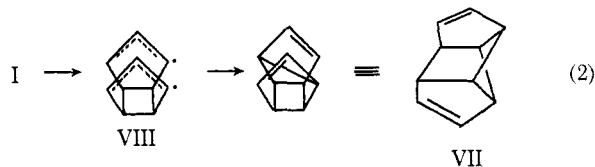


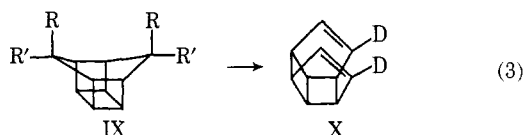
Hypostrophene sublimes readily under reduced pressure at room temperature as colorless plates; the nmr spectrum (CDCl_3) of the material at room temperature consists of two singlet absorptions at τ 3.9 (4 H) and 6.8 (6 H).

The nmr spectrum of hypostrophene indicates that the degenerate rearrangements shown in eq 1, if they are occurring at all, must be slow with respect to the nmr time scale. Unfortunately, attempts to demonstrate the degenerate isomerization by having the nmr absorptions coalesce upon raising the temperature were thwarted due to the inception of a nondegenerate irreversible rearrangement of I leading to an isomeric compound having the proposed structure VII [nmr (CDCl_3) τ 3.7 (bs, 2 H), 4.3 (bs, 2 H), 7.0 (bs, 2 H), 7.4 (bs, 2 H), and 8.0 (bs, 2 H)]. The appearance of VII sets in at about 80° , at which point the nmr absorptions of hypostrophene remain as two relatively sharp singlets, and, although these absorptions show signs of broadening at temperatures near 100° , the results are inconclusive due to the rapid rearrangement to the isomer VII. It is of interest to note that the conversion of I to VII is "forbidden" by any concerted mechanism⁶ and presumably proceeds (eq 2) *via* the intermediate diradical VIII.



Despite the inability to obtain a definitive answer to the question of possible degenerate rearrangements occurring in hypostrophene by the simple technique of coalescence of nmr absorption bands, recourse to specific deuterium labeling experiments was successful.

Reduction of the caged diketone IV with LiAlD_4 afforded the dideuteriodiol IX ($\text{R} = \text{OH}$; $\text{R}' = \text{D}$), which was converted to the corresponding dideuterio dibromide derivative (IX, $\text{R} = \text{D}$; $\text{R}' = \text{Br}$) in the manner indicated earlier. The nmr spectra of the dideuteriodiol and dibromide were similar to the corresponding perhydro compounds except for the lack of absorptions of relative area two at τ 6.15 and 5.4,



respectively, indicating that the deuterium atoms are at the positions shown in IX, as would be expected from their method of synthesis. However, dehalogenation of the dideuterio dibromide with sodium at 50° produced dideuteriohypostrophene in which the ratio of olefinic to saturated protons was found to be 1:1.5 rather than the 1:3 ratio to be expected from the synthetic conversion given in eq 3. The observed ratio of 1:1.5 is most readily explained by a mechanism involving initial formation of the specific dideuteriohypostrophene X followed by the extensive Cope type rearrangements as shown in eq 1.

(6) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

Dehalogenation of the dideuterio dibromide at -40° with sodium naphthylide in dimethyl ether⁷ and maintenance of the temperature at -40° during subsequent separation steps afforded dideuteriohypostrophene in high yield. The nmr spectrum of this product at -50° possessed an olefinic to saturated proton ratio of 1:3, the expected ratio were no rearrangement occurring. Upon warming to 0° , the intensity of the olefinic peak began to increase while that associated with the saturated protons decreased. At 35° , the ratio was observed to be 1:1.5 and showed no further change with time. This ratio is that to be expected on a time-averaged basis were rearrangement occurring.

This latter result demonstrates that the hypostrophene molecule continually undergoes the sequence of degenerate Cope rearrangements outlined in eq 1. Further chemistry pertaining to the hypostrophene molecule is being studied and will be reported at a later date.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, for financial assistance.

(7) Vicinal dihalides have been dehalogenated with sodium naphthylide [C. G. Scouten, *et al.*, *Chem. Commun.*, 78 (1969)]. The reaction of the dibromide with sodium naphthylide in dimethyl ether at -40° (formally a 1,4 elimination) was extremely rapid and appeared to be complete in approximately 15 sec.

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γ - vs. δ -Hydrogen Abstraction in the Photochemistry of β -Alkoxy Ketones. An Overlooked Reaction of Hydroxy Biradicals

Sir:

Two recent reports^{1,2} on the photochemistry of β -alkoxy ketones of structure 1 confirm an earlier report³ that very little Norrish type II photoelimination or cyclobutanol formation occurs. Instead 1 undergoes tetrahydrofuranol formation and elimination of alcohol. These reports all imply that rates of δ -hydrogen abstraction greatly surpass rates of γ -hydrogen abstraction in the excited states of 1. We report here results which indicate that such a conclusion is incorrect and that γ -hydrogen abstraction in ketones of structure 1 must lead to elimination of alcohol instead of to the normal type II products.⁴

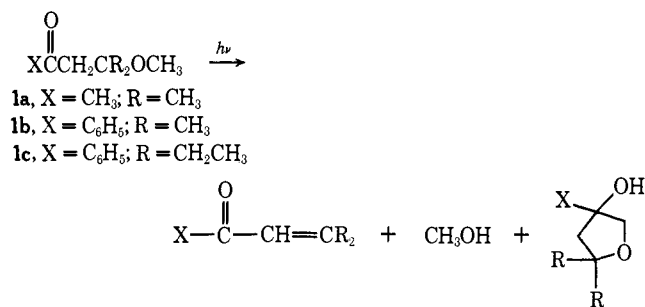
We have studied the photochemistry of β -ethoxypropionophenone (2) and δ -methoxyvalerophenone (3), both of which possess a methylene bonded to oxygen at the δ position relative to the carbonyl. In benzene or *tert*-butyl alcohol, 3130-Å irradiation of 3 yields acetophenone, two cyclobutanols, and two cyclopentanols, the quantum yields for which are listed in Table I. Each cyclic product was collected and identified by its

(1) P. Yates and J. M. Pal, *Chem. Commun.*, 553 (1970).

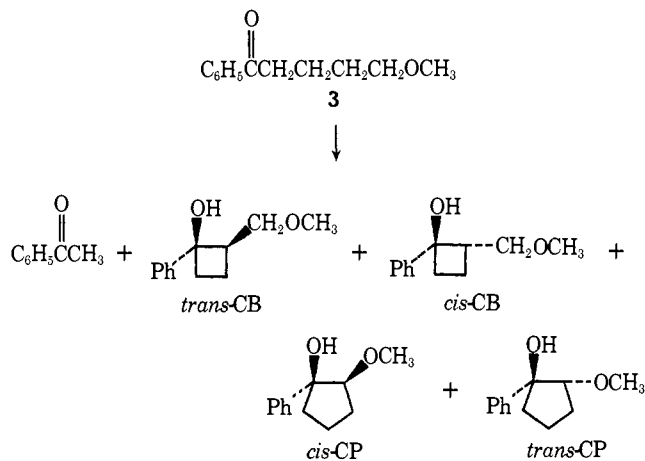
(2) L. M. Stephenson and J. L. Parlett, *J. Org. Chem.*, **36**, 1093 (1971).

(3) D. J. Coyle, R. V. Peterson, and J. Heicklen, *J. Amer. Chem. Soc.*, **86**, 3850 (1964).

(4) For an earlier such suggestion which even the present authors temporarily forgot about, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 108 (1968).



ir, nmr, and mass spectra, which in the case of the two cyclopentanols were identical with spectra of the unambiguously synthesized compounds.



2,5-Dimethyl-2,4-hexadiene quenches all five products from 3 equally. A Stern-Volmer plot in benzene is linear with a slope $k_q\tau$ of $90 M^{-1}$, from which we estimate $1/\tau$ to equal $5.6 \times 10^7 \text{ sec}^{-1}$.⁵ Since the

Table I. Quantum Yields for Product Formation and Ketone Disappearance for δ -Methoxyvalerophenone^a

Measurement	Benzene	<i>tert</i> -BuOH
-Ketone	0.47	0.56
PhCOCH ₃	0.33	0.37
<i>cis</i> -CP	0.019	0.015
<i>trans</i> -CP	0.015	0.085
<i>trans</i> -CB	0.10	0.06
<i>cis</i> -CB	<0.002 ^b	0.03

^a 3130-Å irradiation of 0.10 M ketone solution; products listed in order of retention times on a glpc column packed with 4% QF-1 and 1% Carbowax 20M. ^b None detected.

maximum quantum yield for type II products is 0.46, we further estimate $k_{\gamma\text{-H}} = 2.7 \times 10^7 \text{ sec}^{-1}$ and $k_{\delta\text{-H}} = 2.9 \times 10^7 \text{ sec}^{-1}$. The δ methoxy group deactivates the γ C-H bonds to one-fourth their reactivity in valerophenone⁶ and activates the δ C-H bonds by a factor of 5⁶ so that the normal 20:1 preference for γ : δ hydrogens^{7,8} is reduced to 1:1.

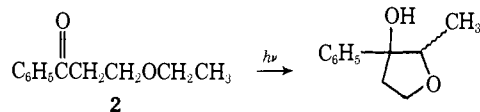
(5) *I.e.*, $k_q = 5 \times 10^9 M^{-1} \text{ sec}^{-1}$: G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, 315, 163 (1970).

(6) P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).

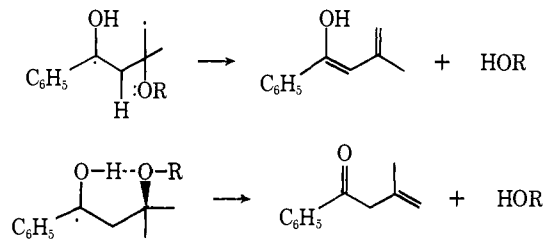
(7) P. J. Wagner, P. A. Kelso, and R. G. Zepp, manuscript in preparation.

(8) For the alkoxy radical analogy, see C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, 86, 1597 (1964).

Irradiation of 2 yields the expected¹⁻³ tetrahydrofuranols quantitatively. Quantum yields for appearance of the two cyclic alcohols are 0.50 in benzene and 0.32 in wet acetonitrile. Only traces of phenyl vinyl ketone could be detected by glpc analysis. Stern-Volmer quenching analysis yields a $k_q\tau$ value equal to $360 M^{-1}$ and thus a $1/\tau$ value of $1.4 \times 10^7 \text{ sec}^{-1}$. We assume that $1/\tau = k_{\delta\text{-H}}$ in 2. The δ C-H bonds of the β -ethoxy ketone are, if anything, slightly less reactive than those of the δ -methoxy ketone.



Application of these results to all that is known about substituent effects on intramolecular hydrogen abstractions⁶ indicates that the triplet-state rate of γ -hydrogen abstraction would equal the rate of δ -hydrogen abstraction in compounds 1a and 1b and would exceed it by a factor of ~ 10 in 1c. Consequently, the 3-alkoxy 1,4 biradicals produced from 1 cannot undergo much normal cyclization or elimination. Since the major photoreaction of 1a is elimination of methanol,³ while 2—which cannot form a 1,4 biradical—undergoes no such elimination, it is clear that the 1,4 biradical produced from 1 must primarily eliminate methanol.⁴ The preference for alcohol elimination over the normal reactions of a 1,4 biradical is very large; it is only with 1c, where γ -hydrogen abstraction must be the major triplet-state reaction, that any normal type II products are observed!



The alcohol elimination may be a four-centered reaction, which is at least 40 kcal exothermic and would yield the dienol of the α,β -unsaturated ketone. Alternatively, intramolecular hydrogen bonding in the biradical might favor an even more exothermic six-centered elimination yielding the β,γ -unsaturated ketone which might isomerize during analysis.⁹ Since hydroxy biradicals are very susceptible to hydrogen bonding,⁶ the latter mechanism might explain why alcohol elimination predominates over other biradical reactions.

Whatever the mechanism for alcohol elimination from these 1,4 biradicals, the behavior of compounds of type 1 illustrates once again how little we know about biradicals.

Acknowledgment. This work was supported by a National Science Foundation Grant.

(9) Professor Yates has kindly informed us that ketone 1c does in fact yield a mixture of α,β - and β,γ -unsaturated ketones.

(10) Alfred P. Sloan Fellow, 1968-1972.

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