is described by C. Y. Meyers and M.-L. Hsu, Abstracts, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975, No. ORGN-45; M.-L. Hsu, Dissertation, University of Southern Illinois, April 1975. See also C. Y. Meyers, T. Parady, V. Kolb, and A. P. Wahner, Abstracts, Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 1976, No. Phys.-Org.-142.
(9) J. F. Bunnett, R. G. Scamehorn, and R. P. Traber, *J. Org. Chem.*, **41**, 3677 (1976).
(10) (a) R. G. Scamehorn and J. F. Bunnett, *J. Org. Chem.*, following paper in this issue. (b) Manuscript in preparation.
(11) Conversion of pinacolone to **2b** is judged to be complete when only a small excess of *t*-BuOK is provided because the pK_a of *t*-BuOH in Me_2SO is much greater than that of ketones such as pinacolone. Cf. E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **85**, 3054 (1963); C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 1721 (1967); W. S. Matthews, J. E. Bares, J. E. Bartmess, F. G. Bordwell, F. J. Cornforth, G. E. Drucker, Z. Margolin, R. J. McCallum, G. J. McCollum and N. R. Vanier, *ibid.*, **97**, 7006 (1975).
(12) J. F. Bunnett in "Investigation of Rates and Mechanisms of Reactions", 3d ed, Part I, E. S. Lewis, Ed., Wiley, New York, N.Y., 1974: (a) p 159; (b) p 405.
(13) N. Kornblum, *Angew. Chem.*, **87**, 797 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).
(14) T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **30**, 3768 (1965); F. G. Bordwell and R. G. Scamehorn, *J. Am. Chem. Soc.*, **93**, 3410 (1971); F. G. Bordwell and A. C. Knipe, *ibid.*, **93**, 3416 (1971). Cf. also Y. Sawaki and Y. Ogata, *ibid.*, **97**, 6983 (1975).
(15) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 164.
(16) N. Kornblum, L. Cheng, R. C. Kerber, M. M. Kestner, B. N. Newton, H. W. Pinnick, R. G. Smith, and P. A. Wade, *J. Org. Chem.*, **41**, 1560 (1976).
(17) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Am. Chem. Soc.*, **86**, 639 (1964); S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).
(18) The radical anion structure presented in steps 3 and 4, Scheme I, shows the extra electron to be located, in effect, in a carbonyl group π^* orbital. Another possible location for it is a benzene ring antibonding π orbital. Transfer of the electron between the two π systems is doubtless rapid; cf. M. Szwarc and J. Jagur-Grodzinski in M. Szwarc, "Ions and Ion Pairs in Organic Reactions", Vol. 2, Wiley, New York, N.Y., 1974, pp 71–85.
(19) (a) D. J. Cram, B. Rickborn, and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960); (b) cf. R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N.Y., 1967, p 140.
(20) A. J. Birch, K. B. Chamberlain, and S. S. Oloyede, *Aust. J. Chem.*, **24**, 2179 (1971).
(21) D. J. Cram and A. C. Day, *J. Org. Chem.*, **31**, 1227 (1966).
(22) R. Huisgen in "Organometallic Chemistry", H. Zeiss, Ed., Reinhold, New York, N.Y., 1960, p 36; K. Herbig, Dissertation, University of Munich, 1960, p 26.
(23) J. F. Bunnett and F. J. Kearley, Jr., *J. Org. Chem.*, **36**, 184 (1971).
(24) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).
(25) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *J. Am. Chem. Soc.*, **89**, 2069 (1967).
(26) R. C. Fuson and J. A. Robertson, *J. Org. Chem.*, **7**, 466 (1942).

Notes

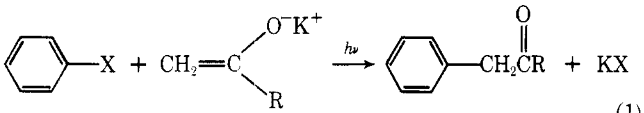
Photostimulated $S_{RN}1$ Reactions of Halobenzenes with Ketone Enolate Ions in Dimethyl Sulfoxide Solution[1a]

Richard G. Scamehorn[1b] and Joseph F. Bunnett*

University of California, Santa Cruz, California 95064

Received August 31, 1976

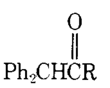
Many ketone enolate ions react with halobenzenes in liquid ammonia, under Pyrex-filtered irradiation, to form α-phenyl derivatives of the ketones.[2-5] Reactions occur, for example, as shown in eq 1. These reactions may be viewed as aromatic nucleophilic substitutions, and they are believed to occur by the $S_{RN}1$ mechanism.[6-9]


(1)

1a, X = Br **2a**, R = CH_3 **3a**, R = CH_3
b, X = I **b**, R = $C(CH_3)_3$ **b**, R = $C(CH_3)_3$

It has also been observed that reactions according to eq 1 occur in dimethyl sulfoxide (Me_2SO) solution.[4,10] We now describe further observations of the reaction in Me_2SO.

Several experiments of descriptive character are summarized in Table I. The reactions of bromo- and iodobenzene with the enolate ions of both acetone and pinacolone occur readily to give high yields of monophenylation products of type **3** often accompanied by small yields of diphenylation products of type **4**.



$$Ph_2CHC(=O)R$$

4a, R = CH_3
b, R = $C(CH_3)_3$

Some preliminary measurements of the rate of reaction of bromobenzene with **2b** are presented in Table II. In most of these experiments, samples withdrawn at various times were analyzed by titration for bromide ion. Results of a typical experiment are displayed in Figure 1. During about the first 40% of the reaction the absolute rate, in M s^{-1}, was nearly constant; later it diminished. We were unable to fit the data for entire experiments to simple rate expressions, such as those for first- and second-order kinetics, and therefore tabulate initial zero-order rate coefficients in Table II.

In Table II, one can see that there was considerable variation in rate among experiments conducted identically or nearly so. For example, compare expt 11, 14, 15, and 16. Changing the concentration of bromobenzene or the enolate ion by a factor of 2 affected the rate very little; compare expt 16 with 17, or 12 and 13 with 11, 14, 15, and 16, or 18 with 19. Experiments 18 and 19 were carried out with a lower intensity of irradiation than the rest; they are based on the same batch of solution of **2b** in Me_2SO, and were performed the same day.

In early work efforts were made to determine the rate of photostimulated reaction of iodobenzene with **2a** and **2b**. We found that a substantial fraction of the reaction occurred before irradiation was started. Study of the photostimulated reaction with bromobenzene was more attractive because the dark reaction is much slower. We report elsewhere[11] a study of the kinetics of the dark reaction of **2b** with iodobenzene.

Spectrophotometric studies between 300 and 400 nm showed weak absorption by bromobenzene, strong absorption by **2b**, and very strong absorption ($A > 3$) by the enolate ions of **3a** and **3b** and by the reaction solution from expt 16, Table II, after 27 min irradiation (60% reaction). The very strong absorption by product enolate ions is perhaps a reason for the diminution in zero-order rate at later stages of reaction; see Figure 1.

Also noteworthy is that typical reaction mixtures, although initially colorless to the eye, became yellow on exposure to the atmosphere. This complicates transfer of solution aliquots, as in the dispensing of portions of a master reaction solution into tubes intended to be removed for analysis at different

Table I. Product Yields in Photostimulated Reactions of Halobenzenes with Ketone Enolate Ions in Dimethyl Sulfoxide Solution

Expt no.	Substrate, concn	Enolate, concn	Irradn time, min	Products, % 3^a	4^b
1	**1b**,[c] 0.05 M	**2a**,[e] 0.20 M	60	81[g]	11[i]
2	**1b**, 0.03 M	**2a**, 0.25 M	60	88	4
3	**1b**, 0.049 M	**2b**,[f] 0.40 M	62	99	
4	**1a**,[d] 0.10 M	**2b**, 0.40 M	90	87[h]	~9[j]

[a] Product is **3a** if **2a** used, or **3b** if **2b** used. [b] Product **4a** if **2a** used, or **4b** if **2b** used. [c] Registry no., 591-50-4. [d] Registry no., 108-86-1. [e] Registry no., 35648-48-7. [f] Registry no., 51742-96-2. [g] Registry no., 103-79-7. [h] Registry no., 6721-67-1. [i] Registry no., 781-35-1. [j] Registry no., 58343-20-7.

Table II. Rates of Photostimulated Reaction of Bromobenzene with Potassium Pinacolone Enolate in Dimethyl Sulfoxide Solution

Expt no.	[**1a**], M	[**2b**], M	Temp,[a] °C	No. of lamps[b]	$10^5 k_0$, M s^{-1}
11	0.05	0.20	26–30	16	1.8
12	0.025	0.20	29–32	16	1.6
13	0.025	0.20	30.5–32.5	16	2.0
14	0.05	0.20	31–34	16	3.0
15	0.05	0.20	35–34	16	4.0
16	0.05	0.20	34	16	1.7
17	0.025	0.10	34–34.5	16	1.7
18[c]	0.025	0.10	34	4	0.88
19[c]	0.127	0.10	34	4	0.77

[a] Temperatures at beginning and end of irradiation are given, in that order. [b] Number of lamps used in photochemical reactor. [c] Experiments 18 and 19 utilized the same batch of solution of **2b** in Me_2SO, and were conducted differently from the rest; see Experimental Section.

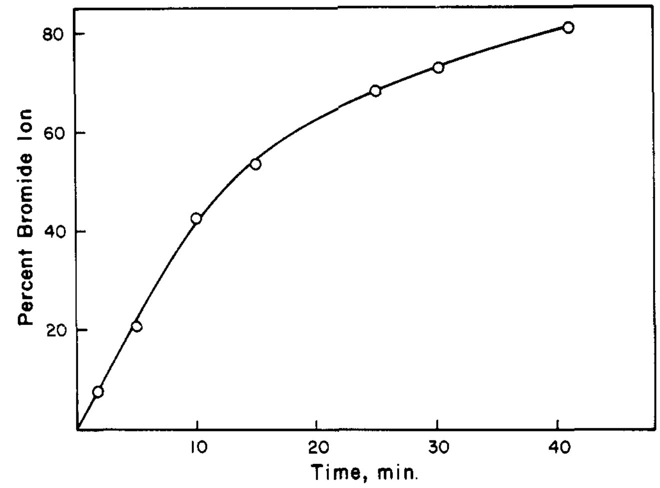


Figure 1. Bromide ion release as a function of time in the reaction of bromobenzene with potassium pinacolone enolate (**2b**) in Me_2SO. Data of expt 17, Table II.

times. In any future experiment of that type, rigorous exclusion of dioxygen during transfer operations should be ensured.

We report elsewhere[11] that, in competitive photostimulated reaction of a mixture of **1a** and **1b** with **2b** in Me_2SO, the iodobenzene/bromobenzene reactivity ratio is about 6.

Investigation of this photostimulated reaction is not being continued.

Experimental Section

Materials and solvents were obtained and purified as described elsewhere.[11] Product determinations were made by GLC as there described.

3,3-Dimethyl-1,1-diphenyl-2-butanone (4b). A flask containing a solution of 2.85 g of iodobenzene, 2.50 g of 3,3-dimethyl-1-phenyl-2-butanone (**3b**), and 3.20 g of *t*-BuOK in 250 ml of liquid ammonia was fitted with a condenser cooled with solid CO_2 in 2-propanol and a drying tube, placed in a Rayonet photochemical reactor fitted with "350-nm" lamps and irradiated for 2 h with occasional interruptions to spray the exterior with 2-propanol and wipe away the frost. The solvent was allowed to evaporate, water and dilute HCl were added, the mixture was extracted with diethyl ether, and the extract was evaporated. The residue was crystallized from methanol: yield 1.15 g (33%); mp 131–131.5 °C; NMR (CCl_4) δ 1.13 (s, 9 H), 5.43 (s, 1 H), 7.10 (s, 10 H); IR (KBr pellet) 704, 741, 1060, 1370, 1401, 1456, 1479, 1502, 1590, 1700, and 2976 cm^{-1}; MS *m/e* 252 (M^+), 167 (likely Ph_2CH^+). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.46; H, 8.05.

Kinetic Procedure. A single-neck 100-ml flask with a gas inlet side arm and short condenser was purged with N_2. A weighed portion of *t*-BuOK, slightly in excess of the ketone to be used, was placed in the flask and then 50 ml of Me_2SO was added through the condenser by means of a syringe. After being stirred for several minutes, the solution was alternately evacuated and flushed with N_2 for at least three cycles. The system was placed in a Rayonet Model RPR-100 photochemical reactor equipped with 16 "350-nm" fluorescent tubes rated at 24 W. (In expt 15–19, Table II, the flask was placed in a glass vessel within the reactor containing water preheated to 34 °C). The ketone and halobenzene were added in the dark, the solution was swirled for mixing, and an aliquot was removed to ascertain how much dark reaction had occurred. Another aliquot was removed and placed in an N_2-flushed, screw cap test tube wrapped with aluminum foil. (This portion was maintained at reaction temperature until the end of the period of irradiation, when it was quenched.) Irradiation was begun and aliquots were removed at recorded times by syringe, through the condenser with N_2 flowing slowly, and delivered into dilute HNO_3 in water for quenching. Halide ion in the quenched aliquots was determined by potentiometric titration with standard $AgNO_3$.

For expt 18 and 19, Table II, the reaction solution was prepared under N_2 in a flask in the dark, and 5-ml aliquots were transferred to screw cap test tubes flushed with argon. The tubes were placed in a "merry-go-round" within the reactor which rotated during irradiation, which was performed with only 4 of the usual 16 lamps in service. Tubes were removed for quenching at recorded times.

Registry No.—Dimethyl sulfoxide, 67-68-5.

References and Notes

(1) (a) Research supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. (b) On sabbatical leave from Ripon College, 1975–1976.
(2) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).
(3) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 3020 (1973).
(4) J. F. Bunnett and J. E. Sundberg, *Chem. Pharm. Bull.*, **23**, 2620 (1975).
(5) J. F. Bunnett and J. E. Sundberg, *J. Org. Chem.*, **41**, 1702 (1976).
(6) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463 (1970).
(7) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Am. Chem. Soc.*, **88**, 5662 (1966).
(8) G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968).
(9) N. Kornblum, *Angew. Chem.*, **87**, 797 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).
(10) J. F. Bunnett, R. G. Scamehorn, and R. P. Traber, *J. Org. Chem.*, **41**, 3677 (1976).
(11) R. G. Scamehorn and J. F. Bunnett, *J. Org. Chem.*, preceding paper in this issue.