# PHOTOCHEMISTRY OF δ-HALOKETONES. ANCHIMERIC

ASSISTANCE IN THE FORMATION OF β-HALODIRADICALS

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Because of the intense interest in β-haloradicals,[1] we have exploited the regiospecific γ-hydrogen abstraction in triplet ketones[2] by studying the photochemistry of three δ-halovalerophenones. We have already reported that the intermediate halodiradicals undergo β-cleavage of halogen atoms.[3] We now wish to report that the δ-halogens enhance the rate of triplet state γ-hydrogen abstraction which normally leads only to type II elimination and cyclization products.[4]
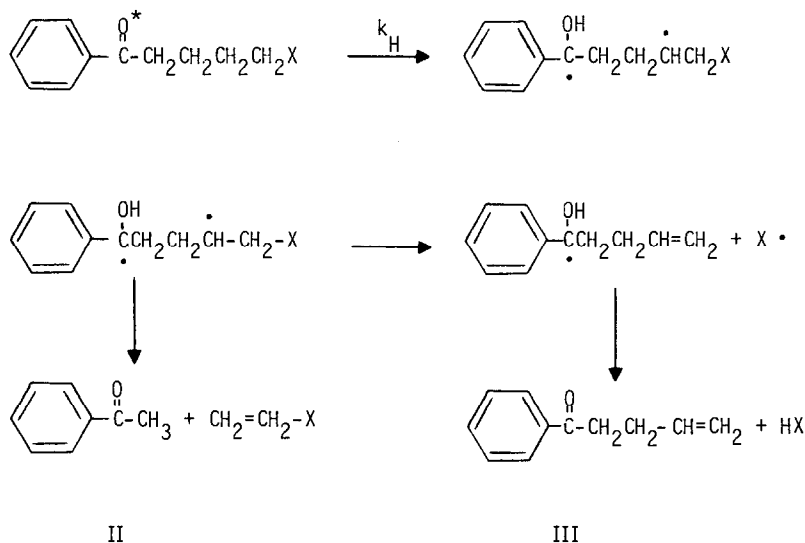
II   III

As already reported, the fraction of the diradical which loses X shows the expected increase in the order Cl < Br < I. Formation of both acetophenone(II) and 4-benzoyl-1-butene(III)

TABLE.   Photokinetics for $PhCOCH_2CH_2CH_2CH_2X$.[a]

X	Φ_{II}	Φ_{III}	$k_q\tau$, M^{-1}	k_H, 10^7 s^{-1}
H	0.43	–	40 ± 2	12.5
Cl	0.58	0.10	230 ± 10	2.2
Br	0.05	0.55	90 ± 3	5.6
I	< 0.002	0.43	30 ± 2	16.7

[a] in benzene containing 0.1 M pyridine

is quenched by typical triplet quenchers; the two products are quenched with equal efficiency.
Quantitative Stern-Volmer quenching plots are illustrated in Figure 1; the slopes equal $k_q\tau$,
where τ is the triplet lifetime and k_q is the bimolecular rate constant for quenching. The
value of k_q is known to equal 5-6 x 10^9 M^{-1} s^{-1} for exothermic energy transfer[5] and does not
vary significantly with ketone structures.[6] As indicated in the table, triplet lifetimes
decrease, and hence triplet decay rates increase, in the same order Cl < Br < I.

The apparent parallel between product ratios and triplet decay rates a priori could mean
that normal type II elimination and elimination of HX were competing triplet state reactions.
However, such is not in fact the case. In the first place, the percentage change in product
ratio is far greater than the percentage change in $1/\tau$. More importantly, we have shown inde-
pendently that alkyl halides do not react sufficiently rapidly with triplet ketones for any
direct interaction between triplet carbonyl and δ-X to compete with γ-hydrogen abstraction.
Ethyl iodide and butyl bromide (1 M) do not quench triplet butyrophenone (lifetime = 130 nsec[7]),
so that the rate constant for bimolecular interaction cannot exceed 10^6 M^{-1} s^{-1}. Likewise γ-
chloro and γ-bromobutyrophenone do not eliminate HX and merely undergo type II elimination.
Since γ-substituents interact with triplet carbonyls some 3-10 times faster than do δ-substitu-
ents,[8] we can safely conclude that the δ-halovalerophenone triplets undergo only γ-hydrogen
abstraction.

The triplet lifetimes of the ketones are therefore determined completely by k_H. The k_H
values in the table equal the $1/\tau$ values derived from the Stern-Volmer slopes, with
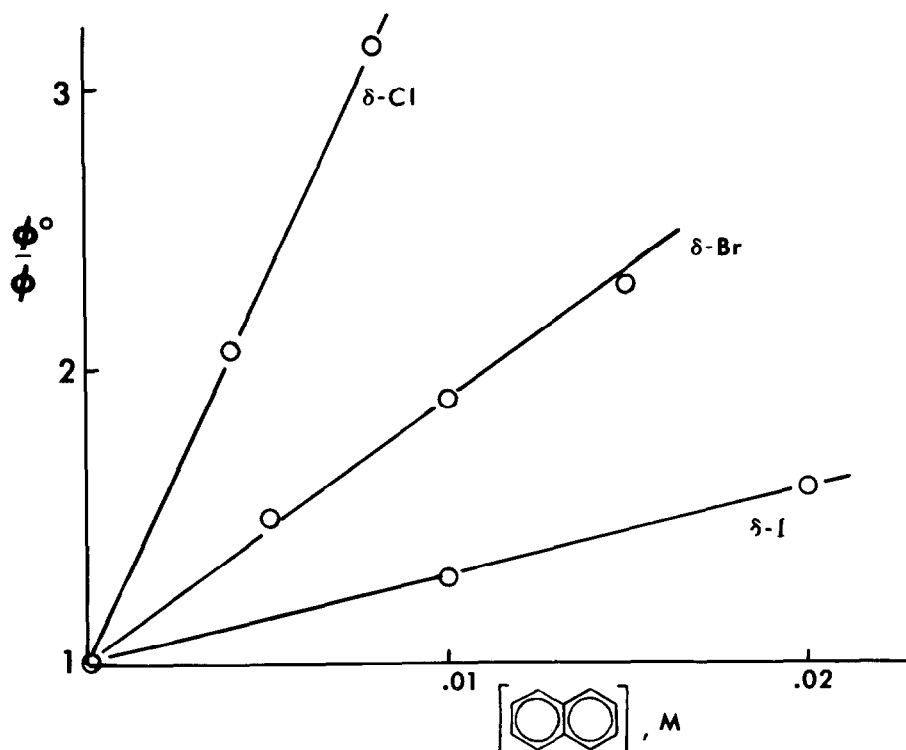
Stern-Volmer plots for quenching of δ-Halovalerophenones

$k_q = 5 \times 10^9$ M^{-1} s^{-1}. The substantial inductive effects of δ-substituents on k_H values have already been reported in detail.[7] A δ-Cl decreases k_H to 1/6 its value in valerophenone. The σ_I values for Br and I are slightly lower than that for Cl[9] so that the k_H value for V-I and V-Br should be, respectively, 45% and 10% greater than that for V-Cl if only inductive effects are important. The actual k_H values indicate that δ-bromo and iodo groups enhance rates of hydrogen abstraction by 230% and 530%, respectively (after correction for differing inductive effects). There is no reason to anticipate any heavy atom effects on k_H, since there is no spin inversion necessary in the conversion of triplet ketone to triplet diradical.[10,11] Therefore we must conclude that the rate enhancements represent another example of the anchimeric assistance which is known to substantially accelerate hydrogen abstraction by bromine atoms.[1] As usual, the n,π* triplet benzoyl group mimics the behavior of alkoxy radicals in displaying only minor[12] anchimeric assistance. The important difference is that exact enhancements can be measured; such was not possible in the alkoxy radical system studied.[12]

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