CHEMISTRY LETTERS, pp. 1261-1264, 1981.

PHOTOFRAGMENTATION REACTIONS OF THIOCARBONYL COMPOUNDS

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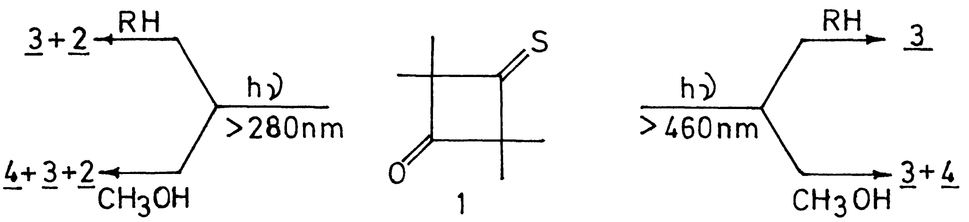
Preferential yield of ring expansion and rearrangement products through α-cleavage of tetramethyl-3-thio-1,3-cyclobutanedione (1) and 3-mercapto-2,2,4-trimethyl-3-pentenoic acid β-(thio lactone) (2) involving diradical and carbene has been observed upon photolysis of 1 and 2.

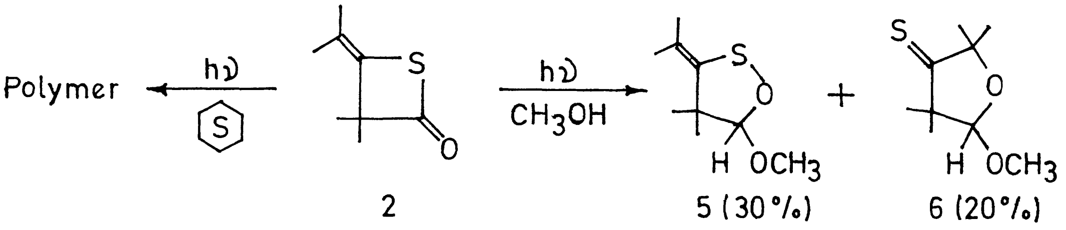
In order to explore the generality of the recently discovered Norrish Type I α-cleavage reactions of thiocarbonyl compounds[1] photochemistry of 1 and 2 were investigated[2]. Irradiation (> 460 nm, Corning filter CS-3.70; 450 W medium pressure mercury lamp) of 1 (0.04 M) in non-hydroxylic solvents (cyclohexane, benzene, diethyl ether) resulted in the formation of 3, a sulfur incorporation product (eq.1)[3]. Photoproduct 3 is believed to result from the sulfur incorporation of the intermediate diradical 7 or carbene 7a by the ground state thione. Though substantial evidence for this pathway is not provided such sulfur incorporation in other systems have been reported[4]. Similar irradiation of 1 in methanol gave a 1:1 adduct 4 along with 3[5]. Interestingly, excitation of the carbonyl absorption of 1 (> 280 nm, Pyrex filter; or >230 nm, quartz filter)[6] in the above solvents gave 2 along with 3 and 4. Neither of these irradiations gave evidence for the formation of dimethylketene or dimethylthioketene. These, if formed, are expected to be trapped in methanol and we did not find any such 1:1 adducts and in non-hydroxylic solvents these might dimerise but no spectral evidence for the formation of dimerisation products were seen. 2 is believed to be the result of α-cleavage from the localised $n\pi^*$ state of carbonyl chromophore whereas 3 and 4 are the results of such a process from the $n\pi^*$ state of thiocarbonyl chromophore (scheme 1).



(1)

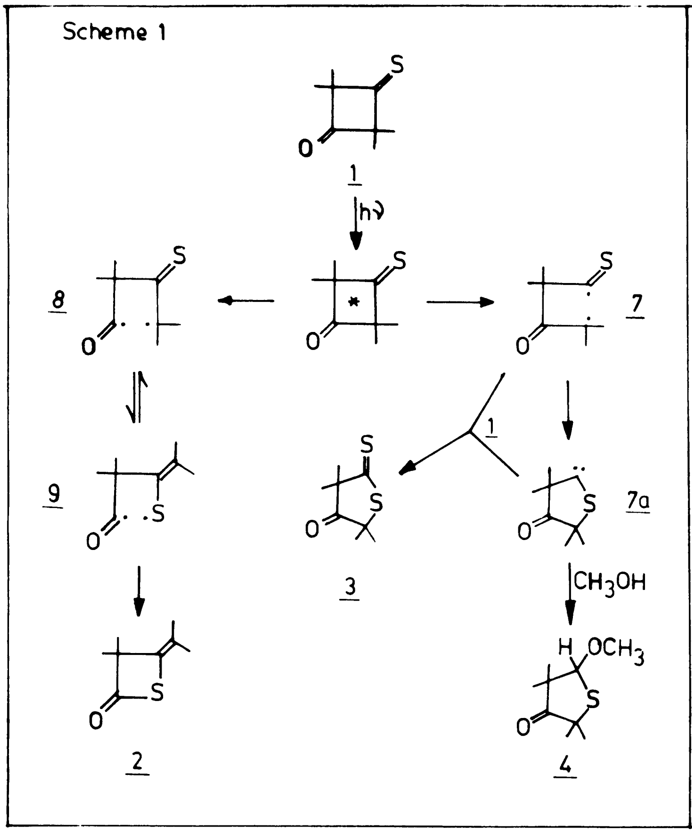
Solvent	Product yields (%)	(excitation >280 nm)	
	2	3	4
RH(Cyclohexane, Benzene, diethyl ether)	5	40	-
Methanol	8	30	15

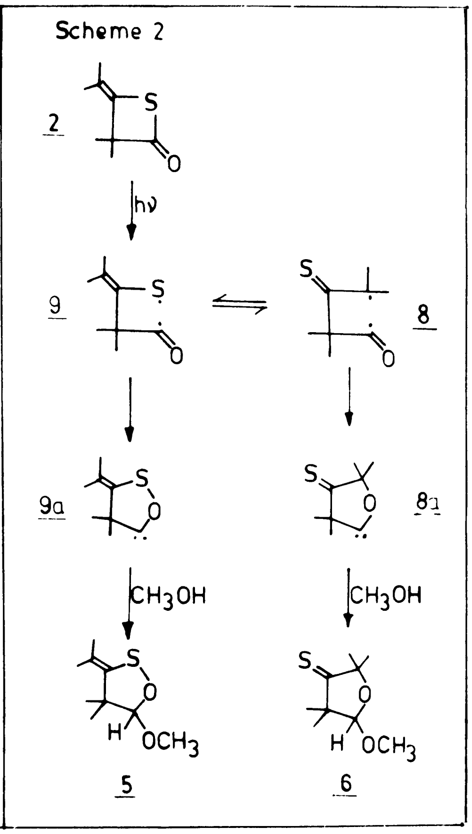
In an attempt to probe the behaviour of diradicals 8 and 9, generated independently, thiolactone (2) was excited (>280 nm, Pyrex filter) in hydrocarbon solvents and this resulted in slow polymerisation and no identifiable products were obtained[7]. Interestingly, irradiation of 2 (0.02 M) in methanol gave rise to 1:1 adducts 5 and 6 (eq.2)[8]. These adducts are expected to derive from carbenes as illustrated in Scheme 2.



(2)

Salient features of our results are the following: (a) Selectivity in the α-cleavage with respect to carbonyl and thiocarbonyl chromophores could be achieved by selective excitation of 1. (b) Diradicals 8 and 9 generated from 1 and 2 neither eliminate carbonmonoxide nor undergo cleavage to thioketene and ketene. This is in contrast to the behaviour of similar 1,4-diradicals derived from tetramethyl-1,3-cyclobutanedione and the corresponding β-lactone[9] but similar to those derived from the corresponding dithione and β-dithiolactone[1]. (c) Of the three diradicals (7-9) derived from 1, only 7 undergoes ring expansion. The formation of ring expansion product from 7 is particularly noteworthy, since the failure of similar 1,4-diradical from





tetramethyl-1,3-cyclobutanedione to undergo ring expansion is attributed to the poor nucleophilicity of the radical centre due to α-carbonyl group[10].

(d) While diradicals **8** and **9** generated from **1** failed to yield ring expansion products, those generated from **2** gave ring expansion products[11]. Interestingly, although the primary photochemical process of closely similar molecules viz. tetramethylcyclobutanedione, -thiodione and -dithione and the corresponding β-lactone, β-thiolactone and β-dithiolactone is the same, namely α-cleavage, the resultant diradicals exhibit widely varying behaviour.

Attempts are underway to understand the above features and to explore the mechanism of α-cleavage reactions of thiocarbonyl chromophore[12].

References

1. K. Muthuramu and V. Ramamurthy, J.C.S. Chem. Comm., 243 (1980).
K. Muthuramu and V. Ramamurthy, J. Org. Chem., **45**, 4532 (1980).
2. Absorption spectra of **1** is discussed in the following paper: K.N. Tantry, P.K. Basu, V. Ramamurthy, C.N.R. Rao, E.A. Seddon and J.C. Green, Tetrahedron Letters, 4787 (1979).

3. Spectral data for photoproduct 3:
PMR ($CDCl_3$): δ 1.41 (s, 6 H) and 1.67 (s, 6 H); CMR ($CDCl_3$): δ 27.8, 28.1, 61.2, 63.4, 216.5 and 242.9; IR (CCl_4): 1745 cm^{-1} (C=O stretching) and 1115 cm^{-1} (C=S stretching); UV (cyclohexane): λ_{max}225 nm ($\varepsilon \sim 2570$); 310 nm ($\varepsilon \sim 10,070$) and 478 ($\varepsilon \sim 20$); Mass Spec.(70 eV): M^+ ion at m/e 188.

4. E.H. Hoffmeister and D.S. Tarbell, Tetrahedron, 21, 35, 2857 and 2865 (1965).

5. Spectral data for photoproduct 4:
PMR (CCl_4): δ 1.18 (s, 3 H), 1.27 (s, 3 H), 1.42 (s, 6 H), 3.35 (s, 3 H) and 4.90 (s, 1 H); IR (neat): 1740 cm^{-1} (C=O stretching); Mass Spec. (70 eV) M^+ ion is located at m/e 188.

6. Irradiation above 280 nm, results in the excitation of both carbonyl and thiocarbonyl chromophores of 1. This results in the formation of 3 and 4, the products due to α-cleavage of thiocarbonyl chromophore.

7. β-thiolactone (2) possess electronic absorption bands at 328 nm ($\varepsilon \sim 42$); 258 nm ($\varepsilon \sim 2000$) and 226 nm ($\varepsilon \sim 4300$).

8. Spectral data for photoproducts 5 and 6

   5 PMR (CCl_4): δ 1.32 (s, 6 H), 1.83 (s, 3 H), 1.90 (s, 3 H), 3.47 (s, 3 H) and 4.60 (s, 1 H); IR (neat): 760 cm^{-1} (S-O stretching); Mass Spec. (70 eV): M^+ ion at m/e 188.

   6 PMR (CCl_4): δ 1.30 (s, 3 H), 1.33 (s, 3 H), 1.53 (s, 6 H), 3.30 (s, 3 H) and 4.73 (s, 1 H); IR (neat): 1150 cm^{-1} (C=S stretching) and 1090 cm^{-1} (C-O stretching); UV (cyclohexane): λ_{max} 260 nm (n,σ^*); 305 nm (π,π^*) and 500 nm (n,π^*).

9. N.J. Turro and T. Cole, Tetrahedron Letters, 3451 (1969).

10. D.R. Morton and N.J. Turro, Adv. Photochem, 9, 197 (1969). For an exception see: K. Kimura, M. Takamura, A. Kunai and Y. Odaira, J.C.S. Chem. Comm., 685 (1974).

11. This differential behaviour may have its origin on the spin states of these diradicals. Attempts are underway to ascertain this proposition.

12. Financial support by the Department of Science and Technology, Government of India, is gratefully acknowledged. K.M. thanks the University Grants Commission, New Delhi, for a senior research fellowship.

(Received July 14, 1981)