Reactions of α-Halo Ketones with Nucleophiles[1]

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Received October 9, 1984

Abstract: *p*-Nitro- or *p*-cyanophenacyl chloride or the 1,1-dimethyl derivatives react with the anion of 2-nitropropane to form the C-alkylation product by a radical chain mechanism ($S_{RN}1$). With the 1,1-dimethyl derivatives, the free radical substitution is photostimulated and occurs in competition with ionic reactions leading to the oxiranes **5** and hydroxy ketones **6**. When K^+ is used as the counterion, the $S_{RN}1$ process is favored by complexation with 18-crown-6. *p*-Nitro-1,1-dimethylphenacyl chloride gives substitution products with diethyl malonate or diethyl methylmalonate anions via the $S_{RN}1$ process, but with PhS^- or *p*-$MeC_6H_4SO_2^-$, substitution occurs by competing ionic and radical processes. Propylacetylenide anion reacts to form the oxirane **13a** while diethyl phosphite or thiophosphite anions yield the enol phosphate **14a** or thiophosphate **14b**. 1,1-Dimethylphenacyl chloride reacts by nonradical processes to give the oxirane with acetylenide anions, the substitution products with PhS^- or *p*-$MeC_6H_4SO_2^-$ and a mixture of the enol phosphate, and oxirane **16** with diethyl phosphite anion. With $Me_2C{=}NO_2^-K^+$, mainly the oxirane is formed in Me_2SO but mainly substitution via the $S_{RN}1$ chain is observed in HMPA.

α-Halocarbonyl compounds are potential substrates for substitution by an electron-transfer chain reaction ($S_{RN}1$) involving reactions 1-3 (Scheme I).

The radical anion of *p*-nitrophenacyl bromide is known to decompose (reaction 1) in aqueous solution to yield the *p*-nitrophenacyl radical with a rate constant of 4.1×10^4 s^{-1} while the radical anion of *p*-nitrobenzyl bromide, a known substrate for $S_{RN}1$ processes, decomposes only slightly faster ($k = 1.7 \times 10^5$ s^{-1}).[3] Some carbonyl derivatives, such as the α-halomercurials ($RCOCH_2HgX$), will participate in the $S_{RN}1$ process with nitronate anions ($R_2C{=}NO_2^-$), but in this instance, the carbonyl group does not seem to play an important role in the reaction since similar substitution processes are observed for simple 1°-, 2°-, or 3°-alkylmercury halides.[4] Similarly, α-nitro ketones and esters undergo $S_{RN}1$ substitutions with nitronate anions.[5,6]

One indication that α-halo ketones may be susceptible to electron-transfer chain reactions is the observation that $Ph_2C(Br)CONMe_2$ undergoes reductive dehalogenation by $MeO^-/Me_2C(OMe)_2$, a process suggested to involve the reactions of Scheme II.[7]

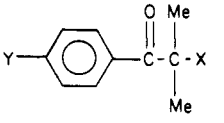
Results and Discussion

Reactions of *p*-nitro- or *p*-cyanophenacyl chlorides **1a** and **b** with 1 equiv of $Me_2C{=}NO_2^-K^+$ in EtOH or Me_2SO yield the elimination products **2a** and **b** from the alkylation product expected for the $S_{RN}1$ process (reaction 7). In EtOH, isolated yields of

$$p\text{-}YC_6H_4COCH_2Cl + Me_2C{=}NO_2^- \xrightarrow{25\ ^\circ C}$$
1a, Y = NO_2
1b, Y = CN
$$[p\text{-}YC_6H_4COCH_2CMe_2NO_2] \rightarrow \underset{\mathbf{2}}{p\text{-}YC_6H_4COCH{=}CMe_2} \quad (7)$$

2a and **2b** were 31% (20-min reaction period) and 16% (90 min), respectively. A radical chain substitution mechanism is supported by the observation that 10 mol % of $(t\text{-Bu})_2NO\cdot$ completely suppressed the formation of **2** in EtOH or Me_2SO.

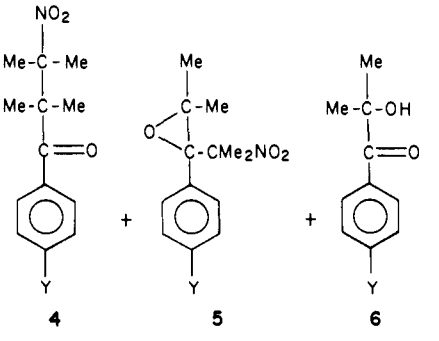
To avoid the consumption of the nucleophile in the elimination process, and to decrease the probability of direct S_N2 substitution, we have studied the reactions of the 1,1-dimethylphenacyl halides **3** with a variety of nucleophiles. Reaction of **3** with $Me_2C{=}NO_2^-$



3

a, Y = NO_2, X = Cl
a', Y = NO_2, X = Br
b, Y = CN, X = Cl
c, Y = H, X = Cl

in Me_2SO (Table I) yielded mixtures of **4-6**. In the case of **3c**



4 **5** **6**

the reactions were further complicated by products of reactions 8 and 9.

The C-alkylation products **4a-c** were not formed in the presence of $(t\text{-Bu})_2NO\cdot$, and the yield of **4** was lower in the dark than with sunlamp irradiation. Conversely, the yields of **5** and **6** were higher

$$\mathbf{3c} + Me_2C{=}NO_2^- \rightarrow \underset{\mathbf{7}}{Me_2C(Cl)NO_2} + PhCOCMe_2^- \xrightarrow{H^+}$$
$$\underset{\mathbf{8}}{PhCOCMe_2H} \quad (8)$$

$$Me_2C{=}NO_2^- + Me_2C(Cl)NO_2 \xrightarrow{S_{RN}1}$$
$$\underset{\mathbf{9}}{Me_2C(NO_2)CMe_2(NO_2)} + Cl^- \quad (9)$$

Scheme I. $S_{RN}1$ Mechanism

$$RC(=O)CH_2X^{\cdot-} \rightarrow RCOCH_2\cdot + X^- \quad (1)$$
$$RCOCH_2\cdot + A^- \rightarrow RCOCH_2A^{\cdot-} \quad (2)$$
$$RCOCH_2A^{\cdot-} + RCOCH_2X \rightarrow RCOCH_2A + RCOCH_2X^{\cdot-} \quad (3)$$
$$\overline{RCOCH_2X + A^- \rightarrow RCOCH_2A + X^-}$$

Scheme II

$$Ph_2C(Br)CONMe_2^{\cdot-} \rightarrow Ph_2\dot{C}CONMe_2 + Br^- \quad (4)$$
$$Ph_2\dot{C}CONMe_2 + CH_3O^- \rightarrow Ph_2CHCONMe_2 + CH_2O^{\cdot-} \quad (5)$$
$$CH_2O^{\cdot-} + Ph_2C(Br)CONMe_2 \rightarrow CH_2O + Ph_2C(Br)CONMe_2^{\cdot-} \quad (6)$$
$$\overline{Ph_2C(Br)CONMe_2 + CH_3O^- \rightarrow CH_2O + Ph_2CHCONMe_2 + Br^-}$$

(1) "Electron Transfer Processes", Part 34. This work was supported by Grants CHE-7823866 and CHE-8119343 from the National Science Foundation.

(2) Postdoctoral Fellow of the Consejo Superior de Investigaciones Cientificas (Spain), 1979-1981.

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Table I. Reaction of Phenacyl Halides (3) with $Me_2C{=}NO_2^-M^+$ in Me_2SO[a]

substrate	M^+	conditions[b]	time, min	4 (%)[c]	5 (%)[c]	6 (%)[c]
3a	Li^+	hν	80	38	7	36
3a	K^+	hν	80	41 (36)	16 (6)	32 (26)
3a	K^+	dark	80	29	19	36
3a	K^+	hν, 10 mol % DNB	45	28	16	31
3a	K^+	hν, 10 mol % DBNO	80	0	18	69
3a	K^+–18-crown-6	hν	80	77	10	10
3a′	Li^+	hν	45	19	45	24
3a′	K^+	hν	15	8 (6)	62 (45)	4 (1)
3a′	K^+	hν, 20 mol % DBNO	15	0	61	5
3a′	K^+–18-crown-6	hν	45	51	28	4
3a′	K^+–18-crown-6	dark	45	40	28	11
3a′	K^+–18-crown-6	hν, 20 mol % DNB	45	27	48	5
3a′	K^+–18-crown-6	hν, 20 mol % DBNO	45	0	78	6
3b	K^+	hν	60	51 (40)	12	18
3b	K^+	dark	60	9	19	48
3b	K^+	hν, 15 mol % DNB	60	7	18	32
3b	K^+	hν, 15 mol % DBNO	60	0	21 (14)	49 (39)
3b	K^+–18-crown-6	hν	60	69	5	12
3c	Li^+	hν	900	8	0	<5[d,e]
3c	K^+	hν	900	4	60	12[e]
3c	K^+–18-crown-6	hν	900	14 (7)	0	15 (11)[e,f]
3c	K^+–18-crown-6	dark	900	0	<5	39[e,g]
3c	K^+–18-crown-6	hν, 25 mol % DBNO	900	0		15[e,g]
3c	K^+ (HMPA)	hν	150	39	9	12[h]

[a] Standard conditions: the α-halo ketone (1 mmol) in Me_2SO was added with stirring under N_2 to $Me_2C{=}NO_2^-M^+$ in Me_2SO, prepared in situ from Me_3COM or Me_3COK/18-crown-6 (1/1) (1.05 mmol) and Me_2CHNO_2 (1.05 mmol) to give solution with $[Li^+]$ = $[K^+$–18-crown-6] = 0.1 M; $[K^+]$ = 0.3 M ($Me_2C{=}NO_2K$ was initially insoluble in Me_2SO). [b] hν: irradiation with a 275-W sunlamp at ca. 50 cm. Dark: flash was wrapped with aluminum foil. DNB = *p*-dinitrobenzene. DBNO = $(t\text{-Bu})_2NO\cdot$. [c] Yield by ^1H NMR analysis; numbers in parentheses represent yields of isolated products by TLC. [d] 18% of **9** isolated. [e] **3c**, **7**, and **8** were detected (<25%). [f] 7% of **9** isolated. [g] **9** not detected. [h] 2% of **9**.

in the dark or in the presence of the nitroxide. We thus have competing free radical and ionic reactions leading to **4** or a mixture of **5** and **6**, respectively.

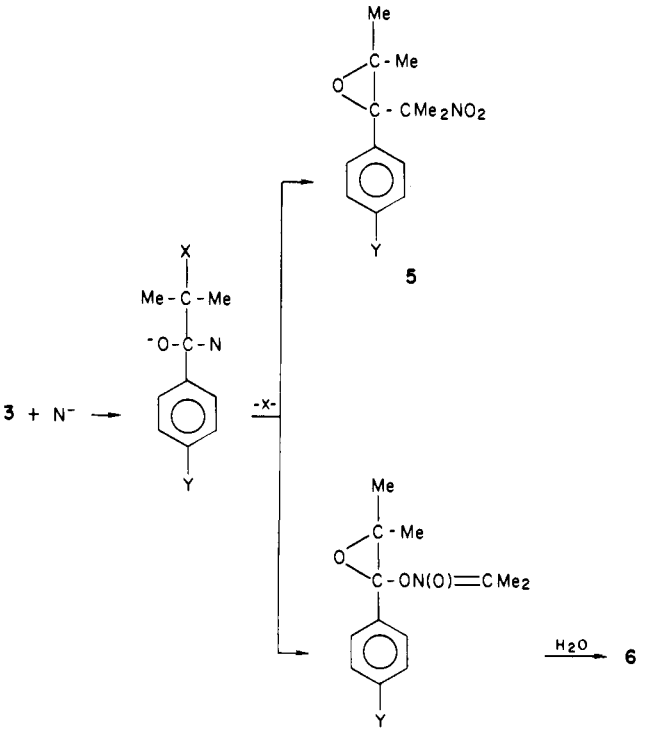
Products **5** and **6** are apparently formed by nucleophilic attack at the carbonyl group by the nitronate anion (N^-, Scheme III). The hydroxy ketone **6a** was not formed from **5a** under the hydrolytic workup employed, nor was **6a** formed under the reaction conditions from a reaction between **5a** and N^-.

By use of K^+–18-crown-6 as the counterion, it was possible to obtain reasonable yields of the $S_{RN}1$ products **4a** and **b** in the photostimulated reactions of **3a** (77%), **3a′** (51%), and **3b** (69%). Under these conditions, **3c** gave only 14% of **4c** in Me_2SO although in HMPA (K^+, hν) the yield of **4c** was increased to 39%. From experiments in the dark, it appears that spontaneous (thermal) initiation of the $S_{RN}1$ process follows the order **3a**, **3a′** > **3b** > **3c**. This order parallels the ease of formation of $3^{-}\cdot$ from **3** as measured by electrochemical reduction.

The counterion had an effect not only upon the competition between the radical **4** and ionic (**5** and **6**) components of the reaction but also upon the partitioning of the ionic products between **5** and **6**. The experiments of Table I involved homogeneous experiments initially 0.1 M in Li^+ or K^+–18-crown-6 and initially heterogeneous experiments with 0.3 M $Me_2C{=}NO_2^-K^+$. In all cases the yield of **4** (or the ratio **4**/(**5** + **6**)) was higher for the K^+–18-crown-6 experiments than for Li^+ or the heterogeneous $Me_2C{=}NO_2^-K^+$ experiments. The yield of **5**, and in most cases the ratio **5**/**6**, was higher for the heterogeneous $Me_2C{=}NO_2^-K^+$ reactions than for the homogeneous reactions (Li^+ or K^+-18-crown-6). For **3a′** and **3c** the heterogeneous reactions with $Me_2C{=}NO_2^-K^+$ were reasonably selective, giving 62% (**5a**/**6a** = 16) and 60% (**5c**/**6c** = 5) yields of **5a** and **5c**, respectively.

Although the ratios of **4**/(**5** + **6**) appear to reflect the competition between electron transfer and nucleophilic attack, one could imagine that both types of products are formed from an initial electron transfer to yield $Me_2\dot{C}NO_2$-*p*-$YC_6H_4\dot{C}(O^-)CMe_2X$. Escape from the cage of the ketyl radical anion followed by elimination of X^- would give the $S_{RN}1$ chain and product **4**. Collapse of the caged radical pair followed by internal nucleophilic displacement of X^- could yield **5** and **6**. However, if both types of products result from an initial electron transfer, it is not obvious why irradiation or the nature of the counterion and solvent has such a large effect on the ratio of the products. Since ionic

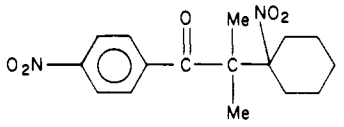
Scheme III



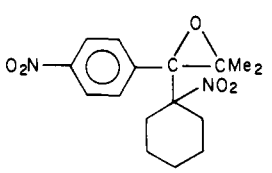
association seems to definitely favor the formation of **5** and **6**, the results may indicate that $Me_2C{=}NO_2^-K^+$ is less associated in HMPA than in Me_2SO–18-crown-6. Alternately, the anion may be equally reactive in both solvent systems, but 18-crown-6 may lead to a slight retardation of the $S_{RN}1$ radical chain process by virtue of hydrogen-transfer reactions.

Reaction of the anion of nitrocyclohexane with **3a** (Me_2SO, K^+, hν, 2 h) yielded **10** and **6a** in 77% and 17% isolated yields. In the dark, the yield of **10** decreased to 56%. With irradiation but in the presence of 8 mol % of $(t\text{-Bu})_2NO\cdot$, **10** was not formed and **6a** (35%) and oxirane **11** (14%) were isolated.

Table II presents data for the reaction of **3a** with the nucleo-

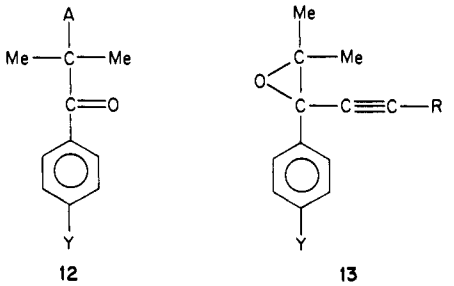


10



11

philes $(EtO_2C)_2CH^-$, $(EtO_2C)_2CMe^-$, PhS^-, $p\text{-}MeC_6H_4SO_2^-$, $n\text{-}PrC{\equiv}C^-$, $(EtO)_2PO^-$, and $(EtO)_2PS^-$. The malonate, benzenethiolate, and *p*-tolylsulfinate anions yielded mainly the substitution products **12a–d**, the acetylenide gave the oxirane **13a**

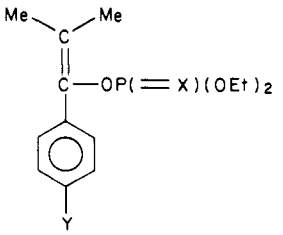


12

a, Y = NO_2, A = $(EtO_2C)_2CH$
b, Y = NO_2, A = $(EtO_2C)_2CMe$
c, Y = NO_2, A = PhS
d, Y = NO_2, A = $p\text{-}MeC_6H_4SO_2$
e, Y = NO_2, A = $EtO_2CCH(CN)$
f, Y = H, A = PhS
g, Y = H, A = *n*-BuS
h, Y = H, A = $p\text{-}MeC_6H_4SO_2$

13

a, Y = NO_2, R = *n*-Pr
b, Y = H, R = *n*-Pr
c, Y = H, R = Ph



14

a, Y = NO_2, X = O
b, Y = NO_2, X = S
c, Y = H, X = O

while diethyl phosphite or thiophosphite anions yielded the enol phosphate and thiophosphate (**14a** and **b**).

The formation of **12a** and **b** clearly occurred by the $S_{RN}1$ chain. The yields were increased by sunlamp irradiation, and the formation of **12a** and **b** was completely suppressed by 10 mol % of $(t\text{-}Bu)_2NO\cdot$. Small amounts of the hydroxy ketone **6a** were formed, possibly by a mechanism similar to that of Scheme III. Surprisingly, the reaction of **3a** with ethyl cyanoacetate anion gave **12e** in good yield in the presence or absence of $(t\text{-}Bu)_2NO\cdot$ or galvinoxyl (Table III).

Reaction of **3a′** with $(EtO_2C)_2CMe^-K^+$ in Me_2SO failed to yield the substitution product, even with irradiation. A 22% yield of the hydroxy ketone **6a** was obtained, but the major product appeared to be a dimer of $p\text{-}O_2NC_6H_4COCMe_2$ (42%) with four different methyl groups whose chemical shifts (δ 0.94, 1.47, 1.53, 1.63) were consistent with the oxirane **15**, possibly formed by the reactions of Scheme IV. ^1H NMR of the crude reactions mixtures indicated that **15** was also a minor reaction product of **3a** with $(EtO_2C)_2CMe^-$. The bromo ketone **3a′** had a much greater reactivity than the chloro ketone **3a** in the ionic reactions of Schemes III and IV.

The reactions of PhS^- or $p\text{-}MeC_6H_4SO_2^-$ with **3a** (Table II) to give **12c** and **d** involved both ionic and free radical processes (Figures 1 and 2). The reactions were photostimulated but also occurred, albeit at a slower rate, in the presence of $(t\text{-}Bu)_2NO\cdot$ or galvinoxyl. A substitution of the S_N2 type to yield **12c** and **d** may be occurring with these nucleophiles. The sulfone **12d** was not formed by halogen exchange to give $p\text{-}O_2NC_6H_4COCMe_2^-$

Table II. Reaction of $p\text{-}O_2NC_6H_4COCMe_2Cl$ (**3a**) with Nucleophiles[a]

nucleophile	conditions[b]	product (yield)[c]
$(EtO_2C)_2CH^-K^+$	Me_2SO, *hν*, 75 min	**12a** (49%), **6a** (22%)
$(EtO_2C)_2CH^-K^+$	Me_2SO, dark, 75 min	**12a** (36%)[d]
$(EtO_2C)_2CH^-K^+$	Me_2SO, *hν*, 10 mol % DBNO, 75 min	**12a** (0%)[d]
$(EtO_2C)_2CMe^-K^+$	Me_2SO, *hν*, 90 min	**12b** (62%), **6a** (5%)[e]
$(EtO_2C)_2CMe^-K^+$	Me_2SO, dark, 90 min	**12b** (30%)[d,e]
$(EtO_2C)_2CMe^-K^+$	Me_2SO, *hν*, 10 mol % DBNO, 90 min	**12b** (0%),[d] **6a** (17%)[e]
PhS^-K^+	EtOH, 120 min	**12c** (77%)[f]
PhS^-K^+	Me_2SO, *hν*, 120 min	**12c** (97%)
$p\text{-}MeC_6H_4SO_2^-Na^+$	Me_2SO, *hν*, 390 min	**12d** (100%)
$n\text{-}PrC{\equiv}C^-Li^+$	THF, −60 to 25 °C, 720 min	**13a** (67%)
$(EtO)_2PO^-K^+$	Me_2SO, *hν*, 120 min	**14a** (35%)[d,g]
$(EtO)_2PO^-K^+$	THF, 0 °C, 10 mol % DBNO, 60 min	**14a** (77%)[d]
$(EtO)_2PO^-K^+$	THF, *hν*, 900 min	**14a** (75%)[d]
$(EtO)_2PO^-K^+$[h]	THF, 900 min	**14a** (72,[d] 55%)
$(EtO)_2PS^-K^+$	Me_2SO, *hν*, 780 min	**14b** (85%)[d]
$(EtO)_2PS^-K^+$	THF, 180 min	**14b** (70,[d] 46%)

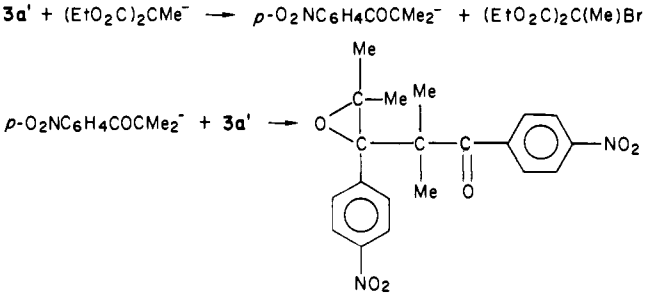
[a] Reactions were conducted at room temperature under N_2 with 1 equiv of the nucleophile. [b] *hν*: irradiation with a 275-W sunlamp at ca. 50 cm. Dark: flask wrapped with aluminum foil. DBNO = $(t\text{-}Bu)_2NO\cdot$. [c] Isolated yield except as noted. [d] ^1H NMR yield. [e] **15** detected (<15%). [f] $p\text{-}O_2NC_6H_4COCHMe_2$ detected (~5%). [g] 50% of **3a** recovered. [h] Two equivalents of $(EtO)_2PO^-K^+$.

Table III. Reactions of $p\text{-}O_2NC_6H_4COCMe_2Cl$ (**3a**) with $N{\equiv}CCHCO_2Et^-K^+$

conditions[a]	%**12e**[b]
Me_2SO, 40 °C, *hν*, 90 min	63
Me_2SO, 40 °C, *hν*, 7 mol % DBNO, 90 min	69
Me_2SO, 40 °C, 11 mol % galvinoxyl, 90 min	58
DMF, −20 °C, 60 min	38
DMF, −20 °C, 13 mol % DBNO, 60 min	39
DMF, −20 °C, O_2, 60 min	39

[a] Reactions were performed with a 1/1 ratio of reactants, 0.4 M in Me_2SO and 0.09 M in DMF. *hν*: irradiation with a 275-W sunlamp at ca. 50 cm. Dark: flask wrapped with aluminum foil. DBNO = $(t\text{-}Bu)_2NO\cdot$. [b] By ^1H NMR.

Scheme IV



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and $p\text{-}MeC_6H_4SO_2Cl$ since reactions of either $PhCOCMe_2^-$ or $p\text{-}O_2NC_6H_4COCMe_2^-$ with $p\text{-}MeC_6H_4SO_2Cl$ failed to yield the sulfone. Diethyl phosphite and thiophosphite anions reacted in a modified Perkov reaction[8] to yield the enol phosphate and thiophosphates (**14a** and **b**) in reactions that were not inhibited by $(t\text{-}Bu)_2NO\cdot$.

Table IV presents data for the reactions of **3c** with nucleophiles other than $Me_2C{=}NO_2^-$. All the products are those expected from ionic processes. C-Alkylation was not observed with $(EtO_2C)_2CMe^-$, even with irradiation. Reaction with PhS^-, *n*-BuS^-, or $p\text{-}MeC_6H_4SO_2^-$ yielded the substitution products **12f–h**

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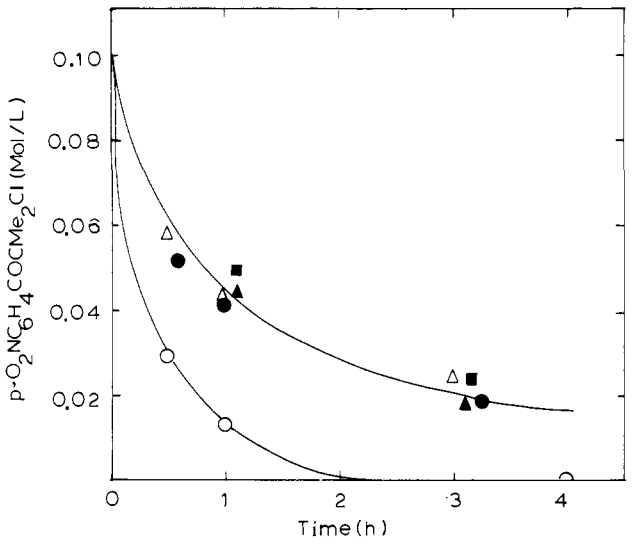


Figure 1. Reaction of 0.1 M p-$O_2NC_6H_4COCMe_2Cl$ (**3a**) with 0.1 M PhS^-K^+ in EtOH at 0 °C; (○) irradiation with a 275-W sunlamp; (●) dark; (△) sunlamp with 8 mol % $(t\text{-Bu})_2NO\cdot$; (▲) 27 mol g $(t\text{-Bu})_2NO\cdot$ in the dark; (■) 12 mol % p-dinitrobenzene in the dark.

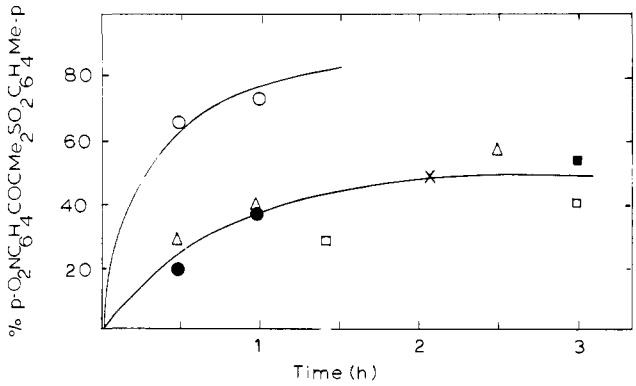
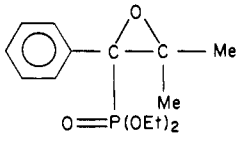


Figure 2. Reaction of 0.2 M p-$O_2NC_6H_4COMe_2Cl$ (**3a**) with 0.2 M p-$MeC_6H_4SO_2^-Na^+$ in Me_2SO at 40 °C; (○) irradiation with 275-W sunlamp; (●) dark; (△) sunlamp with 10 mol % galvinoxyl; (□) saturated with O_2 in the dark; (×) 11 mol % p-dinitrobenzene in the dark; (■) sunlamp with 5 mol % $(t\text{-Bu})_2NO\cdot$.

by processes which were neither photostimulated nor inhibited by $(t\text{-Bu})_2NO\cdot$. Acetylenides in THF yielded the oxiranes **13b**



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and **c** while $(EtO)_2PO^-$ gave a mixture of the Perkov product **14c** and the oxirane **16** in a 1.6:1 ratio (^1H NMR of the distilled reaction product).

Experimental Section

Reagents. α-Chloro-p-nitroacetophenone (**1a**),[9] α-chloroisobutyrophenone (**3c**),[10] and diethyl thiophosphite[11] were prepared according to the literature. α-Chloro-p-cyanoacetophenone (**1b**) was prepared by the chlorination of p-cyanoacetophenone with sulfuryl chloride in $CHCl_3$ to give **1b** in 74% yield, mp 91–95 °C (lit.[12] mp 98–100 °C). α-Chloro-p-nitroisobutyrophenone (**3a**) was prepared from p-nitroisobutyrophenone[13] in 70% yield by reaction with Cl_2 in acetic acid, mp 54–57 °C; ^1H NMR ($CDCl_3$) δ 1.90 (s, 6), 8.25 (s, 4); IR (KBr) 1685, 1527, 1354 cm^{-1}; HRMS calcd for $C_{10}H_9NO_3$ (P-HCl) 191.058 25, found 191.055 94. Anal. Calcd for $C_{10}H_{10}ClNO_3$: C, 52.75; H, 4.44; Cl, 15.57. Found: C, 52.88; H, 4.43; Cl, 15.60.

Bromination of p-nitroisobutyrophenone by Br_2 in CCl_4 formed α-bromo-p-nitroisobutyrophenone (**3a'**) in 95% yield, mp 59–60 °C; ^1H NMR ($CDCl_3$) δ 2.02 (s, 6), 8.23 (s, 4); IR (Nujol) 1680, 1530, 1350 cm^{-1}; HRMS calcd for $C_{10}H_{10}BrNO_3$ 270.984 40, found 270.984 20.

Reduction of p-nitroisobutyrophenone with Sn in concentrated hydrochloric acid/EtOH gave p-aminoisobutyrophenone in 95% yield, mp 107–109 °C; ^1H NMR ($CDCl_3$) δ 1.19 (d, 6, J = 7 Hz), 3.44 (sept, 1, J = 7 Hz), 4.15 (br s, 2), 6.62 (d, 2, J = 9 Hz), 7.70 (d, 2, J = 9 Hz); IR (KBr) 3400, 3330, 3225, 1642, 1588 cm^{-1}. Diazotization followed by treatment with CuCN gave p-cyanoisobutyrophenone in 72% yield, mp 45–47 °C: ^1H NMR ($CDCl_3$) δ 1.14 (d, 6, J = 7 Hz), 3.46 (sept, 1, J = 7 Hz), 7.72 (d, 2, J = 9 Hz), 8.02 (d, 2, J = 9 Hz); IR (KBr) 2230, 1677 cm^{-1}. Chlorination with Cl_2 in HOAc followed by TLC with CCl_4 eluent gave α-chloro-p-cyanosiobutyrophenone (**3c**) as an oil in 60% yield: ^1H NMR ($CDCl_3$) δ 1.90 (s, 6), 7.81 (d, 2, J = 9 Hz), 8.26 (d, 2, J = 9 Hz); IR (CCl_4) 2225, 1690 cm^{-1}; HRMS calcd for $C_{11}H_{10}ClNO$ 270.04509, found 207.04475.

Lithium *tert*-butoxide was prepared and had a neutralization equivalent of 78.5 (calcd 80.1). Solvents were distilled from calcium hydride and stored under N_2 over molecular sieves.

General Procedures. Solutions of nucleophiles were prepared immediately before use by addition of the conjugate acid under N_2 to a molar equivalent of lithium or potassium *tert*-butoxide in the desired solvent. Acetylenides were prepared by reaction with *n*-butyllithium. The solutions were deoxygenated by bubbling nitrogen for 15–30 min followed by the addition via syringe of a deoxygenated solution of the substrate. For irradiated experiments, a 275-W sunlamp was positioned ca. 50 cm from the Pyrex reaction flask. For reactions in the dark, the flask was wrapped with aluminum foil. The crude products obtained by hydrolysis and Et_2O extraction were analyzed by ^1H NMR by using DMF, Me_2SO, or CH_2Br_2 as internal standards. Separations by TLC were performed on silica gel with pure compounds extracted by $CHCl_3$ or Et_2O.

α-Isopropylidene-p-nitroacetophenone (2a). A solution of 1.37 g of **1a** in 9 mL of warm EtOH was added to $Me_2C{=}NO_2^-K^+$ prepared from 0.61 g of 2-nitropropane in 10 mL of EtOH. After 20 min, the mixture was poured into water and extracted with ether to give 1.50 g of product. By TLC (hexane–ethyl acetate, 4:1) of a 0.42-g aliquot there was obtained 0.12 g of **2a** (31%), mp 103–106 °C: ^1H NMR ($CDCl_3$) δ 2.07 (d, 3, J = 1 Hz), 2.27 (d, 3, J = 1 Hz), 6.74 (7, 1), 8.05 (d, 2, J = 8 Hz), 8.31 (d, 2, J = 8 Hz); IR (KBr) 1655, 1594, 1517, 1341 cm^{-1}. HRMS calcd for $C_{11}H_{11}NO_3$ 205.013 90, found 205.013 62. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.37; H, 5.41; N, 6.83. Found: *m/e* 205.01362; C, 64.17; H, 5.41; N, 6.76. In a similar experiment in Me_2SO (72 min), the yield of **2a** by ^1H NMR was 22%. With 10 mol % of $(t\text{-Bu})_2NO\cdot$, **2a** was not detected (Me_2SO, 75 min).

α-Isopropylidene-p-cyanoacetophenone (2b). Reaction of 1.72 g of **1b** with $Me_2C{=}NO_2^-K^+$ prepared from 0.85 g of 2-nitropropane in 25 mL of EtOH for 1.5 h gave 1.51 g of a crude oil which by TLC afforded 16% of **2b**, mp 70–75 °C: ^1H NMR ($CDCl_3$) δ 2.06 (d, 3, J = 1 Hz), 2.25 (d, 3, J = 1 Hz), 6.70 (m, 1), 7.72 (d, 2 J = 8 Hz), 8.02 (d, 2, J = 8 Hz); IR (KBr) 2222, 1660, 1608 cm^{-1}; HRMS calcd for $C_{12}H_{11}NO$

Table IV. Reaction of $PhCOCMe_2Cl$ (**3c**) with Nucleophiles[a]

nucleophile	conditions[b]	product (yield)[c]
$(EtO_2C)_2CMe^-K^+$	Me_2SO, 25–50 °C, 23 h	**6c** (62,[d] 37%[e])
PhS^-K^+	Me_2SO, 5.5 h	**12f** (74%)[f]
PhS^-K^+	EtOH, *hν*, 3 h	**12f** (39%)[f,g]
PhS^-K^+	EtOH, dark, 3 h	**12f** (36%)[f,g]
PhS^-K^+	EtOH, *hν*, 5 mol % DBNO, 3 h	**12f** (38%)[f,g]
n-BuS^-K^+	Me_2SO, 2 h	**12g** (67%)[f]
p-$MeC_6H_4SO_2^-Na^+$	Me_2SO, 60 °C, 16 h	**12h** (82%)
p-$MeC_6H_4SO_2^-Na^+$	Me_2SO, *hν*, 13 h	**12h** (41%)[d]
p-$MeC_6H_4SO_2^-Na^+$	Me_2SO, dark, 20 mol % DBNO, 13 h	**12h** (42%)[d]
n-$PrC{\equiv}C^-Li^+$	THF, −60 to 25 °C, 12 h	**13b** (96%)
$PhC{\equiv}C^-Li^+$	THF, −60 to 25 °C, 12 h	**13c** (57%)
$(EtO)_2PO^-K^+$	Me_2SO, 50 °C, 36 h	**14c** (34%)[d] **16** (22%)[d]

[a] Reactions conducted at room temperature under N_2 with 1 equiv of nucleophile unless otherwise noted. [b] *hν*: irradiation with a 275 W sunlamp at *ca.* 50 cm; dark: flask was wrapped with aluminum foil; DBNO = $(tert\text{-Bu})_2NO\cdot$. [c] Isolated yield except as noted. [d] Yield by ^1H NMR. [e] 87% of $(EtO_2C)_2CHMe$ recovered. [f] $PhCOCMe_2H$ (**8**) detected (<20%). [g] Yield by GLC.

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184.076 24, found 184.076 37. Anal. Calcd for $C_{12}H_{11}NO$: C, 77.80; H, 6.00; N, 7.56. Found: C, 77.69; H, 6.18; N, 7.44. In a similar experiment with 10 mol % of $(t\text{-Bu})_2NO\cdot$, **2b** was not detected by ^1H NMR (1.5 h).

α-(2-Nitro-2-propyl)-*p*-nitroisobutyrophenone (4a). The chloro ketone **3a** (4.23 g) in Me_2SO was added to $Me_2C{=}NO_2^-K^+$ prepared from 1.66 g of 2-nitropropane (total volume 50 mL) and allowed to react for 2 h in ordinary laboratory light. Hydrolysis and ether extraction followed by digestion of the crude solid in 200 mL of refluxing pentane for 10 h and recrystallization from hexane–benzene gave 1.71 g (33%) of **4a**, mp 107–109 °C: ^1H NMR ($CDCl_3$) δ 1.38 (s, 6), 1.79 (s, 6) 7.57 (d, 2, J = 9 Hz), 8.23 (d, 2, J = 9 Hz); IR (KBr) 1686, 1539, 1526, 1352 cm^{-1}; HRMS calcd for $C_{13}H_{16}NO_3$ (P–NO_2) 234.113 03, found 234.113 27. Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.70; H, 5.77; N, 10.00. Found: C, 55.91; H, 5.90; N, 10.01. Analysis of the crude reaction product by ^1H NMR gave a yield of **4a** of 42% and a yield of **6a** of 16%.

2,2-Dimethyl-3-(*p*-nitrophenyl)-3-(2-nitro-2-propyl)oxirane (5a). Reaction of 0.272 g of **3a′** with $Me_2C{=}NO_2^-K^+$ (from 0.094 g of 2-nitropropane) in 3.3 mL of Me_2SO with sunlamp irradiation for 15 min gave by TLC (benzene–ethyl acetate, 8:1) 6% of **4a**, 1% of **6a**, and 45% of **5a**, mp 140–144 °C: ^1H NMR ($CDCl_3$) δ 1.04 (s, 3), 1.36 (s, 3), 1.53 (s, 3), 1.70 (s, 3), 7.25 (d, 2, J = 8 Hz), 8.35 (d, 2, J = 8 Hz); IR (KBr) 1520, 1348 1330, 1250, 948, 850 cm^{-1}; HRMS calcd for $C_{13}H_{16}NO_2$ (P–NO_2) 234.113 03, found 234.113 82. Anal. Calcd for $C_{13}H_{16}N_2O_5$: C, 55.70; H, 5.77; N, 10.00. Found: C, 55.71; H, 5.81; N, 9.92. Reaction of **5a** (0.50 mmol) and $Me_2C{=}NO_2^-Li^+$ (0.60 mmol) in Me_2SO (2 mL) for 1 h followed by hydrolysis and Et_2O extraction gave a quantitative recovery of **5a**.

α-(2-Nitro-2-propyl)-*p*-cyanoisobutyrophenone (4b). Irradiation of 0.209 g of **3b** and $Me_2C{=}NO_2^-K^+$ (from 0.098 g of 2-nitropropane) in 4 mL of Me_2SO for 1 h gave, after digestion of the crude solid reaction product in 15 mL of refluxing pentane (16 h), 40% of **4b**, mp 124–128 °C: ^1H NMR ($CDCl_3$) δ 1.37 (s, 6), 1.79 (s, 6), 7.46 (d, 2, J = 8 Hz), 7.70 (d, 2, J = 8 Hz); IR (KBr) 2230, 1679, 1530, 1342, cm^{-1}; HRMS calcd for $C_{14}H_{16}NO$ (P–NO_2) 214.123 19, found 214.123 40. Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.21; N, 10.76. Found: C, 64.72; H, 5.87; N, 11.29.

2,2-Dimethyl-3-(*p*-cyanophenyl)-3-(2-nitro-2-propyl)oxirane (5b) and α-Hydroxy-*p*-cyanoisobutyrophenone (6b). Repetition of the previous experiment in the presence of 15 mol % of $(t\text{-Bu})_2NO\cdot$ afforded by TLC (benzene–ethyl acetate, 13:1) **5b** (14%) and **6b** (39%) as oils. Oxirane **5b**: ^1H NMR ($CDCl_3$) δ 1.03 (s, 3), 1.35 (s, 3), 1.50 (s, 3), 1.67 (s, 3), 7.77 (s, 4); IR (neat) 2260, 1350, 1240, 964, 829 cm^{-1}; HRMS calcd for $C_{14}H_{16}NO$ (P–NO_2) 214.123 19, found 214.123 62. Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.21; N, 10.76. Found: C, 64.33; H, 6.12; N, 10.59. Hydroxy ketone **6b**: ^1H NMR ($CDCl_3$) δ 1.61 (s, 6), 3.36 (br s, 1), 7.76 (d, 2, J = 9 Hz), 8.18 (d, 2, J = 9 Hz); IR (neat) 3470, 2225, 1678 cm^{-1}; HRMS calcd for $C_{11}H_9NO$ (P–H_2O) 171.068 41, found 171.068 75. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.81; H, 5.87; N, 7.40. Found: C, 68.73; H, 5.89; N, 7.21.

α-(1-Nitro-1-cyclohexyl)-*p*-nitroisobutyrophenone (10) and α-Hydroxy-*p*-nitroisobutyrophenone (6a). Addition of 0.626 g of **3a** in 2 mL of Me_2SO to the K^+ salt prepared from 0.355 g of nitrocyclohexane in 5 mL of Me_2SO, followed by 2 h irradiation, gave, after hydrolysis, ether extraction, and digestion in 100 mL of refluxing pentane (8 h), 0.583 g of **10** (66%), mp 127–129 °C (from hexane–benzene): ^1H NMR ($CDCl_3$) δ 0.9–2.2 (m), 1.33 (s), 2.72 (br d, 2), 7.52 (d, 2, J = 9 Hz), 8.24 (d, 2, J = 9 Hz); IR (KBr) 1682, 1535, 1521, 1353 cm^{-1}; HRMS calcd for $C_{16}H_{20}NO_3$ (P–NO_2) 274.144 33, found 274.143 22. Anal. Calcd for $C_{16}H_{20}N_2O_5$: C, 59.98; H, 6.31; N, 8.75. Found: C, 59.92; H, 6.40; N, 8.75.

The pentane soluble reaction product afforded an additional 11% of **10** and 17% of **6a** as an oil isolated by TLC (benzene–ethyl acetate, 4:1): ^1H NMR ($CDCl_3$) δ 1.64 (s, 6), 3.27 (br s, 1), 8.38 (s, 4); IR (neat) 3450, 1690, 1525, 1352 cm^{-1}; HRMS calcd for $C_9H_8NO_4$ (P–CH_3) 194.045 34, found 194.045 78. Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.40; H, 5.31; N, 6.70. Found: C, 57.30; H, 5.49; N, 6.56. Repetition of the reaction in the dark gave by TLC 56% of **10** and 29% of **6a**.

2,2-Dimethyl-3-(1-nitro-1-cyclohexyl)-3-(*p*-nitrophenyl)oxirane (11). Reaction of 0.412 g of **3a** with the K^+ salt of nitrocyclohexane (from 0.236 g of nitrocyclohexane) in 5 mL of Me_2SO in the presence of 8 mol % of $(t\text{-Bu})_2NO\cdot$ with sunlamp irradiation for 2 h gave by TLC (benzene-ethyl acetate, 4:1) 35% of **6a** and 14% of **11**: ^1H NMR ($CDCl_3$) δ 0.9–2.3 (m), 1.03 (s), 1.50 (s), 7.73 (d, J = 9 Hz), 8.29 (d, J = 9 Hz); IR (KBr) 1520, 1360, 1335, 1255, 851 cm^{-1}; HRMS calcd for $C_{16}H_{20}NO_3$ (P–NO_2) 274.144 32, found 274.144 20. Anal. Calcd for $C_{16}H_2N_2O_5$: C, 59.98; H, 6.31. Found: C, 59.46; H, 5.76. Compound **10** was not detected in this reaction.

Reactions of the Anion of 2-Nitropropane with 3c. The reactions of $Me_2C{=}NO_2^-M^+$ with **3c** in Me_2SO gave mixtures of products not easily separable by distillation but partially resolved by TLC. However, analysis by ^1H NMR of the methyl singlets was possible. Yields in Table I are based on the chemical shifts for the known $PhCOCMe_2CMe_2NO_2$ (**4c**, δ 1.40, 1.77),[14] $PhCOCMe_2OH$ (**6c**, δ 1.54), $PhCOMe_2Cl$ (**3c**, δ 1.88), $O_2NCMe_2CMe_2NO_2$ (**9**, δ 1.73), $Me_2C(Cl)NO_2$ (**7**, δ 2.13), and $PhCOCMe_2H$ (**8** δ 1.15, 1.26). In the presence of K^+–18-crown-6 in Me_2SO, **4c** (7%), **6c** (11%), and **9** (7%) were isolated by TLC by using C_6H_6 as the eluent. The heterogeneous reaction with 0.3 M $Me_2C{=}NO_2^-K^+$ in Me_2SO gave predominately (60%) a product with four methyl singlets at δ 0.98, 1.31, 1.47, and 1.63, which by analogy with **5a** and **b** can be assigned to the oxirane **5c**. Distillation at 100 °C (0.1 torr) gave a mixture enriched in **5c** but still contaminated with **3c** and **6c**.

Diethyl (2-(*p*-Nitrobenzoyl)-2-propyl)malonate (12a). Reaction of 486 mg of **3a** with the anion from 340 mg of diethyl malonate in 6 mL of Me_2SO for 75 min with irradiation gave by distillation a fraction, bp 145–160 °C (1 torr), from which 22% of **6a** was isolated by TLC (benzene–ethyl acetate, 4:1). Distillation also yielded **12a** (49%), bp 147–149 °C (0.01 torr): ^1H NMR (CCl_4) δ 1.29 (t, 6, J = 7 Hz), 1.36 (s, 6), 4.10 (s, 1), 4.18 (q, 4, J = 7 Hz), 7.64 (d, 2, J = 8 Hz), 8.25 (d, 2, J = 8 Hz); IR (neat) 1790, 1736, 1700, 1531, 1356 cm^{-1}; HRMS calcd for $C_{15}H_{16}NO_6$ (P–C_2H_5O) 306.7 77, found 306.097 22. Anal. Calcd for $C_{17}H_{21}NO_7$: C, 58.10; H, 6.04. Found: 58.13; H, 6.02.

Diethyl Methyl(2-(*p*-nitrobenzoyl)-2-propyl)malonate (12b). The reaction of 3.07 g of **3a** with $(EtO_2C)_2CMe^-K^+$ prepared from 2.63 g of diethyl methylmalonate in 37 mL of Me_2SO was irradiated for 1.5 h. Hydrolysis and ether extractions gave a liquid which was distilled to give **6a** (5%), bp 98–108 °C (0.1 torr), and **12b** (62%), bp 145–152 °C (0.01 torr): ^1H NMR ($CDCl_3$) δ 1.28 (t, 6, J = 7 Hz), 1.37 (s, 6), 1.67 (s, 3), 4.23 (q, 4, J = 7 Hz), 7.70 (d, 2, J = 9 Hz), 8.14 (d, 2, J = 9 Hz); IR (neat) 1728, 1699, 1529, 1353 cm^{-1}; HRMS calcd for $C_{16}H_{18}NO_6$ (P–C_2H_5O) 320.113 42, found 320.112 38. Anal. Calcd for $C_{18}H_{23}NO_7$: C, 59.16; H, 6.36. Found: C, 59.35; H, 6.50.

Reaction of Diethyl Methylmalonate Anion with 3a′ and 3c. Irradiation of 0.304 g of **3a′** and $(EtO_2C)_2CMe^-K^+$ (from 0.189 g of diethyl methylmalonate) in 4 mL of Me_2SO for 1 h gave by TLC (benzene–ethyl acetate, 16:1) 13% of **6a** and 26% of 2,2-dimethyl-3-(2-(*p*-nitrobenzoyl)-2-propyl)-3-(*p*-nitrophenyl)oxirane (**15**), mp 125–132 °C: ^1H NMR ($CDCl_3$) δ 0.94 (s, 3), 1.47 (s, 3), 1.53 (s, 3), 1.63 (s, 3), 7.48 (d, 2, J = 9 Hz), 8.12 (d, 2, J = 9 Hz), 8.31 (s, 4); IR (KBr) 1670, 1512, 1340, 1253, 934, 850 cm^{-1}. Anal. Calcd for $C_{20}H_{20}N_2O_6$: N, 7.29. Found: N, 7.08.

Reaction of 2.76 g of **3c** with $(EtO_2C)_2CMe^-K^+$ (from 2.63 g of diethyl methylmalonate) in 40 mL of Me_2SO for 4 h at room temperature and 19 h at 50 °C gave by distillation 87% of recovered diethyl methylmaonate and 37% of **6c**, bp 121–124 °C (14 torr) [lit.[15] bp 125 °C (12 torr)]: ^1H NMR (CCl_4) δ 1.54 (s, 6), 4.00 (br s, 1), 7.5 (m, 3), 8.1 (m, 2).

α-(Phenylthio)-*p*-nitroisobutyrophenone (12c). Reaction with PhS^-K^+ (prepared from 1.78 g of benzenethiol) with 3.67 g of **3a** in 43 mL of Me_2SO for 2 h with irradiation yielded after hydrolysis and ether extraction **12c** (97%), mp 89–90 °C from hexane: ^1H NMR ($CDCl_3$) δ 1.53 (s, 6), 7.28 (s, 5), 8.30 (s, 4); IR (KBr) 1676, 1518, 1352 cm^{-1}; HRMS calcd for $C_{16}H_{15}NO_3S$ 301.077 27, found 301,075 91. Anal. Calcd for $C_{16}H_{15}NO_3S$: C, 63.76; H, 5.03; S, 10.64. Found: C, 63.91; H, 5.05; S, 10.41. In EtOH with room light the reaction (2 h) gave 77% of **12c** recrystallized from hexane. For the reaction in Figure 1, the consumption of **3a** was followed by hydrolyzing aliquots and analyzing by ^1H NMR.

α-(*p*-Methylbenzenesulfonyl)-*p*-nitroisobutyrophenone (12d). To a stirred solution of 342 mg of sodium *p*-tolylsulfinate in 4 mL of Me_2SO was added 436 mg of **3a** in 4 mL of Me_2SO. The solution was irradiated for 6.5 h, poured onto ice, and extracted with ether to give 675 mg of **12d** (100%), which upon recrystallization from hexane–benzene had mp 115–116 °C: ^1H NMR ($CDCl_3$) δ 1.65 (s, 6), 2.47 (s, 3), 7.30 (d, 2, J = 9 Hz), 7.65 (d, 2, J = 9 Hz), 8.06 (d, 2, J = 9 Hz), 8.30 (d, 2, J = 9 Hz); IR (KBr) 1700, 1526, 1354, 1301, 1155, 1129 cm^{-1}; HRMS calcd for $C_{17}H_{17}NO_5S$ 347.082 75, found 347.082 96. Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.77; H, 4.94; S, 9.23. Found: C, 58.92; H, 4.95; S, 9.11.

The reactions in Figure 2 were initially 0.2 M in **3a** and sodium *p*-tolylsulfinate. The yields of **12d** were determined by hydrolyzing aliquots and analyzing the ether extracts by ^1H NMR. A similar reaction in Me_2SO–EtOH (1.8:1) in the dark at 30 °C for 12 h and 50 °C for 9 h gave 63% of **12d** (by ^1H NMR). No *p*-nitrosoisobutyrophenone could be detected by GLC. Reaction of sodium *p*-tolylsulfinate in Me_2SO with

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O_2 in the dark for 4 h at 40 °C gave a quantitative recovery of unchanged sulfinate.

Ethyl Cyano(2-(*p*-nitrobenzoyl)-2-propyl)acetate (12). The anion from 1.71 g of ethyl cyanoacetate was reacted with 1.73 g of **3a** in 23 mL of Me_2SO for 2 h. Acidification with dilute hydrochloric acid and ether extractions followed by recrystallization from EtOH gave 1.67 g of **12e** (72%), mp 94–96 °C: ^1H NMR ($CDCl_3$) δ 1.36 (t, 3, J = 7 Hz), 1.52 (s, 3), 1.56 (s, 3) 4.32 (q, 2, J = 7 Hz), 4.46 (s, 1), 7.79 (d, 2, J = 9 Hz), 8.35 (d, 2, J = 9 Hz); IR (Nujol) 2260, 1740, 1684, 1528, 1360, cm^{-1}; HRMS calcd for $C_{15}H_{16}N_2O_6$ 304.105 93, found 304.104 87. Anal. Calcd for $C_{15}H_{16}N_2O_5$: C, 59.20; H, 5.31, N, 9.21. Found: C, 59.06; H, 5.39; N, 9.14.

α-(Phenylthio)isobutyrophenone (12f). Reaction of PhS^-K^+ prepared from 1.98 g of benzenethiol with 3.29 g of **3c** in 50 mL of Me_2SO for 5.5 h yielded by distillation **12f** (74%), bp 141 °C (0.45 torr) [lit.[16] bp 133–135 °C (0.1 torr)].

α-(*n*-Butylthio)isobutyrophenone (12g). Reaction with *n*-BuS^-K^+ prepared from 1.70 g of butanethiol and 3.44 g of **3c** in 50 mL of Me_2SO for 2 h gave by distillation **12g** (67%), bp 97 °C (0.2 torr): ^1H NMR ($CDCl_3$) δ 0.84 (m, 3), 1.1–1.5 (m, 4) 1.55 (s, 6), 2.47 (t, 2), 7.2–7.5 (m, 3), 7.9–8.2 (m, 2); IR (neat) 1669 cm^{-1}; HRMS calcd for $C_{14}H_{20}OS$ 236.123 49, found 236.139 95. C, 71.13; H, 8.54; S, 13.56. Found: C, 71.34; H, 8.67; S, 13.75.

α-(*p*-Methylbenzenesulfonyl)isobutyrophenone (12h). Reaction of 2.49 g sodium *p*-tolylsulfinate with 2.44 g of **3c** in 40 mL of Me_2SO for 16 h at 60 °C under ordinary laboratory lighting gave by distillation **12h** (82%), bp 158–163 °C (0.01 torr), mp 48–53 °C: ^1H NMR (CCl_4) δ 1.59 (s, 6), 2.46 (s, 3), 7.5 (m, 7), 8.0 (m, 2); IR (KBr) 1675, 1301, 1148, 1129 cm^{-1}; HRMS calcd for $C_{17}H_{18}O_3S$ 302.097 67, found 302.097 04. Anal. Calcd for $C_{17}H_{18}O_3S$: C, 67.51; H, 6.01; S, 10.60. Found: C, 67.72; H, 6.05; S, 10.53. In Me_2SO–EtOH (1.8:1) at 60 °C for 18 h, the crude yield of **12h** was 16% and isobutyrophenone could not be detected by GLC.

Reactions of *p*-Nitroisobutyrophenone and Isobutyrophenone Enolate Anions with *p*-Methylbenzenesulfonyl Chloride. Addition of 0.268 g of tosyl chloride in 2 mL of THF to *p*-$O_2NC_6H_4COCMe_2^-K^+$ in 12 mL of Me_2SO (from reaction of 0.265 g of *p*-nitroisobutyrophenone and 1 equiv of $CH_3SOCH_2^-K^+$) gave after 1 h in a crude mixture containing some *p*-nitroisobutyrophenone (~5% by ^1H NMR), but **12d** could not be detected by GLC. With $PhCOCMe_2^-K^+$, the reaction gave 19% of isobutyrophenone and **12h** was not detected.

2,2-Dimethyl-3-(*p*-nitrophenyl)-3-(1-pentynyl)oxirane (13a). A solution of *n*-$PrC{\equiv}C^-Li^+$ was prepared by addition of 7 mL of a 3.4 M solution of butyllithium in hexane to 1.42 g of 1-pentyne in 40 mL of THF at −60 °C. After 4.54 g of **3a** was added in 40 mL of THF, the resulting solution was allowed to warm to 30 °C over a 12-h period. Hydrolysis and ether extraction gave by distillation **13a** (67%), bp 135–137 °C (0.25 torr): ^1H NMR (CCl_4) δ 1.00 (t, 3, J = 6 Hz), 1.02 (s, 3), 1.55 (sex., 2, J = 6 Hz), 1.62 (s, 3) 2.22 (t, 2, J = 6 Hz), 7.54 (d, 2, J = 8 Hz), 8.15 (d, 2, J = 8 Hz); IR (neat) 2238, 1516, 1346, 1228, 917, 850 cm^{-1}; HRMS calcd for $C_{15}H_{17}NO_3$ 259.120 85, found 259.121 75. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.47; H, 6.62. Found: C, 69.72; H, 6.84.

2,2-Dimethyl-3-(1-pentynyl)-3-phenyloxirane (13b). Reaction of *n*-$PrC{\equiv}C^-Li^+$ (prepared from 1.90 g of 1-pentyne) with 5.14 g of **3c** in 120 mL of THF for 12 h (−60 to 30 °C) gave **13b** (96%), bp 84 °C (0.4 torr): ^1H NMR (CCl_4) δ 0.95 (t, 3, J = 7 Hz), 0.95 (s, 3), 1.50 (sex., 2, J = 7 Hz), 1.57 (s, 3), 2.17 (t, 2, J = 7 Hz), 7.3 (m, 5); IR (neat) 2238, 1230, 898, 860 cm^{-1}; HRMS calcd for $C_{15}H_{18}O$ 214.135 77, found 214.135 20. Anal. Calcd for $C_{15}H_{18}O$: C, 84.05; H, 8.48. Found: C, 84.37; H, 8.62.

2,2-Dimethyl-3-(2-phenethynyl)-3-phenyloxirane (13c). Reaction of $PhC{\equiv}C^-Li^+$ (prepared from 1.89 g of phenylacetylene) and 3.38 g of **3c** in 80 mL of THF for 12 h (−60 to 30 °C) gave **13c** (57%), bp 130–131 °C (0.25 torr): ^1H NMR ($CDCl_3$) δ 1.07 (s, 3), 1.72 (s, 3), 7.3 (m, 10); IR (neat) 2233, 1240, 904, 866 cm^{-1}; HRMS calcd for $C_{18}H_{16}O$ 248.120 12, found 248.120 20. Anal. Calcd for $C_{18}H_{16}O$: C, 87.05; H, 6.51. Found: C, 87.22; H, 6.70.

Diethyl 2,2-Dimethyl-1-(*p*-nitrophenyl)vinyl Phosphate (14a). Reaction of $(EtO)_2PO^-K^+$ (prepared from 4.31 g of diethyl phosphite and 3.67 g Me_3COK) with 3.39 g of **3a** in 47 mL of THF for 15 h gave after hydrolysis and ether extraction 72% of **14a** by ^1H NMR. A 55% yield was isolated by distillation, bp 156–161 °C (0.15 torr): ^1H NMR (CCl_4) δ 1.20 (t, 6, J = 7 Hz), 1.74 (d, 3, J_{PH}) = 4 Hz), 1.92 (d, 3, J_{PH} = 3 Hz), 3.90 (p, 4, J_{HH} = J_{PH} = 7 Hz), 7.45 (d, 2, J = 9 Hz), 8.13 (d, 2, J = 9 Hz); IR (neat) 1516, 1349, 1271, 1030 cm^{-1}; HRMS calcd for $C_{14}H_{20}NO_6P$ 329.102 83, found 329.104 12. Anal. Calcd for $C_{14}H_{20}NO_6P$: C, 51.06; H, 6.13; P, 9.40. Found: C, 51.05; H, 6.28; P, 9.50.

Diethyl 2,2-Dimethyl-1-(*p*-nitrophenyl)vinyl Thiophosphate (14b). Reaction of $(EtO)_2PS^-K^+$ (prepared from 1.10 g of diethyl thiophosphite) with 1.62 g of **3a** in 23 mL of THF for 3 h gave after hydrolysis, ether extraction, and distillation a 46% yield of **14b**, bp 149–153 °C (0.1 torr): ^1H NMR (CCl_4) δ 1.18 (t, 6, J = 7 Hz), 1.77 (d, 3 J_{PH} = 4 Hz), 1.91 (d, 3, J_{PH} = 3 Hz), 3.94 (p, 4, J_{PH} = J_{HH} = 7 Hz), 7.52 (d, 2, J = 9 Hz), 8.19 (d, 2, J = 9 Hz); IR (neat) 1520, 1347, 1022 cm^{-1}; HRMS calcd for $C_{14}H_{20}NO_5PS$ 345.079 99, found 345.078 91. Anal. Calcd for $C_{14}H_{20}NO_5PS$: C, 48.68; H, 5.85; P, 8.97; S, 9.28. Found: C, 48.76; H, 5.90; P, 9.04; S, 9.25.

Reactions of Diethyl Phosphite or Thiophosphite Anions with 3c. Reaction of $(EtO)_2PO^-K^+$ (from 3.55 g of diethyl phosphite) with 4.69 g of **3c** in 23 mL of Me_2SO at 50 °C for 36 h gave by distillation at 116–118 °C (0.5 torr) a 40% yield of a 1.6:1 mixture of **14c**[17] and an isomer which could not be separated by preparative GLC. By ^1H NMR the isomer was assigned as **16**, 2-(diethoxyphosphinyl)-3,3-dimethyl-2-phenyloxirane. The vinyl methyls of **14c** had δ 1.69 (J_{PH} = 4 Hz) and 1.88 (J_{PH} = 2 Hz), while the oxirane methyls of **16** had δ 0.93 (J_{PH} = 1 Hz) and 1.73 (s). A similar mixture of isomers was observed in the reaction of $(EtO)_2PS^-Na^+$ with **3c** in EtOH at 0–20 °C for 24 h.

Registry No. 1a, 34006-49-0; **1b**, 40805-50-3; **29**, 95249-13-1; **2b**, 95249-14-2; **3a**, 83846-29-1; **3a′**, 42009-04-1; **3b**, 83846-30-4; **3c**, 7473-99-6; **4a**, 72511-02-5; **4b**, 83846-31-5; **4c**, 29973-21-5; **5a**, 83846-32-6; **5b**, 83846-33-7; **5c**, 83846-34-8; **6a**, 83846-35-9; **6b**, 83846-36-0; **6c**, 7473-98-5; **8**·K, 95070-46-5; **9**, 3964-18-9; **10**, 95249-15-3; **11**, 95249-16-4; **12a**, 83846-37-1; **12b**, 83846-38-2; **12c**, 95249-18-6; **12d**, 95249-19-7; **12e**, 95249-20-0; **12f**, 59919-11-8; **12g**, 95249-21-1; **12h**, 74074-84-3; **13a**, 95249-23-3; **13b**, 95249-24-4; **13c**, 95249-25-5; **14a**, 95249-26-6; **14b**, 95249-27-7; **14c**, 10409-55-9; **15**, 95249-17-5; **16**, 95249-28-8; *p*-$NCC_6H_4COOH_3$, 1443-80-7; *p*-$O_2NC_6H_4COCHMe_2$, 10326-99-5; *p*-$H_2NC_6H_4COCHMe_2$, 95249-12-0; *p*-$NCC_6H_4COCHMe_2$, 79341-95-0; $Me_2C{=}NO_2^-K^+$, 28273-55-4; $(EtO_2C)_2CH^-$, 14851-10-6; $(EtO_2C)_2CMe^-K^+$, 30014-62-1; *p*-$MeC_6H_4SO_2^-Na^+$, 873-55-2; $EtO_2CC(CN)^-$, 31124-95-5; *n*-BuS^-K^+, 26385-25-1; *p*-$O_2NC_6H_4COCMe_2^-K^+$, 95249-22-2; *p*-$MeC_6H_4SO_2Cl$, 98-59-9; *n*-$Pr{\equiv}C^-Li^+$, 18643-50-0; $PhC{\equiv}C^-Li^+$, 4440-01-1; $(EtO)_2PO^-K^+$, 54058-00-3; $(EtO)_2PS^-K^+$, 71774-85-1; PhS^-K^+, 3111-52-2; nitrocyclohexane K salt, 12385-03-4.

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