Photostimulated Aromatic SRN1 Reactions

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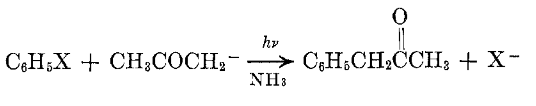
Acetone enolate ion is unreactive with halobenzenes and related substrates in liquid ammonia in the dark, but reaction occurs rapidly when stimulated by near-ultraviolet light, to form phenylacetone in high yields, plus small amounts of 1,1-diphenyl-2-propanone. Phenylacetone was obtained in 57–95% yield from PhI, PhBr, PhCl, PhF, Ph_2S, $Ph_3S^+Cl^-$, Ph_2Se, and $PhNMe_3{}^+I^-$, and in small yield from Ph_2O and $PhOPO(OEt)_2$. An electron transfer, radical mechanism (SRN1) is indicated by the inhibitory effect of radical scavengers (O_2 and di-*tert*-butyl nitroxide).

Bromobenzene does not react with acetone enolate ion in liquid ammonia in the dark, and bromobenzene in liquid ammonia survives exposure to near-ultraviolet radiation. However, under irradiation, bromobenzene and acetone enolate ion react rapidly to form phenylacetone in high yield (eq 1). Even a 150-W tungsten light bulb external to a Pyrex flask causes reaction to occur.



$$C_6H_5X + CH_3COCH_2{}^- \xrightarrow[NH_3]{h\nu} C_6H_5CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + X^- \qquad (1)$$

Several other substituted benzenes, with various nucleofugic groups, also undergo this photochemical reaction, as reported in Table I. With one minor exception, no reaction occurs without irradiation; the exception is that iodobenzene undergoes a slow dark reaction which, in two experiments, consumed about 5 and 15% of it during 3 hr. Most of the reactions of Table I were conducted in Pyrex flasks irradiated by 350-nm ultraviolet lamps in a Rayonet photochemical reactor.[2]

Rather long irradiation times were employed before the great facility of this photochemical reaction was appreciated. In later experiments, portrayed in Figure 1, samples were analyzed at frequent intervals and information as to the dependence of rate on identity of nucleofugic substituent was obtained. These experiments were all conducted in the same way, in the identical flask and with the same disposition of lamps in the reactor, but there may have been some variation of radiation intensity. Nevertheless, the results are at least qualitatively significant. They show the order of mobility: I ~ Br > SPh ≫ Cl > F ≫ OPh. Iodo- and bromobenzene were totally consumed within 5 min, the time of first observation.

Three methods for preparation of acetone enolate ion were employed. For most of the reactions of Table I, as well as for those of Figure 1, it was made by reaction of potassium metal with acetone in ammonia. This reaction,[3] which we also employed to prepare acetone enolate ion for another study,[4] has now been found to reduce about 35% of the acetone to isopropyl alcohol. Acetone enolate ion obtained by the K metal method is thus contaminated by isopropoxide ion.

For runs 11, 12, 13, 21, and 22 of Table I, the enolate ion was prepared by reaction of acetone with KNH_2 which had been formed *in situ* by iron-catalyzed reaction of K metal with the solvent. For runs 15–17, Table I, the enolate ion was made by interaction of acetone with potassium *tert*-butoxide, either supplied as such (run 17) or formed in the ammonia solvent by the remarkably slow reaction of K metal with *tert*-butyl alcohol.

Benzene was a prominent by-product of reactions with the enolate ion prepared by the K metal method, but was scarcely detectable when the enolate had been prepared by the KNH_2 or *t*-BuOK method. The implication that benzene arises from hydrogen atom abstraction from isopropoxide ion is substantiated by the fact (runs 12 and 13) that the benzene yield was increased when isopropoxide ion was intentionally added to enolate prepared by the KNH_2 method.

The virtual absence of benzene as a product from reactions with isopropoxide-free enolate ion shows that the phenyl radical is loath to abstract a hydrogen atom from ammonia.

Reactions with enolate ion prepared by the KNH_2 method were much slower than with preparations by the other methods. The reaction solutions were dark gray, probably owing to colloidal iron metal, and mere exclusion of light may have been responsible. However, it is not clear why the addition of isopropoxide ion (runs 12 and 13) enabled the reactions to occur more rapidly.

In a short series of reactions utilizing enolate prepared by the *t*-BuOK method, the time required to achieve half reaction was found to increase approximately linearly with reactant concentration. These reactions involved bromobenzene in concentrations from 0.1 to 0.6 *M*, with acetone enolate ion always in about threefold excess. One factor contributing to lower reactivity at higher reactant concentrations is the accumulation of crusts on the walls of the reaction flask above the solution; the crusts partially screen the solution from irradiation. Another may be absorption of light by substances in solution, causing a reduction of light intensity in the interior of the flask. Finally, the bimolecular termination steps of a radical chain mechanism (see below) become relatively more important at higher reagent concentrations.

When irradiation was provided by an external 150-W tungsten lamp, 1 hr was required for complete reaction of bromobenzene, in contrast to less than 5 min in the photochemical reactor. At the lower intensity of illumination, study of the effects of other substances on reaction rate was convenient. As shown in Figure 2, reaction was exceedingly slow in the presence of 4.3 mol % of di-*tert*-butyl nitroxide, a radical scavenger.[5]

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[1] Grateful recipient of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina.

[2] Product of Southern New England Ultraviolet Co., Middletown, Conn.

[3] A. J. Birch, *J. Proc. Roy. Soc. New South Wales*, **83**, 245 (1949).

[4] R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972).

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TABLE I

PHOTOCHEMICAL REACTIONS OF MONOSUBSTITUTED BENZENES WITH ACETONE ENOLATE ION IN LIQUID AMMONIA AT −33°

						Products,^{b} %			
Run	Substrate	Registry no.	[Substrate], *M*	[$CH_3COCH_2^-$],^{a} *M*	Time, min	Substrate recovered	C_6H_6	$PhCH_2COCH_3$	$Ph_2CHCOCH_3$
1	PhI	591-50-4	0.087	Nil	180	99	1		
2			0.15	0.51	180^{c}	94	2	2	
3			0.13	0.39	180^{c}	83	4	8	
4			0.14	0.50	180	0	22	67	11
5			0.22	0.75	180	0	*d*	61^{e}	*d*
6			0.14	0.50	5	0	20	67	10
7	PhBr	108-86-1	0.076	Nil	60	95	0.5		
8			0.076	0.43	80^{c}	98	0.3		
9			0.076	0.43	80	0	22	73	6
10			0.060	0.35	5	0	27	64	5
11			0.095	0.38^{f}	50	0	0.5	88	9
12			0.092	0.29^{f,g}	19	0	9	78	9
13			0.089	0.23^{f,h}	15	0	32	58	5
14			0.089	0.42	60^{i}	0	21	65	11
15			0.095	0.24^{j}	11	0	0.6	85	14
16			0.089	0.38^{k}	80^{i}	0	0.3	94	8
17			0.34	1.04^{l}	110	<0.1	<0.1	86^{m}	14
18	PhCl	108-90-7	0.063	0.44	180	0	31	61^{n}	5
19	PhF	462-06-6	0.066	0.48	200	0	31	60^{n}	3
20	PhSPh	139-66-2	0.063	0.44	30	0	26	66^{o}	5
21	$Ph_3S^+Cl^-$	4270-70-6	0.029	0.46^{f}	70	*d*	1	75^{p}	2
22	PhSePh	1132-39-4	0.024	0.30^{f}	30	0	1	95^{q}	3
23	PhOPh	101-84-8	0.072	0.47	250	77	6	14^{n,r}	0
24	$PhNMe_3^+I^-$	98-04-0	0.035	0.44	60	*d*	37	57	1
25	$PhOPO(OEt)_2$	2510-86-3	0.078	0.40	250	*d*	11	13^{s}	0

[a] Prepared from acetone and K metal unless otherwise noted; concentration listed assumes quantitative conversion of acetone to enolate ion. [b] Yield by glpc unless otherwise noted. [c] Dark. [d] Not determined. [e] Isolated and weighed. [f] Prepared from acetone and KNH_2. [g] $(CH_3)_2CHO^-K^+$ (0.13 *M*) also present. [h] $(CH_3)_2CHO^-K^+$ (0.23 *M*) also present. [i] Irradiation by 150-W tungsten bulb. [j] From acetone and *t*-BuOK (0.39 *M*). [k] From acetone and *t*-BuOK (0.47 *M*). [l] From acetone and commercial *t*-BuOK (1.18 *M*). [m] Yield of isolated and weighed phenylacetone, 73%. [n] *Ca.* 1% 1-phenyl-2-propanol also detected. [o] C_6H_5SH (97%) also determined. [p] From 10.2 mmol of $Ph_3S^+Cl^-$, 0.11 mmol of C_6H_6, 7.66 mmol of phenylacetone, 0.10 mmol of diphenylacetone, 2.22 mmol of PhSPh, and 5.28 mmol of PhSH were obtained. [q] PhSeH (83%) also formed, isolated as PhSeSePh. [r] Phenol (20%) also determined. [s] Phenol (71%) also determined.

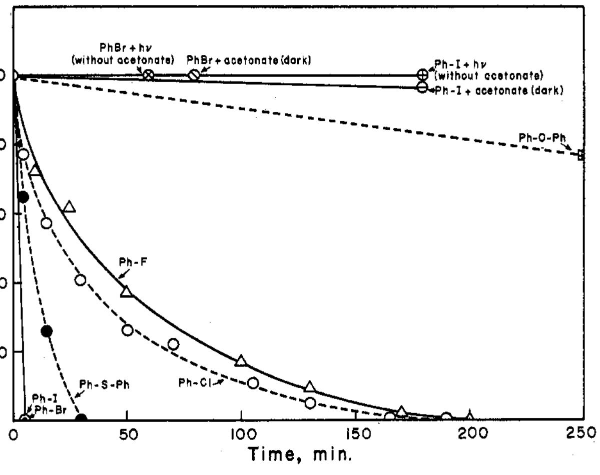

Figure 1.—Per cent of substrate remaining after various times of exposure in the photochemical reactor (see text). Reaction solutions were *ca.* 0.07 *M* in substrate and *ca.* 0.45 *M* in acetone enolate ion (prepared by K metal method), in ammonia at reflux under N_2 atmosphere: ⦸, PhBr + acetone enolate in dark; ⊗, PhBr with illumination but no enolate ion; ⊖, PhI + acetone enolate ion in dark; ⊕, PhI with illumination but no enolate ion.

Even 0.68 mol % of this nitroxide appreciably retarded the reaction. Oxygen is also an inhibitor, as shown by the sluggishness of reaction under air. These experiments testify to a radical chain mechanism.

Reaction Mechanism.—Of three types of mechanism which come to mind, two are easily rejected, while the third gives a good account of the facts.

The possibility that these are photo-SNAr reactions, such as occur between nitrophenyl ethers and diverse nucleophiles,[6] is rejected because those reactions do not display radical characteristics, because bromobenzene, etc., do not show appreciable absorption at wavelengths above 290 nm, and in view of the very short irradiation times which sufficed in most of our experiments. The possibility that phenyl radicals are generated by photolytic homolysis of bonds between carbon and halogen or other nucleofugic groups is rejected because even homolysis of iodobenzene requires long illumination (*ca.* 20 hr) with 253.7-nm light,[7] and photolysis of other halobenzenes is even slower.[8]

The mechanism of Scheme I is compatible with our observations.

This is a photostimulated SRN1 mechanism.[9] Steps 3, 4, and 5 constitute a cycle with radical intermediates,

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[6] E. Havinga, R. O. de Jongh, and M. E. Kronenberg, *Helv. Chim. Acta,* **50**, 2550 (1967); R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Amer. Chem. Soc.,* **87**, 2945 (1965); F. Pietra, *Quart. Rev., Chem. Soc.,* **23**, 519 (1969).

[7] W. Wolf and N. Kharasch, *J. Org. Chem.,* **30**, 2493 (1965).

[8] N. Kharasch, R. K. Sharma, and H. B. Lewis, *Chem. Commun.,* 418 (1966).

[9] J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.,* **92**, 7463, 7464 (1970).

SCHEME I

$$\text{Electron source} + \text{PhX} \xrightarrow{h\nu} [\text{PhX}]\cdot^- + \text{residue} \quad (2)$$

$$[\text{PhX}]\cdot^- \longrightarrow \text{Ph}\cdot + \text{X}^- \quad (3)$$

$$\text{Ph}\cdot + \text{CH}_3\text{COCH}_2^- \longrightarrow [\text{PhCH}_2\text{COCH}_3]\cdot^- \quad (4)$$

$$[\text{PhCH}_2\text{COCH}_3]\cdot^- + \text{PhX} \longrightarrow [\text{PhX}]\cdot^- + \text{PhCH}_2\text{COCH}_3 \quad (5)$$

$$\text{Termination steps} \quad (6)$$

and thus accommodate the inhibition experiments (Figure 2), which indicate a radical chain mechanism.

Oxygen and di-*tert*-butyl nitroxide may interfere with propagation of the reaction chain by trapping phenyl radicals and/or by taking electrons from $[\text{PhCH}_2\text{COCH}_3]\cdot^-$ radical anions, in the latter case being reduced to $\text{O}_2\cdot^-$ and di-*tert*-butylhydroxylamine anion, respectively.[10]

The mechanism of Scheme I is very similar to that previously proposed[4] for condensation of halobenzenes and other substrates with acetone enolate ion stimulated by K metal in liquid ammonia, reactions which have many characteristics in common with these light-stimulated reactions. Photostimulation of *aliphatic* SRN1 reactions has been reported.[11] Irradiation of solutions of halobenzenes with dimethylaniline in methanol gives rise to phenyl radical intermediates, and reaction steps similar to our steps 2 and 3 have been proposed.[12]

The identity of the electron source in step 2 is not clear. Possibilities are the enolate ion itself, or an enolate ion derived from an aldol condensation product of acetone. Further investigation of this question is planned.

Synthetic Utility.—Run 17, Table I, was carried out on a preparative scale and afforded 21 g of pure phenylacetone. The only by-product was 1,1-diphenyl-2-propanone. It demonstrates the potentiality of these reactions for synthesis. In contrast to similar reactions provoked by alkali metals,[4] the phenylacetone obtained in the present study is virtually free of 1-phenyl-2-propanol. In utilization of the present method for the purpose of synthesis, care must be taken to exclude air; see the run under air in Figure 2.

Experimental Section

Reactions Reported in Figure 1.—In a typical run, a solution of potassium acetone enolate was prepared by reaction of 5.4 g (0.138 mol) of potassium metal with 10.4 ml (0.142 mol) of acetone in 320 ml of ammonia under nitrogen in a flask provided with a cold finger condenser cooled by solid CO_2 in 2-propanol. Chlorobenzene (2.0 ml, 0.02 mol) was added, the solution was stirred and kept for 15 min in the dark, and a sample was taken. The reaction flask was then placed in the photochemical reactor equipped with 350-nm lamps, and *ca.* 1-ml samples were taken, by means of a piece of 8-mm glass tubing J-shaped at the lower end, after measured periods of irradiation. Each sample was added to 1 ml of water; the mixture was extracted with 1 ml of diethyl ether and a portion of the ether layer was examined by glpc on a column of 20% Carbowax 20M on Chromosorb P, with thermal conductivity detector. The peaks for chlorobenzene and phenylacetone were suitably corrected for molar response; the per cent of chlorobenzene unreacted plotted in Figure 1 represents (moles chlorobenzene)/(moles chlorobenzene plus moles phenylacetone) and, in view of the substantial amount of benzene formed (see below), is something of an overstatement. When, after 190 min irradiation, chlorobenzene could no longer be detected, the reaction mixture was treated with excess NH_4Cl, 200 ml of diethyl ether was added together with measured amounts of toluene and *p*-dichlorobenzene to act as internal standards, the ammonia was allowed to evaporate, and water was added. The ether layer was washed with water, dried over anhydrous Na_2SO_4, and examined by glpc, suitable molar response corrections being made. Obtained were benzene (31%), phenylacetone (61%), 1,1-diphenyl-2-propanone (5%), and about 1% of material with the same retention time as that of 1-phenyl-2-propanol.

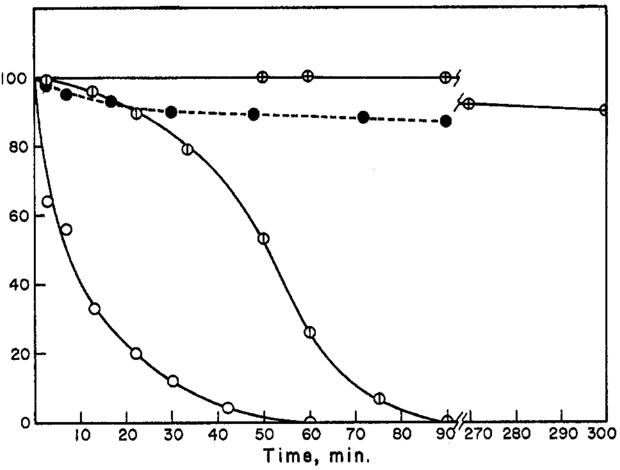

Figure 2.—Per cent of bromobenzene remaining after various times of exposure to external 150-W tungsten lamp, as affected by radical scavengers: ○, without scavengers; ⦶, with 0.68 mol % di-*tert*-butyl nitroxide; ⊕, with 4.3 mol % di-*tert*-butyl nitroxide; ●, under air. In all experiments, PhBr was *ca.* 0.09 *M*, and acetone enolate ion (prepared by K metal method) was *ca.* 0.45 *M*, in ammonia at reflux.

Reactions Reported in Figure 2.—Essentially the same technique was employed, except that irradiation was provided by a 150-W tungsten lamp placed about 10 cm from the wall of the reaction flask and somewhat above it; the flask and lamp were crudely surrounded by aluminum foil to reduce glare into the laboratory.

Reaction of Acetone with Potassium Metal in Ammonia.—To a stirred solution of 6.9 g (0.177 mol) of potassium metal in 360 ml of anhydrous liquid ammonia at reflux was added acetone, drop by drop, until the blue color was discharged; a total of 13.8 ml (0.188 mol) of acetone was required. Excess NH_4Cl was added, followed by diethyl ether (200 ml) and toluene (10 ml), and the ammonia was evaporated through a condenser at −30 to −20°. The toluene was to act as an internal standard for glpc purposes. Glpc analysis of a sample of the remaining ether solution indicated a 32% yield of 2-propanol and 38% recovery of acetone; there were also some small peaks for less volatile substances. Water was added to the evaporation residue, and glpc analysis of a sample of the ether layer indicated 25% of 2-propanol and 38% of acetone. The infrared spectrum of a sample of the 2-propanol formed, isolated by glpc, was identical with that of an authentic sample. The balanced equation, $2\text{CH}_3\text{COCH}_3 + 2\text{K} \rightarrow \text{CH}_3\text{COCH}_2\text{K} + (\text{CH}_3)_2\text{CHOK}$, would accord with the observed consumption of nearly equimolar amounts of potassium and acetone and would call for equimolar amounts of acetone and 2-propanol to appear as products of the experiment described. It is not clear why less 2-propanol than acetone was found, or why these substances account for only 70% of the acetone originally introduced.

Preparative Scale Reaction (Run 17).—Into a 2-l., three-neck, round-bottom flask equipped with magnetic stirrer, dropping funnel, and cold finger condenser cooled by solid CO_2 in 2-propanol, dried and flushed with nitrogen, were placed 100 g (0.89 mol) of potassium *tert*-butoxide and 700 ml of anhydrous ammonia. Not all the potassium *tert*-butoxide dissolved. Acetone (55 ml, 0.75 mol) was added dropwise with good stirring over a

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[10] We thank a referee for pointing out the electron-theft possibility.

[11] N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, **88**, 5662 (1966); G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966); **90**, 347 (1968); N. Kornblum and F. W. Stuchal, *ibid.*, **92**, 1804 (1970).

[12] C. Pac, T. Tosa, and H. Sakurai, *Bull. Chem. Soc. Jap.*, **45**, 1169 (1972).

period of 40 min. After a further 15 min, 25 ml (0.24 mol) of bromobenzene was added *via* the same dropping funnel, the reaction flask was placed in the photochemical reactor equipped with 350-nm lamps, and irradiation was started, the solution being constantly stirred and gently swept with nitrogen. Samples (*ca.* 1 ml) were taken by the procedure described above and analyzed by glpc; after 110 min, the bromobenzene had all reacted. To the reaction mixture, solid NH_4Cl was added until the orange-yellow solution became pale yellow, 350 ml of ether was added, and the ammonia was evaporated. Sufficient water was added to dissolve the inorganic salts and the ether layer was separated. The water layer was extracted with a further 150 ml of ether. The combined ether extracts were washed thrice with 100-ml portions of water saturated with NaCl and dried over anhydrous Na_2SO_4. One-tenth of the ether solution was separated from the rest; measured amounts of toluene and *p*-dichlorobenzene were added to it; glpc analysis of the resulting mixture indicated 86% of phenylacetone and 14% of 1,1-diphenyl-2-propanone to have been formed, but no significant amount of benzene. The remaining nine-tenths of the ether solution was concentrated and distilled under vacuum; 21.0 g (73%) of phenylacetone, bp 103–106° (19 Torr), of purity >98% as judged by glpc and nmr, was isolated.

Registry No.—Acetone enolate ion, 24262-31-5.

Acknowledgments.—We thank Dr. William J. Boyle, Jr., for a sample of di-*tert*-butyl nitroxide, and Professor Frederick D. Greene for suggesting its use.

Mechanisms of SNi Reactions. The Effect of Aralkyl Group Structure on Ion-Pair Return in the Decomposition of Aralkyl Thiocarbonates[1]

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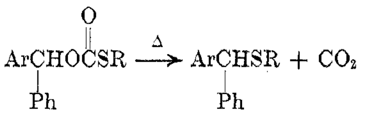
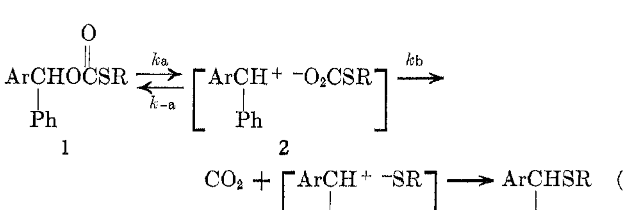
The effect of a change in the nature of Ar in $ArPhCH^+$ on the extent and stereochemistry of ion-pair return accompanying the decomposition of aralkyl *S*-methyl thiocarbonates (eq 2) has been examined by investigating the behavior of *p*-methylbenzhydryl and α-naphthylphenylcarbinyl *S*-methyl thiocarbonates (**1b** and **1c**) and comparison of the results with those obtained earlier with *p*-chlorobenzyhydryl *S*-methyl thiocarbonate. The change from Ar = $p\text{-ClC}_6H_4$ to $p\text{-CH}_3C_6H_4$ leads to a decrease in the percentage of ion pairs **2** undergoing return and to an increase in the fraction doing so with racemization, in accord with the effect expected of a structural change that leads to an increase in the stability of the carbonium ion portion of the ion pair, and, where appropriate, with the results of Goering and Hopf on a related system. In contrast the change from Ar = $p\text{-ClC}_6H_4$ to $\alpha\text{-C}_{10}H_7$, while also leading to a carbonium ion of increased stability, leads to only very small changes in the extent and stereochemistry of ion pair return. The implications of this result are discussed.

Previous work[2] has shown that the thermal decomposition of aralkyl thiocarbonates (eq 1), which occurs



$$\mathrm{Ar\underset{\displaystyle Ph}{CH}O\overset{\displaystyle O}{\overset{\|}{C}}SR \xrightarrow{\Delta} Ar\underset{\displaystyle Ph}{CH}SR + CO_2} \qquad (1)$$

when these compounds are heated in a polar aprotic solvent at 130–170°, takes place *via* the two-step mechanism outlined in eq 2 and that extensive ion-pair



$$\mathrm{\underset{\displaystyle 1}{Ar\underset{\displaystyle Ph}{CH}O\overset{\displaystyle O}{\overset{\|}{C}}SR}\ \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}}\ \underset{\displaystyle 2}{\left[Ar\underset{\displaystyle Ph}{CH^+}\ {}^-O_2CSR\right]} \xrightarrow{k_b} CO_2 + \left[Ar\underset{\displaystyle Ph}{CH^+}\ {}^-SR\right] \longrightarrow Ar\underset{\displaystyle Ph}{CH}SR} \qquad (2)$$

return from **2** to thiocarbonate (step k_{-a}) accompanies the decomposition.

In this earlier study[2] the variation in both the extent and stereochemistry of ion-pair return was investigated for a trio of *p*-chlorobenzhydryl (Ar = $p\text{-ClC}_6H_4$) thiocarbonates as a function of (1) changes in the structure of the thioalkyl (RS–) group and (2) a change from a relatively polar (benzonitrile) to a less polar solvent (bromobenzene). In the present investigation we have explored the effect of changes in the structure of Ar in the carbonium ion portion of **2** on ion-pair return by studying the decomposition of a pair of aralkyl *S*-methyl thiocarbonates in benzonitrile and comparing the results with those obtained earlier[2] for the decomposition of *p*-chlorobenzhydryl *S*-methyl thiocarbonate (**1a**, Ar = $p\text{-ClC}_6H_4$; R = CH_3) in this solvent. The two thiocarbonates chosen for study were *p*-methylbenzhydryl (**1b**, Ar = $p\text{-CH}_3C_6H_4$; R = CH_3) and the α-naphthylphenylcarbinyl (**1c**, Ar = $\alpha\text{-C}_{10}H_7$; R = CH_3) *S*-methyl thiocarbonate.

The reasons for choosing these two particular thiocarbonates were as follows. As judged by the rates of solvolysis of the corresponding aralkyl chlorides in aqueous acetone,[3,4] both $p\text{-CH}_3C_6H_4CHPh^+$ and $\alpha\text{-C}_{10}H_7CHPh^+$ are more stable carbonium ions than $p\text{-ClC}_6H_4CHPh^+$. However, while with Ar = $p\text{-CH}_3C_6H_4$ this increase in carbonium ion stability is achieved with no change in the steric requirements of the Ar group, this is not the case with Ar = $\alpha\text{-C}_{10}H_7$, since α-naphthyl represents a significantly bulkier group than *p*-chlorophenyl. Our interest was first to compare the effect of the change from Ar = $p\text{-ClC}_6H_4$ to $p\text{-CH}_3C_6H_4$ on the extent and stereochemistry of ion-pair return in the thiocarbonate decomposition with the results of Goering and Hopf[5] on the effect of the same change on ion-pair return in the solvolysis of para-substituted benzhydryl *p*-nitrobenzoates. Second, we were interested in the extent to which the change in steric bulk of Ar on going to Ar = $\alpha\text{-C}_{10}H_7$ would have any significant effect on ion-pair return.

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) J. L. Kice, R. L. Scriven, E. Koubek, and M. Barnes, *J. Amer. Chem. Soc.*, **92**, 5608 (1970).

(3) L. Verbit and E. Berlinger, *ibid.*, **86**, 3307 (1964).

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