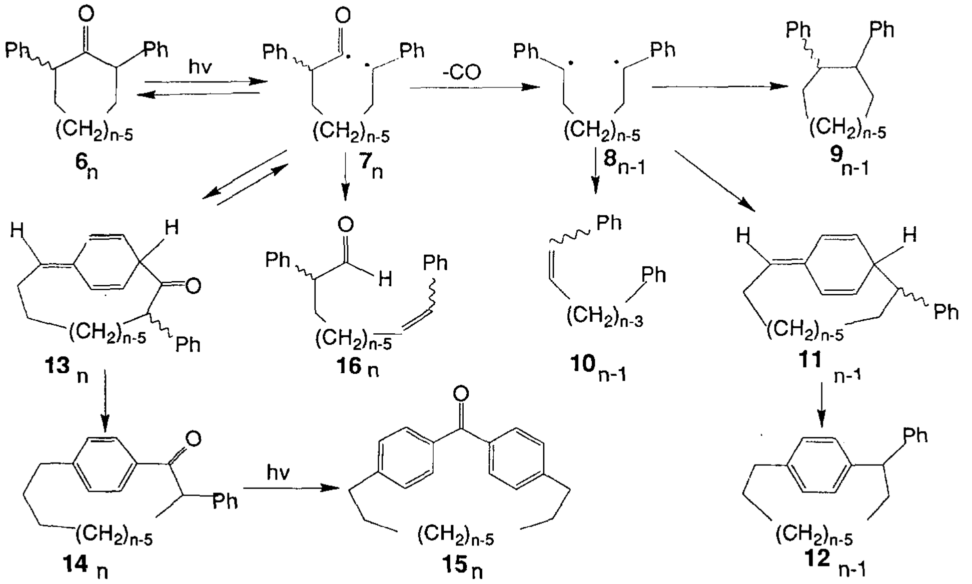
Irradiation of $\mathbf{1}_{12}$ ($R=CH_3$) in DMF gave $\mathbf{3}_{12}$ (R=Me) in >90% yield (by ^1H nmr[6]). This product was recovered unchanged after refluxing in hexane (68°) for 24 h, and decomposed in the GC to give >90% starting ketone, with no evidence of methyl shift to produce the cyclophane. Photolysis of $\mathbf{1}_{12}$ (R=t-Bu) in hexane solvent gave enals exclusively. An approximate deuterium isotope effect on the yield of $\mathbf{4}_{12}$ (R=H) was measured by irradiation of $\mathbf{1}_{12}$-d_5 (C_6D_5 group) and $\mathbf{1}_{12}$ under identical conditions using octadecane as an internal standard. The ratio of $\mathbf{4}_{12}$ to $\mathbf{4}_{12}$-d_5 was 1.7.

The photolysis products of 2,n-diphenylcycloalkanones (n=10,11,12,15) are shown in Scheme 2. Product yields are listed in Table 1.

Table 1. Photolysis products of 2,n-diphenylcycloalkanones $\mathbf{6}_n$.

n	Φ_{-K}[a]	solvent	T(°C)	Percent Yields **9-12**[b]	**14**	$\mathbf{6}_n$ c/t isomer[c]
n=10 cis	0.9	hexane	RT	37	<0.1	3
10 trans	0.9	hexane	RT	64	<0.1	4
11 cis	0.95	hexane	RT	74	<0.1	4
	--	DMF	-78	12	75	11
12 cis	0.8	hexane	RT	80	4	4
	--	hexane	-78	70	23	4
	--	DMF	RT	72	10	2
	--	DMF	-78	11	76	10
12 trans	0.85	hexane	RT	97	<0.1	2
15 cis	0.27	hexane	RT	48	<0.1	10
	--	DMF	-78	18	68	5
15 trans	0.27	hexane	RT	65	<0.1	6

a) In MeOH at 25°C, using $\mathbf{1}_6$ as an actinometer. See Ref. 2c.
b) Decarbonylation products **9**, **10**, **11**, **12**.
c) Cis/trans isomerization of original ketone $\mathbf{6}_n$.



Scheme 2

All isolated products had the correct molecular weight by GC/MS. **13** is postulated by analogy to Scheme 1, but was never detected. $\mathbf{15}_{12}$ was identified by comparison of its ^1H NMR spectrum and its MS fragmentation pattern (EI) to that of an authentic sample.[7] Irradiation of $\mathbf{6}_{12}$ or $\mathbf{6}_{10}$ at 25° in DMF produced ca. 1% $\mathbf{15}_{12}$ or $\mathbf{15}_{10}$, respectively. When $\mathbf{14}_{12}$ was isolated by prep TLC and irradiated for 30 m at 25° in DMF (85% conversion), the yield of $\mathbf{15}_{12}$ increased to 30%. GC/MS detected 15% of an unidentified isomer of $\mathbf{15}_{12}$, the remainder being polymer. Further irradiation decreased the yield of $\mathbf{15}_{12}$.

$\mathbf{9}_{n-1}$ and $\mathbf{11}_{n-1}$ (n=10,11,12,15) were all isolated by prep TLC and identified by 200 MHz ^1H NMR. In $CDCl_3$ the 5.2-6.8 ppm region of **11** exhibited a 5H pattern very similar to **3**, a ring methine in the region 3.1-3.4, and the benzylic methine at 2.8 (dd). **9** showed phenyl peaks ($CDCl_3$) at 7.15(6H), 6.8 (4H), and two methines at 2.9-3.1. Trans-$\mathbf{10}_9$ was isolated by prep TLC and showed a CH_2 triplet at 2.6 ppm and two olefinic protons at 6.25 (m) and 6.40 (d,J=18 Hz). $\mathbf{10}_{10}$ was also detected in the product mixture by its olefinic NMR pattern, but was not isolated. Trans-$\mathbf{16}_{15}$ was partially separated by prep TLC, and showed an aldehyde proton at 9.7 ppm (d,J=3 Hz) and an olefinic pattern at 6.15-6.45 ppm identical to $\mathbf{10}_9$. The aldehyde proton of $\mathbf{16}_{10}$ was also detected in the product mixture from $\mathbf{6}_{10}$ but the enal was not isolated.

Small yields of para coupling products analogous to 3 and **13** have been observed for cumyl radical pairs[8] and phenylacetyl-benzyl pairs.[9] In our case, 3 and **14** can be made the dominant products. This dramatic effect is unique to triplet-derived biradicals. Whether it arises from a geometrical constraint on intersystem crossing or from the subsequent singlet chemistry is a question currently under investigation.

Acknowledgement. The authors are grateful to Prof. Heinz Staab and Dr. Reinhold Alt for samples of **15**. CED thanks the National Science Foundation (CHE-84-21140) for support. NJT thanks the National Science Foundation and Department of Energy for support.

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4. ^{1}H 200 MHz nmr spectrum of 3_{12} (R=H) (δ, ppm, $CDCl_3$): 6.72 (d,1H), 6.36 (d,1H), 5.78 (m,1H), 5.66 (m,1H), 5.41 (m,1H), 3.96 (m,1H), 2.74 (m,1H), 1.1-2.6 (m,19H).

5. Identified by nmr as phenylcycloalkanone and unsubstituted cyclophane, derived by a formal decarbonylation of **2**.

6. ^{1}H 300 MHz nmr spectrum of 3_{12} (R=CH_3) (δ, ppm, $CDCl_3$): 6.66 (dd,1H), 6.30 (dd,1H), 5.45 (m,3H), 2.86 (m,1H), 2.4 (m,1H), 2.10 (m,2H), 1.1-1.72 (m,19H).

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(Received in USA 17 June 1986)