Thiophenol-Promoted Radical Chain Reduction of α-Substituted Isobutyrophenones by 1,3-Dimethyl-2-phenylbenzimidazoline

Dennis D. Tanner* and Jian Jeffrey Chen[1]

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Received May 29, 1991

The reductions of α-haloacetophenones and α-halopropiophenones by 1,3-dimethyl-2-phenylbenzimidazoline (DMBI) have been reported to proceed via an electron-transfer free-radical chain mechanism. The reduction of α-haloisobutyrophenones did not proceed by the chain sequence. We now report that initiated reductions of α-bromo- and α-chloroisobutyrophenones (IIIa,b) have been found to be promoted by the addition of thiophenol. Isobutyrophenone was formed as the major product via a free-radical chain process. During the PhSH-promoted DMBI reduction of IIIa,b a minor product, α-(phenylthio)isobutyrophenone (IV), was also formed via nucleophilic substitution. The chain propagation steps involve the efficient hydrogen atom transfers between $PhCOCMe_2^{\bullet}$ and PhSH and between $PhS^{\bullet}$ and DMBI. The facile hydrogen transfer between $PhS^{\bullet}$ and DMBI was confirmed by carrying out the radical-chain reduction of PhSSPh with DMBI.

Introduction

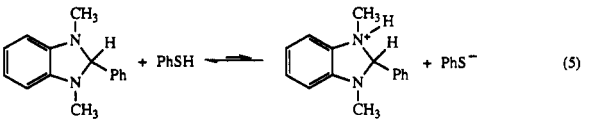
The reduction of α-bromo- and α-chloroacetophenone (Ia and Ib) and α-bromo- and α-chloropropiophenone (IIa and IIb) by 1,3-dimethyl-2-phenylbenzimidizoline (DMBI) was recently reported.[2] The reduction products, acetophenone and propiophenone, were formed by an electron-transfer hydrogen atom abstraction chain mechanism (see Scheme I).[2] The reduction of α-bromo- and α-chloroisobutyrophenone (IIIa and IIIb), however, did not appear to proceed by a chain sequence since the addition of either an initiator (AIBN) or an inhibitor (dinitrobenzene, DNB), additives which had been an effective chain initiator and inhibitor for the reduction of the primary (Ia,b) and secondary (IIa,b) halo ketones, did not significantly affect the yield of the reduction products. The tertiary halo ketones, IIIa,b, were involved in the radical process since they acted as efficient inhibitors when they were present during the reduction of the α-haloacetophenones and α-halopropiophenones. The observation that chain reduction did not take place with the α-haloisobutyrophenones was rationalized by assuming that hydrogen atom transfer between the tertiary radical $PhCOCMe_2^{\bullet}$ and DMBI was too inefficient to carry the chain (eq 3). It was anticipated that the chain reaction would be facilitated by the addition of a chain-transfer agent which itself produces a radical that could carry the chain. As anticipated, the addition of thiophenol increases the yield of the reduction products significantly. The present report describes a study of this enhanced reduction.

Results and Discussion

Reduction of α-Haloisobutyrophenones by DMBI in the Presence of PhSH. The DMBI reductions of the α-haloisobutyrophenones (IIIa,b) were carried out using the same conditions as previously reported for the DMBI reductions of Ia,b and IIa,b (degassed, THF, 61 °C).[2] Radical initiation (AIBN) and inhibition (*p*-DNB) were used to establish whether a free-radical chain mechanism is operative in the PhSH-promoted reduction. The results of these studies are summarized in Table I.

The reduction of α-bromoisobutyrophenone (IIIa) which had been reported[2] as relatively unreactive toward DMBI (reactions 1–3, Table I) was significantly accelerated by the addition of thiophenol (reactions 5–10). An optimum yield of reduction product was obtained when at least 2 equiv of thiophenol were used. In addition to the reduction product, isobutyrophenone, α-(phenylthio)isobutyrophenone (IV) was produced as a minor product (~1–5%). In the presence of *p*-DNB, the formation of the reduction product was inhibited (reactions 6, 8, 10), but the yield of the substitution product IV increased significantly.

Two competitive processes appear to be operative: the reduction product, isobutyrophenone, is formed by a free-radical chain process, while the substitution product, the thio ketone IV, is formed by a heterolytic substitution. In the absence of DMBI, IIIa was unreactive toward PhSH even in the presence of AIBN (reaction 11, Table I). Since DMBI and PhSH are required both for the radical-chain reduction and heterolytic substitution of IIIa, the nucleophilic substitution appears to proceed via the thiolate anion, PhS^-, eqs 5 and 6.



(5)

$$PhS^- + PhCOCMe_2X \rightarrow PhCOCMe_2SPh + X^- \quad (6)$$

The reduction of α-chloroisobutyrophenone (IIIb) was enhanced by PhSH (reactions 12–17), albeit the thermal reaction was much slower than that of the bromide IIIa. Nevertheless, the reduction could be inhibited by DNB (reaction 16) and initiated by AIBN (reaction 17). The yield of the heterolytic substitution product (IV) also increased in the presence of DNB (reaction 16).

Scheme II rationalizes both initiation (AIBN) and inhibition (DNB) and seems to indicate that the thiophenol-promoted reduction proceeds by a short-chain process, Table I, reactions 5–10. The two main chain-transfer steps involve hydrogen atom transfer from PhSH and DMBI (eqs 8 and 9).

Although hydrogen abstraction form PhSH is well documented and hydrogen abstraction by $PhS^{\bullet}$ from C–H has been observed, it is limited by reversibility.[3,4] The major portion of the thiyl radicals produced results in dimerization (reaction 12). A similar mechanistic scheme involving hydrogen abstraction from RSH by an aminyl radical, followed by hydrogen abstraction from the α-carbon of an amine by the $RS^{\bullet}$ radical, was proposed to explain the catalytic effect of thiols in the photoreduction of benzophenone by amines.[5] In order to show unam-

(1) Killam predoctoral fellow, 1987–1990.
(2) Tanner, D. D.; Chen, J. J. *J. Org. Chem.* **1989**, *54*, 3842.
(3) Kice, J. L. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 24, pp 718–22.
(4) Tanner, D. D.; Wada, N.; Brownlee, B. G. *Can. J. Chem.* **1973**, *51*, 1870.

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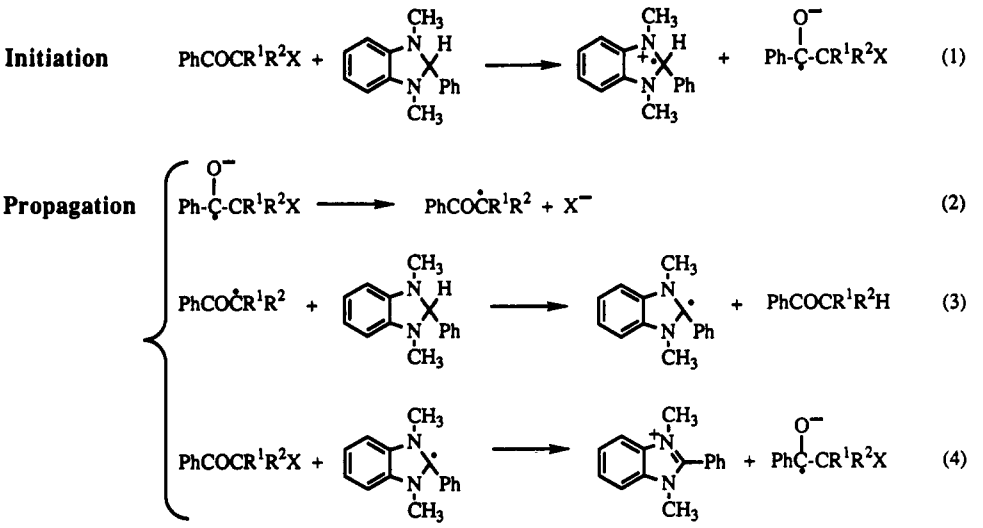
Scheme I



Scheme II

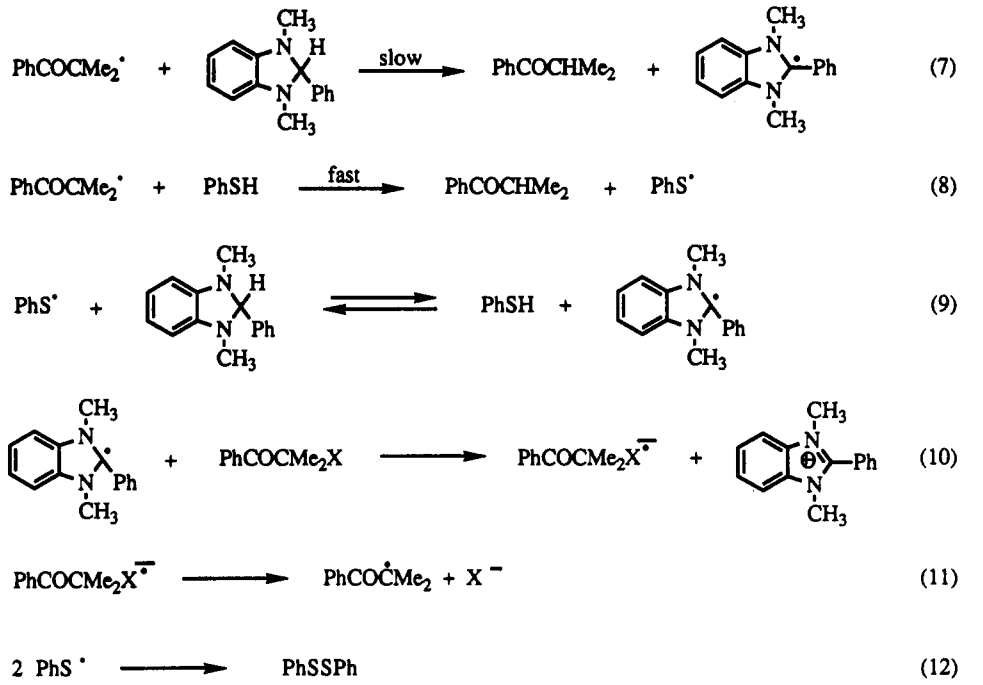


Table I. PhSH-Promoted Reduction of $PhCOCMe_2X$ (IIIa,b) by DMBI

X	reaction	condns[a]	$PhCOCHMe_2$	$PhCOCMe_2X$ (IIIa,b)	$PhCOCMe_2$ SPH (IV)
Br (IIIa)	1	96 h[b]	5.4	89.6	
	2	96 h, 4% AIBN[b]	11.4	79.7	
	3	96 h, 5% *p*-DNB[b]	12.2	79.7	
	4	104 h	19.1	63.4	
	5	104 h, PhSH (0.5 equiv)	79.5	20.5	4.0
	6	104 h, PhSH (0.5 equiv), 10% DNB-*p*	0.2	57.0	18.6
	7	35 h, PhSH	46.9	43.0	4.6
	8	35 h, PhSH (1 equiv), 10% *p*-DNB	2.2	63.4	35.6
	9	20 h, PhSH (2 equiv)	92.7		1.7
	10	20 h, PhSH (2 equiv), 9% *p*-DNB	0.7	52.0	22.2
	11	104 h, PhSH (2 equiv), 8% AIBN[c]	2.6	92.9	
Cl (IIIb)	12	77 h[b]	4.7	84.8	
	13	77 h, 3% AIBN[b]	14.8	81.7	
	14	77 h, 3% *p*-DNB[b]	1.0	92.9	
	15	27 h, PhSH (2 equiv)	14.5	77.8	8.0
	16	27 h, PhSH (2 equiv), 6% *p*-DNB	0.0	79.9	32.7
	17	27 h, PhSH (2 equiv), 6.7% AIBN	96.5		2.6

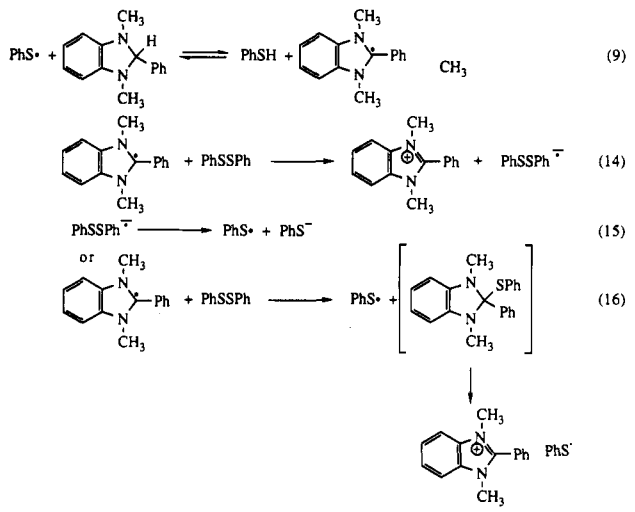
[a] All the reactions were carried out in THF at 61 °C with $[PhCOCMe_2X]$:[DMBI] = 1:2 except where specified in the table [IIIa,b] = 0.05 M. [b] $[PhCOCMe_2X]$:[DMBI] = 1:1. [c] No DMBI was used.

Table II. Reduction of PhSSPh by DMBI at 61 °C

reaction	solvent	condns[a]	PhSH	PhSSPh	$PhSCH_3$[b]
18	THF		0.9 ± 0.9	73.4 ± 10	2.4 ± 0.7
19		7% AIBN	69.0 ± 0.4	20.7 ± 3.0	6.4 ± 0.4
20	C_6H_6			94.0 ± 9.0	
21		10% AIBN	72.2 ± 0.2	24.7 ± 5.0	1.2 ± 0.2

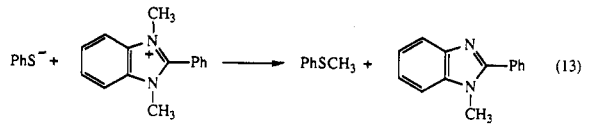
[a] [PhSSPh] = [DMBI] = 0.05 M, 10 h. [b] Small amounts (<6%) 1-methyl-2-phenylbenzimidazole was also observed.

Scheme III



biguously that the abstraction reaction, eq 9, does occur, the reduction of phenyl disulfide by DMBI was investigated.

DMBI Reduction of PhSSPh. The reductions of PhSSPh by DMBI were carried out in THF and in C_6H_6 at 61 °C. The results are shown in Table II. The reduction can be initiated by AIBN to give thiophenol as the major product. Small amounts of methyl phenyl sulfide and 1-methyl-2-phenylbenzimidazole (<6%) were presumably formed by an S_N2 reaction of thiophenoxide with 1,3-dimethyl-2-phenylbenzimidazolium cation (eq 13).[6]



The initiated reduction of phenyl disulfide by DMBI via a free-radical chain sequence can be rationalized by the mechanistic scheme in Scheme III.

A similar radical chain sequence was proposed for the reduction of ArSSAr by *N*-benzyl-1,4-dihydronicotinamide (BNAH).[7]

The chain propagation steps involve hydrogen abstraction by PhS• from DMBI and the regeneration of PhS• from PhSSPh by electron transfer from the DMBI radical. Since the first step in the reaction sequence is no doubt reversible (eq 9, Scheme III), the chain conversion of PhSSPh to PhSH is inefficient since the dimerization of PhS• limits the propagation of the chain, eq 9. In the mechanistic scheme the thiyl radical is regenerated via either electron-transfer fragmentation (eqs 14 and 15) or an S_H2 attack at sulfur (eq 16).[8] S_H2 displacement on sulfur (eq 16), although attractive, is less likely since displacement at sulfur by a tertiary radical would likely be sterically unfavorable.[9]

Table III. PhSH-Promoted Reduction of $PhCOCMe_2SO_2Tol$-*p* (V) and $PhCOCMe_2SPh$ (IV) by DMBI

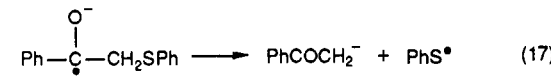
reaction	substrate	condns[a]	product (%) PhCOC-HMe_2
22	IV	60 h, 5% AIBN[b]	16.0
23		43 h, 6 equiv of PhSH, 5% AIBN	94.1
24	V	45 h, 2% AIBN	4.4
25		45 h, 2 equiv of PhSH, 8% AIBN	61.4

[a] 2 equiv of DMBI were used in all reactions except where specified. The reactions were carried out in THF at 61 °C [substrate] = 0.05 M. [b] 1.2 equiv of DMBI were used.

Thiophenol-Promoted DMBI Reduction of α-Phenylthio- and α-(*p*-Toluenesulfonyl)isobutyrophenones. Since the DMBI reduction of α-halo-, α-(phenylthio)- and α-(*p*-toluenesulfonyl)acetophenones have all been shown to proceed via the same ET hydrogen abstraction chain mechanism,[10] we can reasonably assume that the corresponding tertiary substrates, α-(phenylthio)- and α-(*p*-toluenesulfonyl)isobutyrophenones IV and V would show a similar reactivity toward DMBI as that of α-haloisobutyrophenones. Table III summarizes the results of the DMBI reductions of IV and V in the absence and presence of thiophenol.

The initiated (AIBN) reductions of IV and V in the absence of PhSH proceed sluggishly to give low yields of isobutyrophenone. As in the DMBI reductions of IIIa,b reductions of IV and V could be promoted by PhSH, see Table III. These results are consistent with the ET free-radical chain mechanism shown in Scheme II for the PhSH-promoted DMBI reductions of IIIa,b (Scheme II, X = SPh or *p*-$TolSO_2$).

The results of the DMBI reductions of IV and V support the proposal made by Russell[11] that the ketyl radical anions of α-thiylketones cleave to give an enolyl radical and a thiolate anion (eq 11, Scheme II, X = SPh). However, α-phenylthio ketone radical anions have been proposed to undergo cleavage to give an enolate ion and a thiyl radical (eq 17);[12] however no direct evidence was presented for this suggestion.



Cleavage to give the enolate anion might be consistent with a mechanism which involves thiol-promoted reduction, see Scheme IV.

Scheme IV

$$\text{(a) } ZH + PhSH \rightleftharpoons ZH_2^+ + PhS^- \quad (18)$$

$$PhCOCR_2SPh + PhS^- \rightarrow PhCOCR_2SPh^{\bullet -} + PhS^\bullet \quad (19)$$

$$PhCOCR_2SPh^{\bullet -} \rightarrow PhCOCR_2^- + PhS^\bullet \quad (20)$$

$$PhCOCR_2^- + PhSH \rightarrow PhCOCR_2H + PhS^- \quad (21)$$

(5) Stone, P. G.; Cohen, S. G. *J. Phys. Chem.* **1981**, *85*, 1719.
(6) A closely related example is the demethylation of 7-methylguanosine by lithium 2-methylpropane-2-thiolate in HMPA. Hecht, S. M.; Kozarich, J. W. *J. Chem. Soc., Chem. Commun.* **1973**, 387.
(7) Oae, S.; Nagata, T.; Yoshimura, T.; Fuzimori, K. *Tetrahedron Lett.* **1982**, *23*, 3189.
(8) (a) Pryor, W. A.; Pickering, T. L. *J. Am. Chem. Soc.* **1962**, *84*, 2705. (b) Otsu, T.; Kinoshita, Y.; Imoto, M. *Makromol. Chem.* **1964**, *73*, 225.
(9) Tanner, D. D.; Brownlee, B. G. *Can. J. Chem.* **1973**, *51*, 3366.
(10) Tanner, D. D.; Chen, J. J.; Chen, L.; Luelo, C. *J. Am. Chem. Soc.*, in press.
(11) Russell, G. A.; Mikol, G. J. *J. Am. Chem. Soc.* **1966**, *88*, 5498.
(12) (a) Fox, M. A.; Triebel, C. A. *J. Org. Chem.* **1983**, *48*, 835. (b) Kunugi, A.; Muto, A.; Mirai, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1262.

or alternatively

$$\text{(b)}\ PhCOCR_2SPh + Z^{\bullet} \rightarrow Z^{+} + PhCOCR_2SPh^{\bullet -} \quad (22)$$

$$PhCOCR_2SPh^{\bullet -} \rightarrow PhCOCR_2^{-} + PhS^{\bullet} \quad (20)$$

$$PhS^{\bullet} + ZH \rightarrow PhSH + Z^{\bullet} \quad (23)$$

$$PhCOCR_2^{-} + PhSH \rightarrow PhCOCR_2H + PhS^{-} \quad (21)$$

Reduction by the sequence given in Scheme IVa uses DMBI as a base only, while in the mechanism depicted in Scheme IVb DMBI is a hydrogen atom source and its radical acts as an electron-transfer agent. Both alternative mechanisms describe a radical-chain process. The sequence outlined in Scheme IVa could easily be tested since an alterntive proton acceptor should facilitate the reduction.

When the sulfide IV was allowed to react with thiophenol in the presence of a tertiary amine, triethylamine (TEA), no reduction product was observed. The thiol-promoted DMBI reduction of IV, Scheme IVa, can, therefore, be eliminated as the mechanistic pathway leading to reduction product. Scheme IVb is also proposed to proceed via an enolate anion; however, in this scheme catalysis by thiolate is not required; i.e., PhSH only serves as a proton source after the product determining cleavage (eq 21). The proposal[12] that sulfide cleavage of the ketyl of IV proceeds by a mechanism involving an enolate anion (eq 20) is not consistent with (DMBI/PhSH) catalysis. Ketyl cleave to give an enolate anion, eq 17, is therefore not a viable pathway.

Reaction of α-Haloisobutyrophenones with Thiophenol in the Presence of Triethylamine (TEA). Since α-(phenylthio)isobutyrophenone (IV) was formed by a heterolytic pathway during PhSH-promoted DMBI reductions of the α-haloisobutyrophenones (IIIa,b), the reaction of IIIa,b with another tertiary amine, triethylamine (TEA), in the presence of PhSH was investigated. The results of these studies are shown in Table IV.

The reaction of α-bromoisobutyrophenone (IIIa) with $PhSH/NEt_3$ in THF and CH_3CN gave both reduction and substitution products (reactions 26–32). The ratio of these two products depends upon the solvent used; more reduction product was observed in THF than in the more polar solvent, CH_3CN. Moreover, the reaction proceeds much more readily in CH_3CN than in THF. Control experiments showed that the reduction product did not arise from the substitution product IV since IV was unreactive under the condition of the reaction. Similarly, IIIa is unreactive toward TEA in the absence of PhSH (rt, CH_3CN, 10 h). In both solvents, the reactions carried out in the presence of either dinitrobenzene (DNB) or molecular oxygen are not inhibited, nor is the product distribution affected (reactions 27, 29, 30, and 32, Table IV).

The reaction of α-chloroisobutyrophenone (IIIb) proceeded more slowly than that of IIIa (reactions 33–39). In both THF and CH_3CN no reduction product was observed. The reaction of IIIb was not affected by DNB or oxygen.

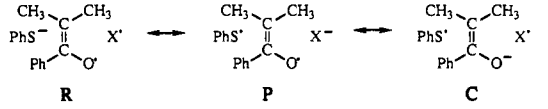
Since the mechanism for the formation of the substitution product is proposed to be a heterolytic process, substitution reactions of the halo ketones at the least hindered carbon should be favored. In accord with this proposal the ratio of substitution vs reduction products for the TEA/PhSH reaction of Ia, IIa, and IIIa show this reactivity pattern, Table V.

When a weaker base, *N,N*-dimethylaniline (DMA), was used in the reaction of IIIa with PhSH, the reaction proceeded more slowly (compare reactions 40 and 26, Table IV). Qualitatively, this observation is consistent with a reaction mechanism for TEA/PhSH halo ketone reactions where PhS^- is involved in the rate-determining step. Since neither inhibition nor initiation was observed, there is no evidence that a radical chain process is involved in the reaction.

Substitution products are most likely formed by an $S_N2(C)$ process, see eq 24.

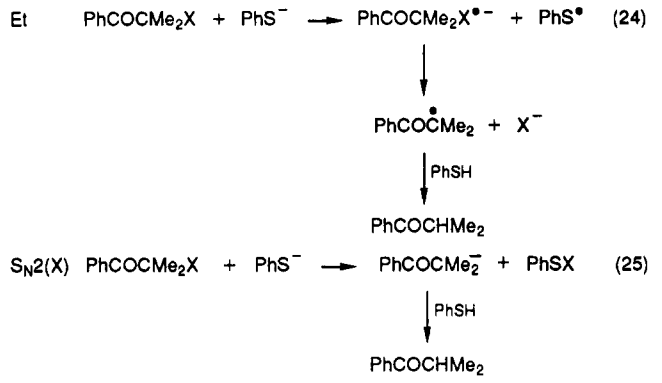
$$PhCOCR^1R^2X + PhS^{-} \rightarrow PhCOCR^1R^2SPh + X^{-} \quad (24)$$

Although the direct S_N2 substitution on tertiary carbon in pure aliphatic systems is extremely rare because of a competing S_N1 reaction, tertiary α-halocarbonyl compounds are believed to undergo S_N2 reactions.[13] Since the S_N1 reaction is retarded by the electron-withdrawing carbonyl, a valence-bonding configuration mixing model has been proposed to account for the enhanced S_N2 reactivity of α-halo ketones. This model might also explain the relative insensitivity of the S_N2 reaction of α-halo ketones to steric effects. For the substitution reaction of thiophenoxide with α-haloisobutyrophenones three configurations (R, P, and C) are used to build the S_N2 reaction



profile. The enolate configuration (C), which is impossible for pure alkyl halides makes an important contribution to the transition state and decreases the steric effect associated with the usual S_N2 reaction.

The reduction product formed from the reaction of PhS^- and $PhCOCMe_2X$ (IIIa–b) could be formed by an electron transfer (ET) sequence, eq 24, or by a nucleophilic substitution on the halogen atom (SN2(X)),[15] eq 25. Although



these two processes have been proposed for the reactions of PhS^- or other nucleophiles with α-substituted alkyl halides,[16–19] we have no direct evidence to support or differentiate between these two mechanistic pathways.

The competition between $S_N2(C)$ and ET or $S_N2(X)$ is controlled by steric crowding at the α-carbon and the halide being substituted. $S_N2(C)$ substitution is favored for the less sterically hindered primary and secondary keto

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(19) Beadle, C. D.; Bowman, W. R.; Prousek, J. *Ibid.* **1984**, *25*, 4979.

Table IV. Reaction of $PhCOCMe_2X$ (IIIa,b) with $PhSH/NEt_3$

X	reaction	solvent	condns[a]	$PhCOCHMe_2$	$PhCOCMe_2SPh$	$PhCOCMe_2X$
Br	26	THF	1 h	55.2	18.5	22.1
	27		1 h, 5% *p*-DNB	53.8	20.8	26.3
	28		20 min	39.1	11.7	41.0
	29		20 min, 100% *m*-DNB	36.3	12.3	51.5
	30	CH_3CN	O_2,[b] 1 min	2.4	99	
	31		2.5 min	3.5	98	
	32		67% *p*-DNB	2	97	
Cl	33	THF	18 h		6.5	98.8
	34		17 h[d]		15.3	87.4
	35		86 h[d]		54.3	44.6
	36	CH_3CN	12 min		26.9	68
	37		12 min, O_2[b]		26	75.7
	38		12 min, 6% *m*-DNB		31.3	69.6
	39		50 min		86.0	5.7
Br	40	HF	DMA,[c] 64 h[d]	8.3	2.8	79.7

[a] All reactions were carried out at room temperature in degassed solvents unless specified with $[PhCOCMe_2X]:[PhSH]:[NEt_3] = 1:2:2$ [IIIa,b] = 0.05 M. [b] In the presence of air. [c] *N,N*-Dimethylaniline (DMA) was used instead of TEA. [d] The returns were carried out at 61 °C.

Table V. Reaction of $PhCOC(R_1)(R_2)Br$ with TEA/PhSH in THF in 23 °C

reactants	reaction time[a] (min)	products	ratio
Ia	0.8	$PhCOCH_3/PhCOCH_2SPh$	0/100
IIa	12	$PhCOCH_2(CH_3)$/ $PhCOCHCH_3SPh$	0/100
IIIa	60	$PhCOCH(CH_3)_2/PhCOC(CH_3)_2SPh$	55/100

[a] All the reactions were carried out in THF at room temperature under oxygen. [Reactant] = 0.05 M; $[PhSH] = [NEt_3]$ = 0.1 M.

halides. The ET or $S_N2(X)$ pathways are more favorable for the bromides than for the chlorides. Only in the case of the sterically hindered bromo ketone IIIa is the $S_N2(C)$ pathway in competition with either the ET (or $S_N2(X)$) pathway.

Experimental Section

Materials. The preparation or purification of α-haloisobutyrophenones, isobutyrophenone, 1,3-dimethyl-2-phenylbenzimidazoline, 1,3-dimethyl-2-phenylbenzimidazolium iodide, and *p*-di-*tert*-butylbenzene has been described previously.[2] THF (Aldrich HPLC grade) was freshly distilled from $LiAlH_4$, and CH_3CN (Aldrich, HPLC grade) was distilled from CaH_2.

Phenyl disulfide (Eastman) was recrystallized from ethanol whereas hexamethylbenzene (Aldrich) from ether.

Thiophenol, thioanisole, and 1-methyl-2-phenylbenzimidazole were obtained from Aldrich and used as received.

α-(Phenylthio)isobutyrophenone was prepared according to the literature procedure:[20] bp 160–170 °C (3.5 mmHg) [lit.[20] 141 °C (0.45 mmHg)]; ^1H NMR δ 1.6 (s, 6 H), 7.25–7.6 (m, 8 H), 8.2–8.32 (m, 2 H); MS *m/e* 256 (M^+), 238, 223, 151, 105, 91, 77, 51, 41, and 28.

General Procedure for the Reaction of α-Substituted Isobutyrophenones with Thiophenol in the Presence of Triethylamine or DMBI. An aliquot of a THF solution of the ketone (0.05 M), a standard (*p*-di-*tert*-butylbenzene or hexamethylbenzene, 0.02 M), the amine (DMBI or Et_3N, 0.1 M), PhSH (0.1 M), and the additive was placed in a reaction ampoule, degassed, sealed under vacuum, and thermostated at the specified temperature for the specified time (see Tables I–IV). The ampoule was opened and analyzed by GC using a HP5840A gas chromatograph interfaced to a HP5840A integrator. A stainless steel column (20 ft × $^1/_4$ in.) packed with 5% SE-30 on chromsorb WAW DMCS 60/80 mesh was used. The area ratios were converted to concentration ratios by using standard calibration curves constructed from known mixtures of reactants and products. The yields listed in Tables I–IV were calculated from the curves. Products were identified by a comparison of their retention times, GC/MS and GC/IR spectra with those of authentic samples.

General Procedure for the Reduction of Disulfides by DMBI. An aliquot of a THF solution of PhSSPh (0.05 M), *p*-di-*tert*-butylbenzene (0.02 M), DMBI (0.05 M), and the additive was placed in a reaction ampoule. The same procedure as was used for the reduction of α-haloisobutyrophenone was followed. A partially soluble light yellow salt, 1,3-dimethyl-2-phenylbenzenedazolium phenylthiolate (IV), precipitated from the reaction mixture and was isolated by filtration: mp 121–132 °C; ^1H NMR δ 3.86 (6 H), 7.3–8.0 (m, 14 H). Although no direct evidence for the saltlike structure is available the chemcial shifts of the protons in IV are identical to those of its perchlorate salt.

(20) Russell, G. A.; Ros, F. *J. Am. Chem. Soc.* 1985, *107*, 2506.