Tetrahedron Letters,Vol.25,No.26,pp 2801-2804,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

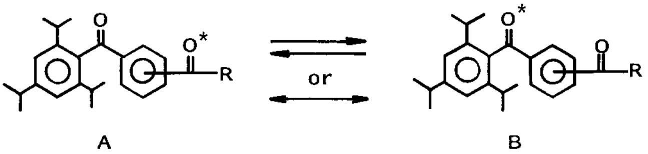
PHOTOREDUCTION OF 2,4,6-TRIISOPROPYLBENZOPHENONES WITH S-BUTYLAMINE[1]

Yoshikatsu Ito,* Nobuhiro Kawatsuki, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

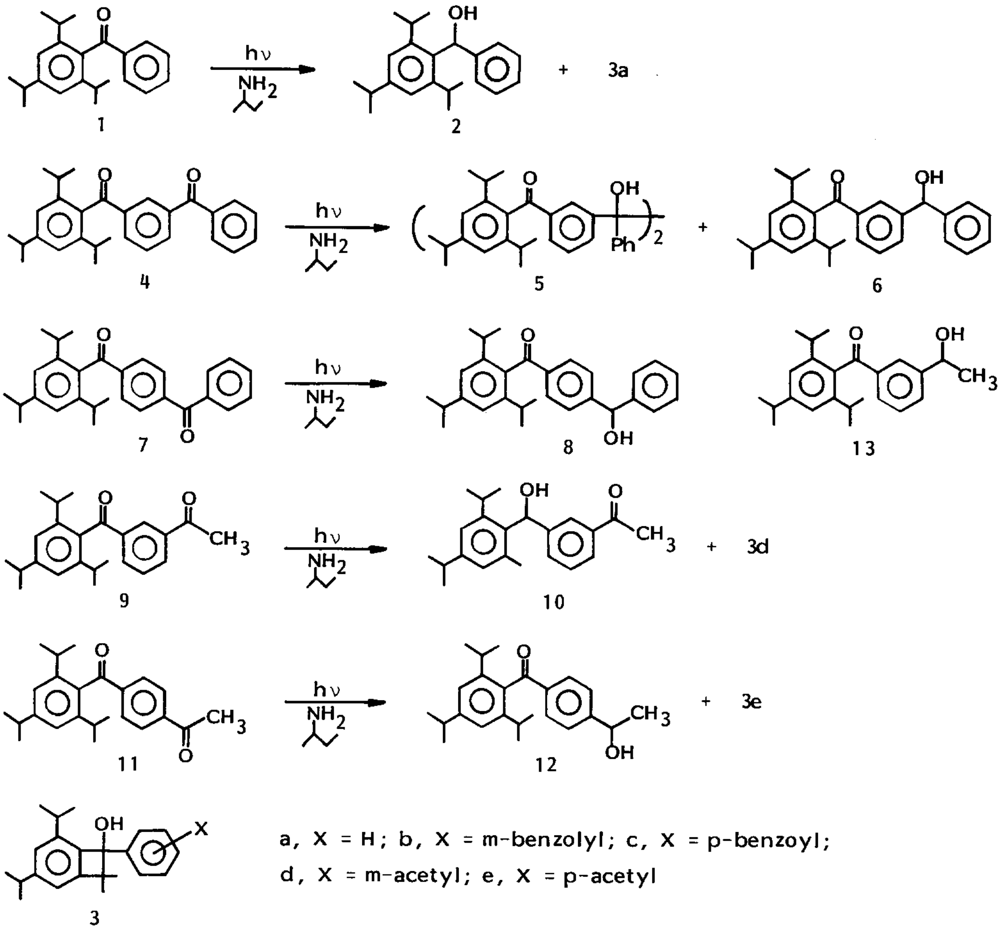
Summary: Photoreduction products and quenching rates by s-butylamine of triplets of the title ketones 1, 4, 7, 9, and 11 indicate that the electronic excitation in 9 in completely shifted toward the hindered carbonyl group rather than the acetyl carbonyl, while that in 11 is distributed over both of the carbonyl groups in a molecule.

It is a fundamental problem to see whether the n,π* excitation in aromatic diketones can be described as an intramolecular energy migration or a resonance between A and B. We have shown in the previous paper, mainly based on the results of spectroscopic and triplet lifetime measurements, that the energy migration is the case for the meta-substituted diketones (R = Ph or 2,4,6-triisopropylphenyl) and the resonance is the case for the para-substituted ones (R = Ph or 2,4,6-triisopropylphenyl).[2] In order to confirm this difference we then studied the photoreduction of a series of 2,4,6-triisopropylbenzophenones 1, 4, 7, 9, and 11 with s-butylamine (BA).



Upon photolysis without BA these triisopropylbenzophenones produce quantitatively the corresponding benzocyclobutenols 3, as is already reported.[3] In the presence of the amine (0.5 - 1.0 M) photoreduction of the carbonyl group occurred (Table I). It can be seen that 1 and 9, where the hindered carbonyls are reduced, and the para-substituted diketones (7 and 11) give products of a hydrol type and that the meta-substituted diketone (4) and benzophenone,[4a] where the unhindered carbonyls are reduced, give products of a pinacol type as major products.[5]

Table I demonstrates that only one of the two carbonyl groups in these diketone molecules was selectively reduced. It appears natural from steric hindrance that the reduction of 4 and 7 occurred at the unhindered carbonyl group in each case. It is, however, noticeable that 9 underwent photoreduction only at the hindered carbonyl group and, in sharp contrast, 11 at the acetyl group. In the case of 9 almost all fraction of the excitation must be present on the hindered carbonyl group, as is expected from the intramolecular energy migration: the triplet energy of acetophenone (74.1 kcal/mol) is much higher than that of 1 (69.1 kcal/mol[2]). On the other hand, considering the experimental fact that the acetyl group of 11 was selectively reduced and that its k_q was much larger than k_q values of 1 and 9 but comparable to those of 4 and 7 (vide infra), the excitation energy is probably distributed over both of the carbonyl groups in the case of 11.



a, X = H; b, X = m-benzolyl; c, X = p-benzoyl;
d, X = m-acetyl; e, X = p-acetyl

Quantum yields of 3 as a function of BA concentration (0.005 - 1 M) were measured in benzene and acetonitrile. From slope of a linear[6] plot of $\Phi°/\Phi$ vs. [BA], the value of $k_q\tau$ was obtained according to eq (1), where $\Phi°$ is the quantum yield for the benzocyclobutenols 3 in the absence of BA, k_q is the rate constant for ketone triplet quenching by the amine BA and τ (= $1/(k_d + k_r)$) is the triplet lifetime of the ketones. Since τ is available from usual diene quenching experiments,[7] k_q can be calculated (Table II). The k_q value for 4 and 7 was nearly an order of magnitude larger than that for 1 and 9 and that for 11 was intermediate of them.[8] Thus it seems that in the case of 9 the electronic excitation is localized at the hindered carbonyl group and that in the cases of 4, 7 and 11 the excitation is delocalized over both of the carbonyl groups in the molecule.

In summary, the present results relating to the meta- and para-substituted diketones 9 and 11 are consistent with the representations $A \rightleftarrows B$ and $A \leftrightarrow B$, respectively.

Table I. Quantum Yields for Reduction Products and Benzocyclobutenols in the Presence of s-Butylamine (BA)[a]

starting ketone	solvent	concn. of BA, M	quantum yields[b] hindered C=O redn.	unhindered C=O redn.	benzocyclobutenol
1	C_6H_6	1.0	**2** (0.03)	-	**3a** (0.11)
	MeCN	1.0	**2** (0.14)	-	**3a** (0.05)
4	C_6H_6	0.5	nd	**5** (0.20), **6** (0.03)	nd
	MeCN	0.5	nd	**5** (0.31), **6** (0.09)	nd
7	C_6H_6	0.5	nd	**8** (0.76)	nd
	MeCN	0.5	nd	**8** (0.77)	nd
9	C_6H_6	0.5	**10** (trace)	nd[c]	**3d** (0.043)
	MeCN	0.5	**10** (0.019)	nd[c]	**3d** (0.017)
11	C_6H_6	0.5	nd	**12** (0.004)	**3e** (0.013)
	MeCN	0.5	nd	**12** (0.003)	**3e** (0.010)

[a] A degassed solution of 0.05 M in the starting ketone was irradiated at 313 nm at 25 °C to conversion < 5%. Products other than listed in Table I were negligible by HPLC.

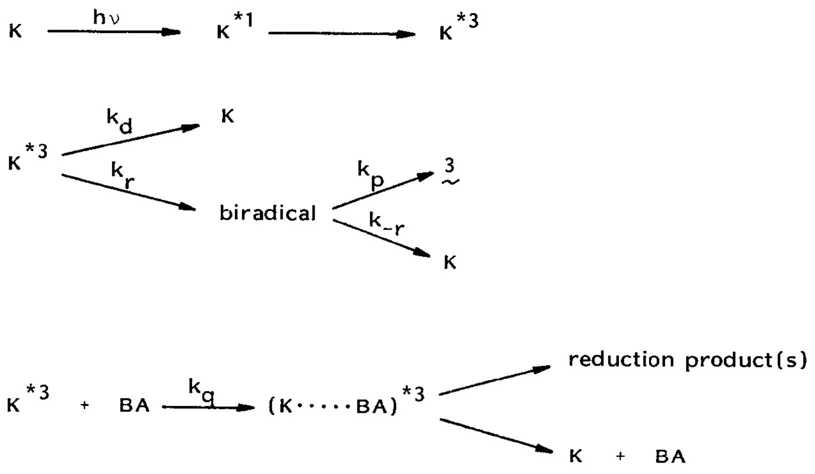
[b] The abbreviation nd denotes that products were not detected even in a preparative run.

[c] The absence of **13** was confirmed by preparation of an authentic sample of **13** by $LiAlH(O\text{-}t\text{-}Bu)_3$ reduction of **9**.

Table II. Quenching Constant ($k_q\tau$) and Quenching Rate (k_q) by s-Butylamine

ketone	$k_q\tau$, M^{-1}		τ in benzene, ns	k_q in benzene, M^{-1} s^{-1}
	C_6H_6	MeCN		
1	5.2	12.6	90[a]	5.8×10^7
4	49.6	51.1	114[a]	4.4×10^8
7	45.2	59.7	91[a]	5.0×10^8
9	9.9	16.3	127	7.6×10^7
11	25.1	26.3	114	2.2×10^8

[a] Reference 2.



$$\Phi^{o}/\Phi = 1 + k_q\tau[BA] \qquad (1)$$

Acknowledgment. We are indebted to the Ministry of Education, Science and Culture of Japan for a financial aid under the special research project on utilization of solar energy.

References and Notes

(1) Photoinduced reaction, part 156.
(2) Ito, Y.; Kawatsuki, N.; Matsuura, T. Submitted for publication.
(3) Ito, Y.; Giri, B. P.; Nakasuji, M.; Hagiwara, T.; Matsuura, T. J. Am. Chem. Soc. 1983, 105, 1117.
(4) (a) Cohen, S. G.; Chao, H. M. J. Am. Chem. Soc. 1968, 90, 165. (b) Cohen, S. G.; Stein, N. M. Ibid. 1971, 93, 6542.
(5) We have found that m-benzoylbenzophenone is photoreduced to a pinacol type (a 1 : 1 mixture of dl and meso isomer, 55 % isolation yield) and that p-benzoylbenzophenone to a hydrol type (68 % isolation yield).
(6) Thus the variation of the $k_p/(k_p + k_{-r})$ value with the amine concentration is not important, as is expected from the previously described effect of pyridine.[7]
(7) Ito, Y.; Nishimura, H.; Umehara, Y.; Yamada, Y.; Tone, M.; Matsuura, T. J. Am. Chem. Soc. 1983, 105, 1590.
(8) Cohen estimated the k_q value for benzophenone as $2.3 \times 10^8\ M^{-1}s^{-1}$ in benzene.[4b]

(Received in Japan 28 February 1984)