Tetrahedron Letters No.39, pp. 3791-3793, 1967. Pergamon Press Ltd. Printed in Great Britain.

A POSSIBLE STERIC EFFECT IN THE PHOTOOXIDATION OF SECONDARY ALCOHOLS BY BENZOPHENONE

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(Received in USA 1 April 1967)

The ability of the benzophenone triplet to abstract hydrogen atoms from substrates such as alcohols is well known (1), and recent papers have concentrated on comparison of ease of hydrogen abstraction in competition studies between two substrates. Walling and Gibian (2) have argued the validity of these studies and have shown that the α-hydrogen atoms from 2-propanol and 2-octanol are abstracted with about equal ease (reactivity 9.3 relative to toluene for the former and 9.6 for the latter). Cohen and Baumgarten (3) have demonstrated that the α-hydrogen atoms from 2-propanol and 2-butylamine are abstracted with equal ease (relative rate 1.00 and 1.06 ± 10%, respectively). Neckers and Schaap (4) have stated that the α-hydrogen atom of *cis*-4-*t*-butylcyclohexanol is abstracted with greater ease than that of the *trans*-isomer. In none of the above studies has any trend of hydrogen abstraction been established among a series of secondary alcohols. We have made such a study and noted a decided trend which is probably of steric origin.

Benzophenone (0.5-3.0 mmoles) was dissolved in a mixture of two pure alcohols (6 - 26 mmoles each) contained in an ampoule. The air in the ampoule was flushed with nitrogen and the ampoule sealed and irradiated for 12 to 30 hours by means of a Sylvania 400 watt (H33 - 1CD) bulb immersed in a constant temperature bath at 25 ± 0.1°C. Mole ratios of the two generated ketones were followed by GLC analysis (Carbowax 1000 and Carbowax 20 M columns) using predetermined calibration curves. The results of the ketone appearance competition studies are shown in Column 1 of Table I:

TABLE I

Competitive Hydrogen Abstraction

Substrate	Relative Reactivity[a]	Material Balance (%)
2-Propanol	1.00	
Cyclohexanol[b]	1.6 ±0.06	95
Cyclopentanol	1.3 ±0.04	94
2-Octanol	1.05 ±0.03	95
2-Heptanol	1.0 ±0.0	92
Methyl-*t*-butylcarbinol[b]	0.9 ±0.02	
3-Heptanol	0.67 ±0.02	96
Methylisobutylcarbinol[b]	0.39 ±0.01	
Methylneopentylcarbinol[b]	0.18 ±0.01	95,100
Diisobutylcarbinol[b]	0.074±0.001	85

[a] Experimental error is average deviation of 3 - 5 individual determinations. [b] Compared to 2-octanol rather than 2-propanol because of the nature of separation of alcohols and ketones on column.

At the suggestion of a referee we set out to show that any disappearance of alcohol did in fact result in formation of the corresponding ketone. Benzophenone (0.10 - 0.23 mmoles) was irradiated in the presence of an alcohol (0.13 - 0.39 mmoles) and an appropriate internal standard (chlorobenzene, *m*-dichlorobenzene, or *o*-dichlorobenzene) for about 25 hours in *t*-butyl alcohol as solvent. The reaction mixtures were then analyzed for remaining alcohol and ketone formed by means of GLC using appropriate calibration curves. The material balance based on amount of starting alcohol was then calculated, and these results are shown in Column 2 of Table I.

The material balance seems to be satisfactory within experimental error except for the case of diisobutylcarbinol. Assuming the rate ratio of tertiary hydrogen to carbinol α-hydrogen to be 1:9[2], one can visualize encroachment of a photochemical process involving the abstraction of tertiary hydrogens in the cases of diisobutylcarbinol and methylisobutylcarbinol which would lead to erroneous results. The rate ratios for diisobutylcarbinol and methylisobutylcarbinol are therefore open to suspicion despite the precision of analytical results.

The overall results nevertheless indicate the usual retardation of reaction associated with steric hindrance as chain-branching is increased. Moreover, judging from the small retardation of hydrogen abstraction of methyl-t-butylcarbinol (rel. reactivity = 0.9) as compared to methylneopentylcarbinol (r.r. = 0.18), the retardation is affected in the same way by branching as the retardation in the esterification of acids [Newman's Rule of Six (5)]. Although stereochemical requirements of the benzophenone triplet have been discussed and demonstrated previously (4,6), we believe that the data in this paper provide the most clear-cut demonstration of such requirements. The technique should be helpful in ascertaining the stereochemical requirements, and perhaps structural features, of photochemical active states of other molecules.

Acknowledgment

One of the authors (M. M.) is indebted to the Department of Health, Education and Welfare, U. S. Government, for an N.D.E.A. Fellowship. Both authors are indebted to the National Science Foundation for a grant in support of this work.

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