peroxide (0.006 M) in 2,3-dimethylbutane was refluxed overnight in a 100-mL round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a calcium chloride drying tube. The products were determined as above. These values are also included in Table V.

Acknowledgment is made for a Faculty Development Grant for research from Missouri Southern State College for support of this project.

Registry No. Cyclohexane, 110-82-7; toluene, 108-88-3; cycloheptane, 291-64-5; cyclooctane, 292-64-8; cyclopentane, 287-92-3; 2,3-dimethylbutane, 79-29-8; 2,2,3,3-tetramethylbutane, 594-82-1; perdeuteriocyclohexane, 1735-17-7; 1-chlorobutane, 109-69-3; *p*-xylene, 106-42-3; *m*-xylene, 108-38-3; *p*-chlorotoluene, 106-43-4; *m*-cyanotoluene, 620-22-4; *m*-nitrotoluene, 99-08-1; *p*-nitrotoluene, 99-99-0; chlorosulfonylisocyanate, 1189-71-5.

Coupling of Enolates of Phenones with 2-Chloro-2-nitropropane[1]

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Lithium enolates of acetophenone, α-methoxyacetophenone, propiophenone, meta- or para-substituted propiophenones, butyrophenone, isovalerophenone, 1-phenyl-1-hexanone, 1-indanone, 1-tetralone, or 1-benzosuberone react with 2-chloro-2-nitropropane in THF by free radical chain processes to produce $ArCOCH(CMe_2NO_2)R$ or $ArCOC(R)=CMe_2$ and when $R \neq H$ the product of oxidative dimerization, $[ArCOC(R)-]_2$. The enolate anion of deoxybenzoin yields in a free radical chain process only the dimerization product.

The radical chain substitution process of Scheme I,[2,3] which has been labeled $S_{RN}1$,[4] has been reported for geminal halo nitroalkanes ($R_2C(NO_2)X$) and N^- = nitroalkane anions,[2,5] enolates of β-dicarbonyl or β-cyano carbonyl compounds,[6,7] malonitriles,[6] aryl thiolates and sulfinates,[8-10] and dialkyl phosphite or thiophosphite anions.[11,13] Similar reactions have been reported in most instances with X = NO_2[5,6,10,12,13] or $ArSO_2$.[9,11,13,14] Lithium enolates of monoketones in THF will also participate in free radical chain substitutions of geminal halo nitroalkanes.[15,16]

Scheme I

$$R_2C(NO_2)X^{-\cdot} \longrightarrow R_2\dot{C}NO_2 + X^-$$

$$R_2\dot{C}NO_2 + N^- \longrightarrow R_2C(NO_2)N^{-\cdot}$$

$$R_2C(NO_2)N^{-\cdot} + R_2C(NO_2)X \longrightarrow R_2C(NO_2)N + R_2C(NO_2)\dot{X}^{-\cdot}$$

Scheme II

$$Me_2C(NO_2)X^{\bullet-} + E^- \longrightarrow \left[X^- + Me_2C{=}NO_2^- + E\bullet\right] \longrightarrow \begin{cases} E\text{-}CMe_2NO_2^{\bullet-} + X^- \\ E\bullet + Me_2C{=}NO_2^- + X^- \end{cases}$$

$$E\bullet + E^- \longrightarrow E\text{-}E^{\bullet-}$$

$$E\text{-}CMe_2NO_2^{\bullet-} + Me_2C(NO_2)X \longrightarrow Me\,C(NO_2)X^{\bullet-} + E\text{-}CMe_2NO_2$$

$$E\text{-}E^{\bullet-} + Me_2C(NO_2)X \longrightarrow Me\,C(NO_2)X^{\bullet-} + E\text{-}E$$

The coupling product **1** (eq 1) is accompanied by the elimination product **2** (eq 2) and the enolate dimerization product (**3**) which is also formed by a free radical chain process (eq 3).[16] The ratio of (1 + 2)/3 depends not only

$$Me_2C(NO_2)X + R'C(OLi){=}CHR \rightarrow \underset{\mathbf{1}}{R'COCH(R)CMe_2NO_2} + LiX \quad (1)$$

$$1 + B^- \rightarrow \underset{\mathbf{2}}{R'COC(R){=}CMe_2} + NO_2^- + HB \quad (2)$$

$$Me_2C(NO_2)X + R'C(OLi){=}CHR \rightarrow \underset{\mathbf{3}}{[R'COCHR-]_2} + Me_2C{=}NO_2Li + LiX \quad (3)$$

upon R and R′ but also on the nature of X, with X = NO_2

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or $ArSO_2$ favoring the formation of the enolate dimerization product.[16] This has led to the suggestion that the reaction proceeds via the mechanism of Scheme II with enolates of monoketones (E^-).[17]

We have applied this reaction to a series of enolates of phenones leading to the aroyl derivatives **a–o**. Table I lists the observed yields of **1–3** under a variety of conditions.

$Y\text{-}C_6H_4COCHRCMe_2NO_2$ (1) $Y\text{-}C_6H_4COC(R)=CMe_2$ (2) $[Y\text{-}C_6H_4COCHR\text{-}]_2$ (3)

a, Y = R = H
b, Y = H, R = OMe
c, Y = H, R = Me
d, Y = *p*-MeO, R = Me
e, Y = *m*-Et_2N, R = Me
f, Y = *p*-Me, R = Me
g, Y = *p*-Cl, R = Me
h, Y = *m*-Cl, R = Me
i, Y = *p*-Br, R = Me
j, Y = *p*-CN, R = Me
k, Y = *m*-NO_2, R = Me
l, Y = H, R = Et
m, Y = H, R = *i*-Pr
n, Y = H, R = *n*-Bu
o, R = H, R = Ph

The free-radical processes responsible for reactions of 1 and 3 were completely inhibited by the presence of 5–10 mol % of $(t\text{-Bu})_2NO\cdot$. Photostimulation had a significant effect on the rate of reactions 1 and 3 at low temperatures, but at room temperature there was little effect of sunlamp irradiation. Spontaneous initiation presumably involves electron transfer between the enolate anion and $Me_2C(NO_2)Cl$ to initiate the chain reaction without evidence of an intermediate charge-transfer complex.

The ratio of coupling products (1 + 2) to enolate dimerization product (3) decreases from acetophenone (where only coupling was observed) to propiophenone ($(1 + 2)/3 \cong 6$ at 0 °C) to isovalerophenone ($(1 + 2)/3 \cong 1$ at 0 °C) to deoxybenzoin where only the enolate dimerization product is observed. The ratio of $(1 + 2)/3$ was higher at lower temperatures which may reflect the tendency for escape of radicals from the cage in Scheme II. With para-substituted propiophenones the overall yield from reaction 1 was increased by inverse addition, i.e., when the solution of the enolate anion was added dropwise to the 2-chloro-2-nitropropane.

Although the coupling reaction of meta- and para-substituted propiophenones occurred readily with a variety of substituents, functional groups in the α-position of acetophenone somehow prevented the reaction from occurring with the exception of the α-methoxy substituent. For $PhC(OLi)=CHY$ reacting with $Me_2C(NO_2)Cl$, little or no reaction occurred for Y = PhS, $PhSO_2$, $MeSO_2$, MeSO, Et_2N, NC, Cl, NO_2, and starting reagents were recovered in high yield. Apparently in these cases the intermediate radical (PhCOCHY) was unable to maintain the chain reaction depicted in Scheme II. The hindered enolate anions from isobutyrophenone or 3,3-dimethylbutyrophenone also failed to undergo reactions 1–3 under the conditions of Table I. Since the amount of dimerization to form 3 increases with steric hindrance of E^-, we would have expected these enolate anions to yield mainly 3. Their failure to react in the chain process may be a result of the inefficiency of the reaction, $E\cdot + E^- \rightarrow E\text{–}E^-\cdot$, when E· is sterically hindered. As a test of this interpretation we studied the reaction of the sterically hindered but easily oxidized enolate anion from 3,3-dimethylbutyrophenone with $Me_2C(NO_2)Cl$ in the presence of the unhindered pinacolone enolate anion. Consistent with the supposition that $t\text{-BuC(OLi)=CH}_2$ but not PhC(OLi)=CHBu-*t* would trap a sterically hindered E·, the only enolate dimerization product formed was the mixed dimer 4 in a yield of 40% (eq 4).

$$PhC(OLi)=CHBu\text{-}t + t\text{-BuC(OLi)=CH}_2 + Me_2C(NO_2)Cl \xrightarrow[10\text{–}30\ ^\circ C,\ 1\ h,\ h\nu]{THF\ (60\%)\text{–}hexane\ (40\%)} PhCOCH(t\text{-Bu})CH_2COBu\text{-}t + Me_2C{=}NO_2Li + LiCl \quad (4)$$

4

In the absence of reactions 1–3, hindered enolate anions reacted with $Me_2C(NO_2)Cl$ to give displacement (S_N2) on halogen (eq 5) in solvents such as THF (53%)–hexane (34%)–HMPA (13%). Reaction 5 with X = Cl was also

$$PhC(OLi)=C(R_1)(R_2) + Me_2X(NO_2)X \rightarrow Me_2C{=}NO_2^- + PhCOC(R_1)(R_2)X \quad (5)$$

5a, X = Cl; R_1 = H; R_2 = *t*-Bu, (78%)
5b, X = Cl; $R_1 = R_2$ = Me (69%)
5c, X = NO_2; R_1 = H; R_2 = Me
5d, X = *p*-$MePhSO_2$; R_1 = H; R_2 = Me

observed in THF for the enolate ion of isovalerophenone particularly when reactions 1 and 3 were inhibited by the presence of $(t\text{-Bu})_2NO\cdot$ (Table I). Although propiophenone enolate failed to yield significant amounts of 5 with X = Cl, the formation of $PhCOCH(CH_3)NO_2$ and $PhCOCH(CH_3)SO_2PhMe\text{-}p$ was observed in reactions with $Me_2C(NO_2)_2$ and *p*-$MePhSO_2CMe_2NO_2$. Nitro group transfer was prevously reported in the reaction of $t\text{-BuC(OLi)=CH}_2$ with $Me_2C(NO_2)_2$ in THF in the presence or absence of $(t\text{-Bu})_2NO\cdot$ and presumably occurs by an ionic process involving nucleophilic addition to the nitrogen atom of the nitro group.[16] The formation of *p*-$MePhSO_2CH(CH_3)COPh$ is more surprising. It is possible that the keto sulfone might be a side product of Scheme II wherein the caged intermediates $|p\text{-}MePhSO_2^-\ Me_2C{=}NO_2^-\ PhCOCHCH_3|$ can collapse to $p\text{-}MePhSO_2CH(CH_3)COPh^-\cdot$ which is oxidized to the keto sulfone by electron transfer to *p*-$MePhSO_2CMe_2NO_2$. Alternately, the keto sulfone might be formed by attack of the free enolate radical on the sulfinate anion.

Small amounts of $O_2NCMe_2CMe_2NO_2$ (6) were observed in certain of the reactions, particularly when $Me_2C{=}NO_2^-$ was added to the reaction mixture or was produced by reaction 5. Presumably the major source of 6 is the known $S_{RN}1$ process of eq 6.[2] An advantage of using the Li^+/THF system is that the ion pair, $Me_2C{=}NO_2^-Li^+$, has a relatively low reactivity to homolytic attack. Thus, although toward $Me_2\dot{C}NO_2$ the relative reactivities of $(EtO_2C)_2CMe^-$ and $Me_2C{=}NO_2^-$ are 10:1 in Me_2SO (K^+[2.2.2]cryptand counterion), the relative reactivities in THF of the lithium ion pairs are >70:1. Since experiments with added $Me_2C{=}NO_2^-Li^+$ in THF in Table I do not give an enhanced yield of the coupling product 1, it appears that the attack of an enolate radical upon $Me_2C{=}NO_2^-Li^+$ in the presence of E^- can be discounted as a viable route to $1^-\cdot$.

$$Me_2C{=}NO_2^- + XCMe_2NO_2 \xrightarrow{h\nu} O_2NCMe_2CMe_2NO_2 + X^- \quad (6)$$

6

Elimination of the elements of HNO_2 from 1 (eq 2) occurred more readily for **1a** than for the coupling products of propiophenones or butyrophenone (**1c–1l**) and was not a factor in the reactions of isovalerophenone. The elimination could be readily achieved by refluxing 1 in methanol containing 10–20% of NaOH for 6–10 h. Under this condition **1c**, **1f**, or **1l** gave 90–100% yields of the elimination products. In the case of the products from the

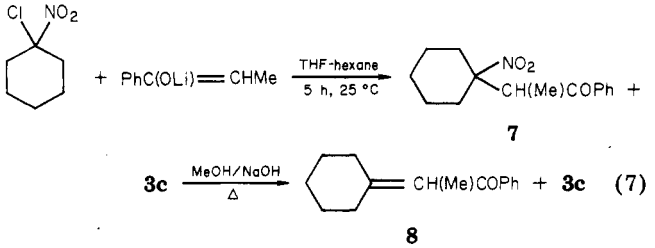
(17) For further discussions of the mechanism of this process, see Russell, G. A.; Mudryk, B.; Ros, F.; Jawdosiuk, M. *Tetrahedron* **1982**, in press.

Table I. Reaction of Y-$C_6H_4C(OLi)=CHR$ with $Me_2C(NO_2)X$ in THF (60%)-Hexane (40%)[a]

Y	R	X	conditions[b]	% yield[c] 1	2	3	5	6
H	H	Cl	−20 °C, 13% HMPA		49, 97,[d] 85[d,e]			
H	OMe	Cl	0-30 °C		66[d]			
H	Me	Cl	32 °C	48	0	37		
H	Me	Cl	25 °C, 10 mol % $(t\text{-Bu})_2NO\cdot$	0	0	0		
H	Me	NO_2	32 °C	10	0	17	24	
H	Me	p-$MePhSO_2$	32 °C	21	0	52	15	
H	Me	p-$MePhSO_2$	32 °C, diluted 5-fold	26	0	47	5	25
H	Me	p-$MePhSO_2$	32 °C, diluted 5-fold, 3 equiv of $Me_2C(NO_2)X$	32	0	54	5	10
H	Me	Cl	0-10 °C	70	0	23		
H	Me	Cl	0-10 °C, diluted 5-fold	78	0	19		
H	Me	Cl	0-10 °C, 2 equiv of $Me_2C(NO_2)Cl$	66	0	22		
H	Me	Cl	0-10 °C, 0.3 equiv of $Me_2C{=}NO_2Li$	52	11	14		
H	Me	Cl	0-10 °C, 13% HMPA	76	4	12		
H	Me	Cl	25 °C, 3 h[e,f]	38	15	12		
p-MeO	Me	Cl	25 °C, 3 h[e,f]	40 (55[g])		13 (0[g])		
m-NEt_2	Me	Cl	25 °C, 3 h[e-g]	50				
p-Me	Me	Cl	25 °C, 3 h[e,f]	43 (52[g])	5 (0[g])	20 (27[g])		
p-Cl	Me	Cl	25 °C, 3 h[e,f]	27 (20[g])	7 (32[g])	14 (26[g])		
m-Cl	Me	Cl	25 °C, 3 h[e,f]	23	23	26		
p-Br	Me	Cl	25 °C, 3 h[e,f]	18	22	9		
p-CN	Me	Cl	25 °C, 3 h[e,f]	4	31	6		
m-NO_2	Me	Cl	25 °C, 3 h[e,f]	2 (31[g])	26 (21[g])	7		
H	Et	Cl	32 °C, 4 h[e]	35		33		
H	Et	Cl	0-10 °C	74		13		
H	n-Bu	Cl	32 °C, 4 h[e]	38		30		
H	i-Pr	Cl	32 °C	4		66		
H	i-Pr	Cl	32 °C[f]			68		
H	i-Pr	Cl	25 °C, 10 mol % $(t\text{-Bu})_2NO\cdot$	0	0	0		
H	i-Pr	Cl	0 °C, 13% Me_2SO	24		32	9	
H	i-Pr	Cl	0 °C, 13% Me_2SO, 10 mol % $(t\text{-Bu})_2NO\cdot$[f]	0	0	0	29	3
H	i-Pr	Cl	0-30 °C, 13% HMPA	35		42	2	28
H	i-Pr	Cl	0-10 °C, 13% HMPA, 2 equiv of $Me_2C(NO_2)Cl$	25		37	7	20
H	i-Pr	Cl	0-30 °C, 13% HMPA, 0.3 equiv of $Me_2C{=}NO_2Li$	29		42	4	36
H	t-Bu	Cl	25 °C, 13% HMPA[f]	0	0	0	78	
H	Ph	Cl	25 °C, 3 h			66		
H	Ph	Cl	25 °C, 3 h, 10 mol % $(t\text{-Bu})_2NO\cdot$[f]	0	0	0		
H	Ph	Cl	25 °C, 24 h[e,f]	0	0	82		

[a] The enolate was generated by reaction of n-butyllithium in hexane with $(i\text{-Pr})_2NH$ in THF at −60 to −70 °C followed by reaction with the ketone at −20 to −30 °C to give a solution of 0.5-1 M in lithium enolate which was reacted with 1 equiv of $Me_2C(Cl)NO_2$ while irradiated with a 275-W sunlamp. [b] Cosolvent in vol %; standard reaction time was 1 h. [c] Yields by ^1H NMR with internal standard. [d] Two equivalents of enolate, yield based on $Me_2C(NO_2)Cl$. [e] Isolated yields. [f] Reactions performed without direct irradiation. [g] Enolate added dropwise to $Me_2C(NO_2)Cl$ in THF.

reaction of 1-chloro-1-nitrocyclohexane with the enolate anion of propiophenone, the coupling product **7** was difficult to separate from **3c**. The crude reaction mixture was thus refluxed with methanolic NaOH to yield **8** (54%), which was easily separated from **3c** (30%) by distillation (eq 7).



(7)

8

The conversion of **1** to **2** can be achieved directly by using 2 equiv of the enolate anion for each equivalent of $Me_2C(NO_2)Cl$.[7] This technique was utilized for the conversion of **9** to **10** where yields (eq 8) are based upon $Me_2C(NO_2)Cl$. In reaction 8, enolate dimerization was not observed for 1-indanone or 1-tetralone but an 18% yield of the oxidative dimerization product (**11c**) was observed for 1-benzosuberone.

Experimental Section

Solvents were distilled from $LiAlH_4$ (THF) or CaH_2(Me_2SO, HMPA) and stored under nitrogen. Diisopropylamine and hexamethyldisilazane were distilled from BaO before use. n-Butyllithium was employed as a 1.55 M solution in hexane (Aldrich Chemical Co.). 2-Chloro-2-nitropropane,[18] 2,2-dinitropropane,[19] and 2-(p-tolylsulfonyl)-2-nitropropane[14,15] were prepared by literature procedures. 1-Chloro-1-nitrocyclohexane was obtained

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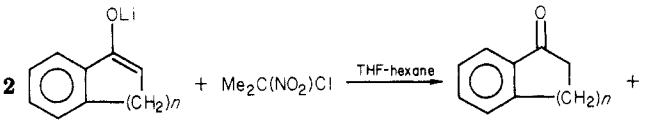
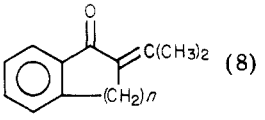


9a, $n = 1$
b, $n = 2$
c, $n = 3$



(8)

10a, 55%
b, 64%
c, 67%

by chlorination of cyclohexanone oxime in CH_2Cl_2 followed by oxidation with HNO_3 in cyclohexane.[29] Isovalerophenone and 3,3-dimethylbutyrophenone were obtained by Friedel–Crafts acylations. The other ketones were obtained from Aldrich Chemical Co. and distilled before use.

Typical Reaction Procedure. A 25-mL three-necked flask equipped with a magnetic stirrer, thermometer, and two rubber septa sealed with Parafilm was flushed with nitrogen via hypodermic needles inserted in the septa. Tetrahydrofuran (5 mL) and 5.2 mmol of diisopropylamine or hexamethyldisilazane were added by syringe, the flask was cooled to −60 °C, and 3.3 mL of 1.55 M *n*-butyllithium 5.1 mmol) in hexane was added by syringe. The flask was kept at −60 °C for 3–5 min, allowed to warm to −10 °C, and then cooled to −30 °C, and the ketone was added dropwise over a 5–10-min period. After 5 min of additional stirring at −30 °C, the cooling bath was removed and the enolate solution allowed to stir for 10–15 min. Additional cosolvents (Me_2SO, HMPA), reagents, or inhibitors were added, and the 2-substituted-2-nitropropane, or its solution in THF for 2,2-dinitropropane or 2-(*p*-tolylsulfonyl)-2-nitropropane, was injected by syringe and the reaction conducted under a small positive pressure of N_2 with a 275-W sunlamp 20–30 cm from the reaction flask. After the desired reaction period, the products were poured into a separatory funnel with 100 mL of water or brine and 40 mL of ether. The ethereal layer was separated and the water layer extracted twice with 15 mL of ether. The combined ether extracts were washed with 25 mL of 0.25 N hydrochloric acid to remove diisopropylamine. When 2,2-dinitropropane or 2-(*p*-tolylsulfonyl)-2-nitropropane were the reactants, the aqueous layer was initially neutralized with dilute hydrochloric acid to assure the extraction of the α-nitro- or α-(*p*-tolylsulfonyl) ketone. The ethereal extracts were dried ($MgSO_4$) and rotary evaporated to give a reaction mixture in which the major products were identified by ^1H NMR, GC, or GS/MS spectroscopy. Pure samples of the reaction products were isolated in all cases by distillation or crystallization from larger scale experiments. The analyses reported in Table I were obtained by complete removal of all the solvent from the reaction product by vacuum evaporation and addition of a known quantity of phthalide as an internal standard. The product yields were then calculated from the integrated ^1H NMR (60 MHz) spectra in $CDCl_3$ of the previously identified products.

2,3-Dimethyl-3-nitro-1-phenyl-1-butanone (1c): bp 105–108 °C (0.1 torr); mp 78.5–79.5 °C; ^1H NMR ($CDCl_3$) δ 1.16 (d, J = 8 Hz, 3 H), 1.59 (s, 3 H), 1.68 (s, 3 H), 4.35 (q, J = 8 Hz, 1 H), 7.3–7.6 (m, 3 H), 7.85–8.05 (m, 2 H); IR ($CHCl_3$) 1355, 1548, 1692 cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.21; H, 6.84; N, 6.21.

2,3-Dimethyl-3-nitro-1-(*p*-anisyl)-1-butanone (1d): bp 180–200 °C (0.01 torr); mp 64.5–65.5 °C; ^1H NMR (CCl_4) δ 1.20 (d, J = 7.5 Hz, 3 H), 1.65 (s, 3 H), 1.68 (s, 3 H), 3.87 (s, 3 H), 4.37 (q, J = 7.5 Hz, 1 H), 7.40 (q, J_{AB} = 9 Hz, ν_{AB} = 0.75 ppm, 4 H); IR (KBr) 1345, 1370, 1580, 1600 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.65; H, 6.84; N, 5.71.

2,3-Dimethyl-3-nitro-1-[*m*-(diethylamino)phenyl]-1-butanone (1e): bp 166–172 °C (0.6 torr); ^1H NMR (CCl_4) δ 1.08 (s, t, J = 8 Hz, 9 H), 1.64 (s, 6 H), 3.2 (q, J = 8 Hz, 4 H), 6.70–7.30 (m, 4 H); IR (CCl_4) 1330, 1365, 1575, 1660 cm^{-1}. Anal. Calcd for $C_{14}H_{19}N_2O_3$: C, 65.96; H, 7.96; N, 9.61. Found: C, 66.86; H, 8.40; N, 9.16.

2,3-Dimethyl-3-nitro-1-(*p*-tolyl)-1-butanone (1f): bp 126–140 °C (0.8 torr); mp 85.5–86.5 °C; ^1H NMR (CCl_4) δ 1.15 (d, J = 8 Hz, 3 H), 1.58 (s, 3 H), 1.70 (s, 3 H), 2.40 (s, 3 H), 4.30 (q, J = 8 Hz, 1 H), 7.49 (q, J_{AB}) = 8 Hz, ν_{AB} = 0.63 ppm, 4 H); IR (KBr) 1330, 1525, 1680 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.32; H, 7.30; N, 5.90.

2,3-Dimethyl-3-nitro-1-(*p*-chlorophenyl)-1-butanone (1g): bp 140–180 °C (0.2 torr); mp 113.5–114.5 °C; ^1H NMR (CCl_4) δ 1.20 (d, J = 8 Hz, 3 H), 1.67 (s, 3 H), 1.73 (s, 3 H), 4.27 (q, J = 8 Hz, 1 H), 7.63 (q, J_{AB} = 8 Hz, ν_{AB} = 0.38 ppm, 4 H); IR (KBr) 1750, 1530, 1675 cm^{-1}. Anal. Calcd for $C_{12}H_{14}ClNO_3$: C, 56.37, H, 5.52; N, 5.48; Cl, 13.86. Found: C, 56.39; H, 5.66; N, 5.52; Cl, 13.85.

2,3-Dimethyl-3-nitro-1-(*p*-bromophenyl)-1-butanone (1i): bp 150–165 °C (0.6 torr); mp 110.5–111.5 °C; ^1H NMR (CCl_4) δ 1.18 (d, J = 8 Hz, 3 H), 1.62 (s, 3 H), 1.70 (s, 3 H), 4.28 (q, J = 8 Hz, 1 H), 7.70 (q, J_{AB} = 8 Hz, ν_{AB} = 0.21 ppm, 4 H); IR (KBr) 1340, 1530, 1675 cm^{-1}. Anal. Calcd for $C_{12}H_{14}BrNO_3$: C, 48.02; H, 4.70; N, 4.67; Br, 26.02. Found: C, 48.03; H, 4.74; N, 4.67; Br, 27.36.

2,3-Dimethyl-3-nitro-1-(*m*-nitrophenyl)-1-butanone (1k): mp 83–85 °C; ^1H NMR δ 1.18 (d, J = 8 Hz, 3 H), 1.70 (s, 6 H), 4.27 (q, J = 8 Hz, 1 H), 7.4–8.3 (m, 4 H); IR (KBr) 1435, 1465, 1535, 1690 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_5$: C, 54.13; H, 5.30; N, 10.52. Found: C, 54.17; H, 5.16; N, 10.30.

2-(2-Nitro-2-propyl)-1-phenyl-1-butanone (1l): bp 118–122 °C (0.1 torr); ^1H NMR ($CDCl_3$) δ 0.79 (t, J = 10.5 Hz, 3 H), 1.46 (s, 3 H), 1.65 (s, 3 H), 1.85 (m, 2 H), 4.33 (d,d, J = 3.5, 10.5 Hz, 1 H), 7.35–7.55 (m, 3 H), 7.90–8.05 (m, 2 H); IR (neat) 1352, 1548, 1685 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.48; H, 7,38; N, 5.86.

2-(2-Nitro-2-propyl)-3-methyl-1-phenyl-1-butanone (1m): bp 115–125 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 0.80 (d, J = 6.5 Hz, 3 H), 0.93 (d, J = 6.5 Hz, 3 H), 1.48 (s, 3 H), 1.85 (s, 3 H), 2.1 (m, 1 H), 4.50 (d, J = 6.5 Hz, 1 H), 7.15–7.65 (m, 3 H), 7.8–8.15 (m, 2 H); IR (neat) 1330, 1550, 1690 cm^{-1}; mass spectrum, m/e (relative intensity) 203.14368 (required for $C_{14}H_{18}O = M^+ - NO_2$, 203.14630, 0.4%), 161 (1), 159 (2.8), 145 (0.9), 105 (100), 77 (37.2), 51 (10).

2-(2-Nitro-2-propyl)-1-phenyl-1-hexanone (1n): bp 126–130 °C (0.1 torr); ^1H NMR ($CDCl_3$) δ 0.73 (t, J = 6.7 Hz, 3 H), 1.15 (m, 4 H), 1.44 (s, 3 H), 1.64 (s, 3 H), 1.8 (m, 2 H), 4.37 (dd, J = 11, 3.1 Hz, 1 H), 7.4–7.7 (m, 3 H), 8.0–8.2 (m, 2 H); IR (neat) 1352, 1545, 1683 cm^{-1}. Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.46; H, 8.03; N, 5.19.

3-Methyl-1-phenyl-2-buten-1-one (2a): bp 77–78 °C (0.9 torr) [lit.[21] bp 133–134 °C (17 torr)]; ^1H NMR ($CDCl_3$) δ 2.00 (d, J = 2 Hz, 3 H), 2.20 (d, J = 2 Hz, 3 H), 6.70 (m, 1 H), 7.2–7.6 (m, 3 H), 7.8–8.2 (m, 2 H); IR (neat) 1620, 1670 cm^{-1}; mass spectrum, m/e (relative intensity) 160.0888 (required for $C_{11}H_{12}O$, 160.08805, 97%), 159 (100), 145 (76), 105 (90), 77 (97), 51 (59).

2-Methoxy-3-methyl-1-phenyl-2-buten-1-one (2b):[22] bp 83–85 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 1.78 (s, 3 H), 1.90 (s, 3 H), 3.37 (s, 3 H), 7.2–7.6 (m, 3 H), 7.8–8.1 (m, 2 H).

2,3-Dimethyl-1-phenyl-2-buten-1-one (2c): bp 76–78 °C (0.3 torr) [lit.[23] bp 134–135 °C (19 torr)]; ^1H NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.83 (s, 3 H), 7.25–7.5 (m, 3 H), 7.7–7.9 (m, 2 H); IR (neat) 1670 cm^{-1}; mass spectrum, m/e (relative intensity) 174.10348 (required for $C_{12}H_{14}O$, 174.10447, 51%), 173 (39), 159 (72), 144 (18), 105 (100), 97 (18), 77 (53).

2,3-Dimethyl-1-(*p*-tolyl)-2-buten-1-one (2f): bp 85–90 °C (0.2 torr); ^1H NMR (CCl_4) δ 1.53 (s, 3 H), 1.77 (s, 6 H), 2.35 (s, 3 H), 7.40 (q, J_{AB} = 8 Hz, ν_{AB} = 0.51 ppm, 4 H); IR (neat) 1590, 1650 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O$: C, 82.92; N, 8.57. Found: C, 82.35; H, 8.57.

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2,3-Dimethyl-1-(*p*-bromophenyl)-2-buten-1-one (2i): bp 130 °C (0.6 torr); ^{1}H NMR (CCl_4) δ 1.55 (s, 3 H), 1.83 (s, 6 H), 7.60 (q, J_{AB} = 9 Hz, ν_{AB} = 0.12 ppm, 4 H); IR (neat) 1575, 1655 cm^{-1}. Anal. Calcd for $C_{12}H_{13}OBr$: C, 56.97; H, 5.18; Br, 31.57. Found: C, 56.55; H, 5.14; Br, 31.86.

2,3-Dimethyl-1-(*p*-cyanophenyl)-2-buten-1-one (2j) was isolated as an oil by column chromatography, using SiO_2 and C_6H_6: ^{1}H NMR (CCl_4) δ 1.58 (s, 3 H), 1.83 (s, 6 H), 7.83 (q, J_{AB} = 8 Hz, 4 H); IR (neat) 1670, 2250 cm^{-1}. Anal. Calcd for $C_{13}H_{13}ON$: C, 78.36; H, 6.58; N, 7.03. Found: C, 79.34; H, 6.53; N, 7.08.

2,3-Dimethyl-1-(*m*-nitrophenyl)-2-buten-1-one (2k): bp 140 °C (0.05 torr); ^{1}H NMR δ 1.67 (s, 3 H), 1.97 (s, 6 H), 7.4–8.9 (m, 4 H).

2-Ethyl-3-methyl-1-phenyl-2-buten-1-one (2l): bp 72–74 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 3 H), 1.49 (s, 3 H), 1.79 (s, 3 H), 2.28 (q, J = 7.4 Hz, 2 H), 7.3–7.55 (m, 3 H), 7.75–8.0 (m, 2 H); IR (neat) 1660 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.91; H, 8.50.

2-Cyclohexylidene-1-phenyl-1-propanone (8) and 2-(1-cyclohexenyl)-1-phenyl-1-propanone (8′)[24] were isolated in a 6:1 ratio by distillation, bp 97–107 °C (0.1 torr); this ratio was established by ^{1}H NMR at δ 1.86 (s, CH_3) for 8 and at δ 1.27 (d, J = 7 Hz, CH_3), 3.96 (q, J = 7 Hz, CH), 5.53 (m, CH) for 8′; IR (neat) 1670 cm^{-1}; mass spectrum m/e (relative intensity) 214.13596 (required for $C_{15}H_{18}O$, 214.13577, 72%), 199 (40), 171 (60), 105 (100), 77 (53).

2-(1-Methyl-1-ethylidene)-1-indanone (10a) was isolated in 52% yield by distillation of the reaction product of 2 equiv of **9a** and 1 equiv of Me_2CNO_2Cl irradiated for 25 min at −40 °C to 0 °C in THF (60%)–hexane (40%): bp 110–112 °C (0.3 torr); mp 101–103 °C (lit.[25] mp 102–103 °C); ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 2.39 (s, 3 H), 3.55 (s, 2 H), 7.2–7.8 (m, 4 H); IR ($CHCl_3$) 1640, 1695 cm^{-1}; mass spectrum, m/e (relative intensity) 172.08835 (required for $C_{11}H_{12}O$, 172.08882, 100%), 158 (55), 130 (64), 129 (30), 77 (13).

2-(1-Methyl-1-ethylidene)-1-tetralone (10b) was isolated in 60% yield by distillation of the reaction mixture of 2 equiv of **9b** and 1 equiv of $Me_2C(NO_2)Cl$ irradiated at 0–30 °C for 75 min in THF (60%)–hexane (40%): bp 91–93 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 3 H), 2.23 (s, 3 H), 2.9 (m, 4 H), 7.1–7.6 (m, 3 H), 8.0–8.2 (m, 1 H); IR (neat) 1610, 1670 cm^{-1}; mass spectrum, m/e (relative intensity) 186.10385 (required for $C_{13}H_{14}O$, 186.10447, 19%), 146 (95), 131 (16), 129 (11), 118 (100), 90 (52).

2-(1-Methyl-1-ethylidene)-1-benzosuberone (10c) was isolated in 60% yield by distillation of the reaction product from 2 equiv of **9c** and 1 equiv of $Me_2C(NO_2)Cl$ irradiated for 2 h at 32 °C in THF (60%)–hexane (40%): bp 100–102 °C (0.1 torr), mp 56–58 °C; ^{1}H NMR ($CDCl_3$) δ 1.92 (s, 3 H), 2.15 (s, 3 H), 1.5–2.5 (m, 4 H), 2.78 (m, 2 H), 7.0–7.45 (m, 3 H), 7.75–8.0 (m, 2 H); IR (neat) 1615, 1665 cm^{-1}; mass spectrum, m/e (relative intensity) 200.12019 (required for $C_{14}H_{16}O$ 200.12012, 100%), 172 (11), 160 (19), 159 (39), 145 (21), 131 (68), 129 (25), 118 (16), 91 (16).

2,3-Dimethyl-1,4-diphenyl-1,4-butanedione (3c) was isolated as the diasteromeric mixture, bp 153–155 °C (0.1 torr), which could be crystallized from hexane to give the meso, mp 67 °C (lit.[26] mp 67 °C), and racemic, mp 83–85 °C (lit.[25] mp 85–86 °C), isomers. The mixture of isomers had the following: ^{1}H NMR ($CDCl_3$) δ 1.18 (d, J = 6.8 Hz, 6 H), 3.82 (m, 2 H), 7.2–7.5 (m, 6 H), 7.7–8.1 (m, 4 H); IR (neat) 1683 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.75; H, 6.88.

2,3-Dimethyl-1,4-di(*p*-anisyl)-1,4-butanedione (3d) was isolated as a single isomer, mp 166–168 °C, by crystallization of a fraction, bp 210–230 °C (0.01 torr): ^{1}H NMR (CCl_4) δ 1.0 (d, J = 16 Hz, 6 H), 3.8 (m, 8 H), 7.4 (q, J_{AB} = 8 Hz, 8 H); IR (KBr) 1660 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_2$: C, 73.60; H, 6.79. Found: C, 73.61; H, 6.80.

2,3-Dimethyl-1,4-di(*p*-tolyl)-1,4-butanedione (3f) was isolated as a mixture of diastereomers, mp 111.5–122.5 °C, from a fraction, bp 210 °C (0.8 torr): ^{1}H NMR (CCl_4) δ 1.20 (d, J = 7 Hz, 6 H), 2.35 (s, 6 H), 3.82 (m, 2 H), 7.46 (q, J_{AB} = 8 Hz, ν_{AB} = 0.65 ppm, 8 H); IR (KBr) 1660 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.64; H, 7.70.

2,3-Dimethyl-1,4-bis(*p*-chlorophenyl)-1,4-butanedione (3g) was obtained as a mixture of diastereomers, mp 130–150 °C, from a fraction, bp 180 °C (0.2 torr): ^{1}H NMR (CCl_4) δ 1.05 (d, J = 8 Hz, 6 H), 3.85 (m, 2 H), 7.63 (q, J = 8 Hz, ν_{AB} = 0.42 ppm, 8 H); IR (KBr) 1660 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.49; H, 4.81; Cl, 21.15. Found: C, 64.41; H, 4.88; Cl, 21.42.

2,3-Dimethyl-1,4-bis(*p*-bromophenyl)-1,4-butanedione (3i): bp 200–230 °C (0.6 torr); ^{1}H NMR δ 1.05, 1.22 (d, J = 6 Hz, 6 H), 3.82 (m, 2 H), 7.42–7.83 (m, 8 H); IR (KBr) 1660 cm^{-1}. Anal. Calcd for $C_{18}H_{16}Br_2O_2$: C, 50.97; H, 3.80; Br, 37.68. Found: C, 51.04; H, 3.77; Br, 37.30.

2,3-Diethyl-1,4-diphenyl-1,4-butanedione (3l)[27] as a mixture of diastereomers had the following: bp 115–160 °C (0.1 torr); mp 85–95 °C; ^{1}H NMR ($CDCl_3$) δ 0.78 (t, J = 7.5 Hz, 6 H), 1.7 (m, 4 H), 3.95 (m, 2 H), 7.3–7.55 (m, 6 H), 7.85–8.10 (m, 4 H); IR ($CHCl_3$) 1682 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.40; H, 7.60.

2,3-Diisopropyl-1,4-diphenyl-1,4-butanedione (3m) was obtained as a mixture of diastereomers: bp 150–157 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 0.85 (d, J = 7 Hz, 6 H), 1.02 (d, J = 7 Hz, 6 H), 2.2 (m, 2 H), 4.31 (m, 2 H), 7.25–7.6 (m, 6 H), 7.8–8.2 (m, 4 H); IR (neat) 1680 cm^{-1}; mass spectrum, m/e (relative intensity) 322.19233 (required for $C_{22}H_{26}O_2$ 322.19329, 2%), 203 (3), 161 (5), 159 (7), 105 (100), 77 (4), 51 (14).

2,3-Di-*n*-butyl-1,4-diphenyl-1,4-butanedione (3n): bp 165–168 °C (0.1 torr); ^{1}H NMR ($CDCl_3$) δ 0.78 (t, J = 6.5 Hz, 6 H), 1.2 (m, 8 H), 1.65 (m, 4 H), 3.90 (m, 2 H), 7.2–7.55 (m, 6 H), 7.8–8.05 (m, 4 H); IR (neat) 1677 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_2$: C, 82.24; H, 8.63. Found: C, 82.37; H, 8.58.

1,2,3,4-Tetraphenyl-1,4-butanedione (3o) was isolated as the racemic isomer by recrystallization from hexane–methanol: mp 148–154 °C (lit.[25] mp 154–160 °C for racemic, 250–251 °C for meso); ^{1}H NMR ($CDCl_3$) δ 5.55 (s, 2 H), 7.07 (s, 10 H), 7.3–7.5 (m, 6 H), 7.85–8.1 (m, 4 H); IR ($CHCl_3$) 1678 cm^{-1}; mass spectrum, m/e (relative intensity) 390.16336 (required for $C_{28}H_{22}O_2$, 390.16198, 1.1%), 371 (1), 285 (2.5), 269 (1.3), 268 (4.5), 179 (2.9), 122 (1.5), 105 (46.7), 79 (51.6), 78 (100), 77 (99.8).

2-*tert*-Butyl-5,5-dimethyl-1-phenyl-1,4-hexanedione (4): bp 100–103 °C (0.3 torr); 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 9 H), 1.15 (s, 9 H), 2.71 (dd, J = 18, 2.6 Hz, 1 H), 3.40 (dd, J = 18, 11.4 Hz, 1 H), 3.84 (dd, J = 11.4, 2.6 Hz, 1 H), 7.3–8.3 (m, 5 H); IR (neat) 1680, 1710 cm^{-1}; mass spectrum, m/e (relative intensity) 274.19317 (required for $C_{18}H_{26}O_2$, 274.19329, 0.02%), 218 (3), 217 (11), 101 (28), 133 (26), 105 (66), 85 (1), 77 (25), 57 (100).

2,2′-Bibenzosuberone (11c) was obtained by crystallization of the distillation residue from the preparation of **10c** from hexane–methanol as material with the following: mp 142–161 °C; IR ($CHCl_3$) 1680 cm^{-1}; mass spectrum, m/e (relative intensity) 318.16062 (required for $C_{22}H_{22}O_2$, 318.16198, 19%), 300 (21), 200 (15), 166 (26), 146 (68), 91 (23), 69 (30), 57 (100).

2-Chloro-3-methyl-1-phenyl-1-butanone. Reaction of the lithium enolate of isovalerophenone with $Me_2C(NO_2)Cl$ in THF (53%)–hexane (332%)–Me_2SO (13%) at 25 °C for 3 h in the presence of 10 mol% of $(t\text{-Bu})_2NO\cdot$ gave the chloro ketone in 35% yield: bp 65–67 °C (0.15 torr); ^{1}H NMR ($CDCl_3$) δ 0.99 (d, J = 6.5 Hz, 3 H), 1.07 (d, J = 6.5 Hz, 3 H), 2.4 (m, 1 H), 4.93 (d, J = 7.2 Hz, 1 H), 7.2–7.7 (m, 3 H), 7.85–8.3 (m, 2 H); IR (neat) 1700 cm^{-1}; mass spectrum, m/e (relative intensity) 198 (0.5), 196.06520 (required for $C_{11}H_{13}OCl$, 196.06550, 1.6%), 154 (2), 105 (100), 77 (63), 51 (25).

2-Chloro-3,3-dimethyl-1-phenyl-1-butanone. Reaction of LDA with 3,3-dimethyl-1-phenyl-1-butanone gave ~40% of 3,3-dimethyl-1-phenyl-1-butanol as a reaction product.[28] Use of lithium hexamethyldisilazane in THF (53%)–hexane (34%)–HMPA (13%) avoided the reduction product. Reaction of the lithium enolate with $Me_2C(NO_2)Cl$ for 1 h at 25 °C gave 68% of the chloro ketone as measured by the ^{1}H NMR singlet at δ 5.16 and identified by GC/mass spectrum, m/e (relative

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intensity) 212 (0.22), 210 (0.79), 156 (1.68), 154 (5.53), 1.05 (100), 77 (27.7).

2-Chloro-2-methyl-1-phenyl-1-propanone. Reaction of isobutyrophenone with lithium hexamethyldisilazane in THF (53%)-hexane (34%)-HMPA (13%) with $Me_2C(NO_2)Cl$ for 1 h at 25 °C gave 78% of the chloro ketone analyzed by the ^1H NMR singlet at δ 1.90 and identified by comparison of the ^1H NMR spectra and gas chromatography retention time with those of an authentic sample.

Reaction of $PhC(OLi)=CHCH_3$ with $Me_2C(NO_2)_2$ and $Me_2C(NO_2)SO_2PhMe$-*p*. In addition to **1c** and **3c** significant amounts of **5c** (X = NO_2) and **5d** (X = *p*-$MePhSO_2$) were formed. These products were identified by GC/MS and analyzed by ^1H NMR. For $PhCOCH(Me)NO_2$ analysis was based on the signal at δ 6.33 (q, J = 7 Hz, 1 H) in $CDCl_3$, while for $PhCOCH(Me)SO_2PhMe$-*p* analysis was based on signals at δ 1.54 (d, J = 7 Hz, 3 H), 2.34 (s, 3 H), 5.27 (q, J = 7 Hz, 1 H) in $CDCl_3$ and the GC/mass spectrum, m/e 288 (M^+), 155 (*p*-$MePhSO_2$), 139 ($C_6H_4SO_2$), 133 (PhCOCHMe).

Registry No. **1c**, 78706-73-7; **1d**, 81096-19-7; **1e**, 81096-20-0; **1f**, 81096-21-1; **1g**, 81096-22-2; **1h**, 81096-23-3; **1i**, 81096-24-4; **1j**, 81096-25-5; **1k**, 81096-26-6; **1l**, 78706-74-8; **1m**, 78706-75-9; **1n**, 81096-27-7; **2a**, 5650-07-7; **2b**, 56985-25-2; **2c**, 52776-41-7; **2f**, 81096-28-8; **2g**, 81096-29-9; **2h**, 81096-30-2; **2i**, 81096-31-3; **2j**, 81096-32-4; **2k**, 81096-33-5; **2l**, 81096-34-6; **3c** (isomer 1), 81096-35-7; **3c** (isomer 2), 73893-85-3; **3d**, 81096-36-8; **3f** (isomer 1), 81096-37-9; **3f** (isomer 2), 81096-38-0; **3g** (isomer 1), 81096-39-1; **3g** (isomer 2), 81096-40-4; **3h**, 81096-41-5; **3i**, 81096-42-6; **3j**, 81120-65-2; **3l** (isomer 1), 81096-43-7; **3l** (isomer 2), 81096-44-8; **3m** (isomer 1), 81096-45-9; **3m** (isomer 2), 81120-49-2; **3n**, 81096-46-0; (±)-**3a**, 81176-44-5; **4**, 81096-47-1; **5a**, 71491-53-7; **5b**, 7473-99-6; **5c**, 14897-67-7; **5d**, 14195-15-4; **6**, 3964-18-9; **8**, 81096-48-2; **2'**, 81096-49-3; **9a**, 81096-50-6; **9b**, 74074-96-7; **9c**, 81096-51-7; **10a**, 5706-00-3; **10b**, 73652-79-6; **10c**, 81096-52-8; **11c**, 81096-53-9; $PhC(OLi)=CH_2$, 55905-98-1; PhC(OLi)=CHOMe, 81096-54-0; PhC(OLi)=CHMe, 70887-62-6; *p*-$MeOC_6H_4C(OLi)$=CHMe, 81096-55-1; *m*-$NEt_2C_6H_4C(OLi)$=CHMe, 81096-56-2; *p*-$MeC_6H_4C(OLi)$=CHMe, 81096-57-3; *p*-$ClC_6H_4C(OLi)$=CHMe, 81096-58-4; *m*-$ClC_6H_4C(OLi)$=CHMe, 81096-59-5; *p*-$BrC_6H_4C(OLi)$=CHMe, 81096-60-8; *p*-$CNC_6H_4C(OLi)$=CHMe, 81096-61-9; *m*-$NO_2C_6H_4C(OLi)$=CHMe, 81096-62-0; PhC(OLi)=CHEt, 62416-33-5; PhC(OLi)=CHBu, 81096-63-1; PhC(OLi)=CH-*i*-Pr, 78706-71-5; PhC(OLi)=CH-*t*-Bu, 81096-64-2; PhC(OLi)=CHPh, 76639-00-4; 2-chloro-2-nitropropane, 594-71-8; 2,2-dinitropropane, 595-49-3; 2-(*p*-tolylsulfonyl)-2-nitropropane, 21272-86-6; 1-chlorol-nitrocyclohexane, 873-92-7; 3,3-dimethy-2-butanone lithium enolate, 70367-67-8; 2-chloro-3-methyl-1-phenyl-1-butanone, 78706-77-1; 2-chloro-3,3-dimethyl-1-phenyl-1-butanone, 71491-53-7; 2-chloro-2-methyl-1-phenyl-1-propanone, 7473-99-6; isobutyrophenone, 611-70-1.

Substitution at Tetracoordinate Sulfur(VI). Rearrangement of 2-Aminoaryl Arenesulfonates to *N*-(2-Hydroxyaryl)arenesulfonamides[1]

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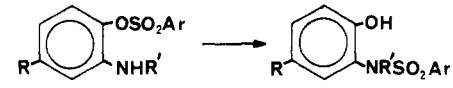
A series of eight 2-aminoaryl arenesulfonates upon treatment by strong bases rearranged intramolecularly to their corresponding *N*-(2-hydroxyaryl)arenesulfonamides as did the related tosylates derived from 2-amino-3-hydroxypyridine, 1-amino-2-naphthol, and 1-amino-8-naphthol. Two mechanisms for these rearrangements were considered likely. The first involves endocyclic nucleophilic attack by nitrogen on sulfonyl sulfur with consequent S–O bond cleavage. The other involves a 1,4-elimination reaction yielding an *o*-quinonimine–sulfinate pair which collapses to the product. Attempts to distinguish between these two alternatives were not conclusive.

Nucleophilic substitution at tetracoordinate hexavalent sulfur (sulfonyl sulfur) is a well-known reaction process. Inversion of configuration at the sulfur atom has been observed in examples subjected to stereochemical analysis.[3-6] These inversion reactions may follow an S_N2-like pathway via a trigonally bipyramidal transition state with the nucleophile (Nu), sulfur atom, and leaving group (L) approximately colinear, but other stereochemical situations are conceivable; e.g., the Nu and L could both be equatorial.

To see if approximate colinearity of Nu, S, and L is actually necessary in order for nucleophilic substitution at sulfur to occur, we are probing the effect of large deviations of the Nu–S–L angle from 180° on the course of substitution reactions. That is, we are synthesizing molecules which appear capable of undergoing endocyclic nucleophilic substitution at sulfur and then determining whether or not they undergo the desired reactions. This article describes one such set of molecules, the 2-aminoaryl arenesulfonates (**1a–8a**), and their base-induced rearrangement to *N*-(2-hydroxylaryl)arenesulfonamides (**1b-8b**, eq 1). As will be seen, it is not clear whether or not these rearrangements occur by nucleophilic substitution at sulfur.



a b (1)

1a,b, Ar = 4-$CH_3C_6H_4$; R = H; R' = H
2a,b, Ar = 4-$CH_3OC_6H_4$; R = H; R' = H
3a,b, Ar = 4-*t*-$C_4H_9C_6H_4$; R = H; R' = H
4a,b, Ar = 4-$CH_3C_6H_4$; R = CH_3; R' = H
5a,b, Ar = 4-$CH_3OC_6H_4$; R = CH_3; R' = H
6a,b, Ar = 4-*t*-$C_4H_9C_6H_4$; R = CH_3; R' = H
7a,b, Ar = 4-$CH_3C_6H_4$; R = H; R' = CH_3
8a,b, Ar = 2,4,6-$(CH_3)_3C_6H_2$; R = CH_3; R' = H

In endocyclic substitution, the nucleophile and leaving group are bonded to one another so that the atom being substituted at, in our case sulfur, is transferred intramolecularly from L to Nu (**9a**) in contrast to exocyclic reactions (**9b**) where ring formation occurs and L is lost.

9a 9b

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