Tetrahedron Letters No. 20, pp 1709 - 1712, 1978. 0040-4039/78/0508-1709. $02.00/0.

PHOTOCHEMISTRY OF PHENYL ALKYL KETONES UNDER PRESSURE. REACTIONS OF 1,4-DIRADICALS.[1]

Robert C. Neuman, Jr.* and Charles T. Berge
Department of Chemistry
University of California
Riverside, California 92521

(Received in USA 21 February 1978; received in UK for publication 23 March 1978)

In a study of the effects of pressure on the thermolysis of a six-membered cyclic azo compound, pressure increased the yield of 1,2-diphenylcyclobutane compared to styrene (Fig. 1).[2] This is consistent with the sole intermediacy of a 1,4-diradical, but styrene formation from a possible concurrent concerted three-bond scission reaction could not be ruled out. Because 1,4-diradicals are intermediates in the photolysis of phenyl alkyl ketones,[3] we decided that pressure effects on the products of these diradicals might provide insight into the cyclic azo compound results.

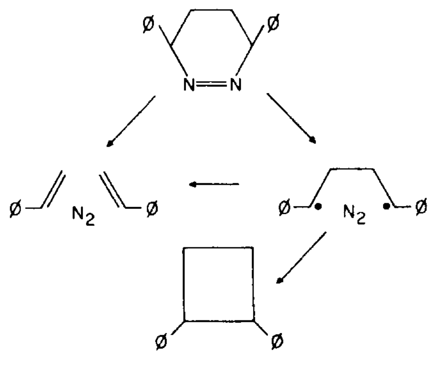

Fig 1

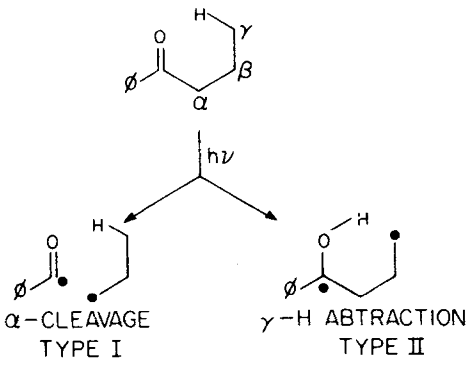

Fig 2

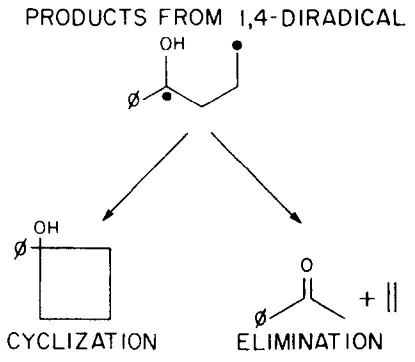

Fig. 3

The two primary photo-processes of phenyl alkyl ketones are α-cleavage and γ-hydrogen abstraction (Fig. 2).[3] The diradical can cyclize, undergo β-scission (Fig. 3), or reabstract the hydroxyl hydrogen to return to starting ketone (a process which we cannot observe). After α-cleavage, the geminate radical pair can recombine or disproportionate to give an olefin and benzaldehyde. Besides our interest in pressure effects on the chemistry of the 1,4-diradical, it seemed possible to us that pressure would favor γ-hydrogen abstraction over α-cleavage and we wished to test this prediction. Homolytic scission reactions such as α-cleavage are markedly inhibited by pressure due to a retardation of the rate of the scission reaction, an increase in rate of the reverse recombination reaction, or an increase in medium viscosity which retards separative diffusion of the radical pair.

Photolyses of butyrophenone (1), valerophenone (2) and α,α-dimethylvalerophenone (3) were carried out in deoxygenated hexane solutions (5×10^{-2}M) to 5-7% conversion.[5,6] Pressure increases the yield of cyclobutanol to elimination product for 1 and 2 (Fig. 4). The effect is comparable to that observed in the cyclic azo compound study (Fig. 5) and this suggests that a diradical intermediate is sufficient to account for the azo compound data.

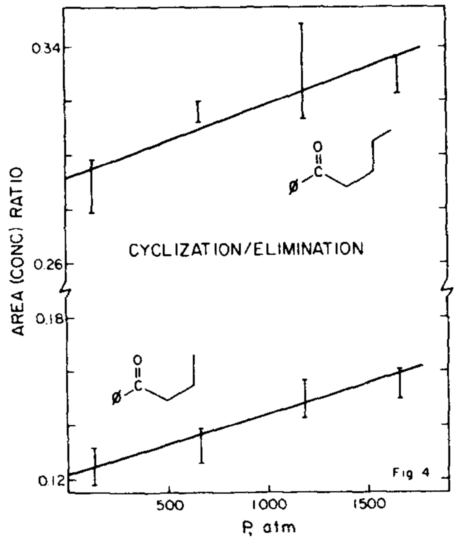

Fig 4

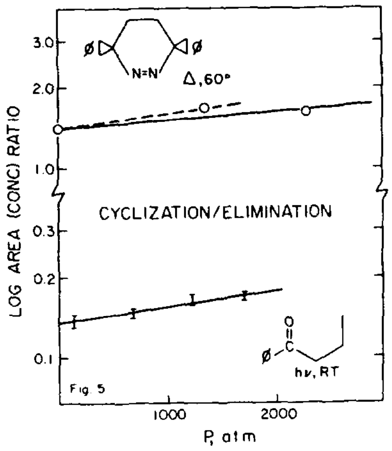

Fig 5

In each of these systems the pressure effect is small. The activation volume for cyclization is only about 1 to 2 cc/mole smaller than that for elimination. This is consistent with the shallow minimum that the diradical presumably occupies on the energy surface. The transition states from diradical to stable products are probably characterized by little bond making or breaking.

An unexpected result has been obtained for α,α-dimethylvalerophenone (3). In contrast with 1 and 2, the cyclization/elimination product ratio for 3 decreases with pressure (Fig. 6). A possible rationale for this follows. At atmospheric pressure the quantum yield for elimination from the 3 diradical is much less than those for 1 and 2.[5a] However, the cyclization quantum yields are all comparable.[5a] This has been interpreted in terms of unfavorable steric interactions in the 3 diradical between the gem-dimethyl pair and the vicinal phenyl and hydroxy substitutents in the conformation required for elimination.[5]

Pressure tends to favor sterically-hindered reactions[7] and we suggest that this phenomenon is responsible for the inverse trend in the cyclization/elimination ratio for 3. If the activation volumes for cyclization and elimination are relatively small, the perturbation due to this steric effect could be sufficient to decrease the elimination activation volume so that this process becomes more favorable under pressure compared to cyclization. α,α-Dimethylbutyrophenone should behave similarly to 3, but results for this system are not yet available.

The 1-phenylcyclobutanols from valerophenone (2) and α,α-dimethylvalerophenone (3) have *cis* and *trans* isomers. From 2, the *trans*/*cis* ratio is *ca* 83% and pressure insensitive. The same ratio from 3 is about 57% at atmospheric pressure and shows a slight pressure sensitivity decreasing to 53% at 1700 atm.

Ketone 3 is the only member of the three systems studied which undergoes competitive α-cleavage and γ-hydrogen abstraction (Fig. 2).[5] Our preliminary data suggest that pressure effectively retards α-cleavage compared to γ-hydrogen abstraction as was predicted. The sum of the absolute chemical yields of products arising from γ-hydrogen abstraction is relatively constant with increasing pressure (Fig. 7); but the yield of benzaldehyde, resulting from α-cleavage, decreases with increasing pressure. All samples were photolyzed under identical conditions for the same length of time at each pressure.

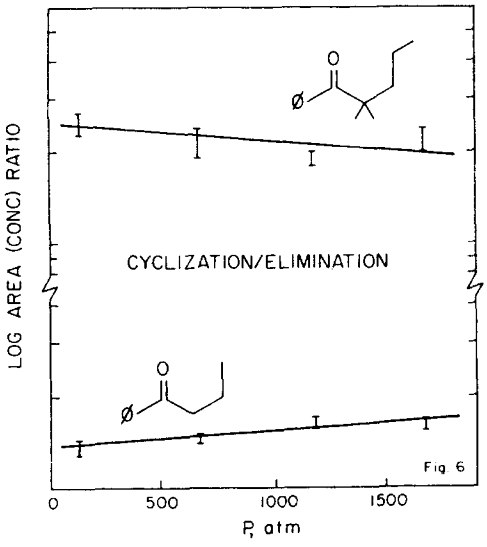

Fig 6

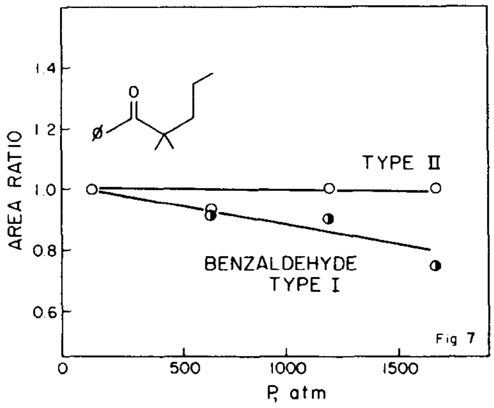

Fig 7

These latter results do not necessarily mean that pressure retards the primary bond scission step leading to the geminate acyl and alkyl radical pair. It is more likely that geminate recombination of these radicals to regenerate the starting ketone is facilitated by pressure because separative diffusion is retarded. Similarly, the constant yield for products from γ-hydrogen abstraction does not fully indicate what is happening in this step since the reversion reaction of the diradical to regenerate starting ketone is invisible. Definitive conclusions on these matters require, among other approaches, studies of effects of pressure on quantum yields.

Acknowledgments. The authors thank the National Science Foundation for support of this work through grant CHE75-19172. We also wish to thank Professors F. Lewis and P. Wagner for helpful discussions.

References

(1) (a) This is part 22 of the series High Pressure Studies. Part 21 is R.C. Neuman, Jr., G.D. Lockyer, Jr., and J. Marin, J. Amer. Chem. Soc., 98, 6975 (1976). (b) Presented at the 2nd International Symposium on Organic Free Radicals, Aix-en-Provence, France, July 17-23, 1977; and the 174th National ACS Meeting, Chicago, August 28-September 2, 1977, ORGN 066.

(2) R.C. Neuman, Jr. and E.W. Ertley, J. Amer. Chem. Soc., 97, 3130 (1975).

(3) See P.J. Wagner, Accounts Chem. Res., 4, 168 (1971).

(4) See (a) R.C. Neuman, Jr., Accounts Chem. Res., 5, 381 (1972), (b) R.C. Neuman, Jr. and R.P. Pankratz, J. Amer. Chem. Soc., 95, 8372 (1973). (c) R.C. Neuman, Jr. and R. Wolfe, J. Org. Chem., 40, 3147 (1975).

(5) Atmospheric pressure photochemical studies are reported by: (a) F.D. Lewis and T.A. Hilliard, J. Amer. Chem. Soc., 94, 3852 (1972). (b) P.J. Wagner and J.M. McGrath, J. Amer. Chem. Soc., 94, 3849 (1972).

(6) Hexane solutions of the phenyl alkyl ketones were photolyzed at room temperature in a high pressure optical cell which has been described (see G.D. Lockyer, Jr., Ph.D. Dissertation, University of California, Riverside, 1975). The light source was a Hanovia Utility Lamp with a medium pressure mercury arc. The light beam was condensed and passed through a Pyrex filter. Products were analyzed by flame ionization GLPC. Authentic samples were isolated and identified to permit quantitative analysis and to verify retention times.

(7) See W.J. LeNoble and T. Asano, J. Amer. Chem. Soc., 97, 1778 (1976).