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THE REACTION OF CARBANIONS WITH 2-SUBSTITUTED-2-NITROPROPANES

SUBSTITUTION AND DIMERIZATION OCCURRING BY RADICAL CHAIN PROCESSES INVOLVING ELECTRON TRANSFER[1]

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Abstract—The reaction of mono-enolate anions with O_2NCMe_2X where $X = Cl$, NO_2, p-$MePhSO_2$ yield coupling ($RCOCH(R')(CMe_2NO_2)$) and enolate dimerization products ($RCOCH(R')CH(R')COR$) by free radical chain mechanisms involving bimolecular substitution or electron transfer reactions between the enolate anion and the intermediate nitro alkane radical anion ($XCMe_2NO_2^{\cdot-}$).

2-Substituted-2-nitropropanes ($XCMe_2NO_2$, $X = Cl$, NO_2, p-$MePhSO_2$) react with carbanions which are weak nucleophiles such as nitronate anions[2–7] or the enolate anions of β-diketones,[5,8] β-keto esters,[5,7,8] or malonic esters to yield substitution products by a photostimulated free radical chain process involving propagation steps 1–3.[3,10] Evidence that the 2-nitro-2-propyl radical is involved

$$XCMe_2NO_2^{\cdot -} \longrightarrow X^- + O_2NCMe_2\cdot \qquad (1)$$

$$O_2NCMe_2\cdot + A^- \longrightarrow O_2NCMe_2A^{\cdot -} \qquad (2)$$

$$O_2NCMe_2A^{\cdot -} + XCMe_2NO_2 \longrightarrow XCMe_2NO_2^{\cdot -} + O_2NCMe_2A \qquad (3)$$

in reaction (2) is furnished by the observation that when $Me_2C{=}NO_2^-$ and $MeC(CO_2Et)_2^-$ are allowed to compete in this process, the ratio of the two substitution products ($O_2NCMe_2CMe_2NO_2$ and $O_2NCMe_2C(Me)$–$(CO_2Et)_2$) are not only independent of the concentration of $XCMe_2NO_2$ employed but are also independent of the nature of the leaving group X (Table 1).[11] We conclude that in these substitutions that the leaving group has left before the new C–C bond has been formed in reaction (2). In competition experiments of this type large effects of solvent and counter-ion are observed upon the relative reactivities (Table 1). Thus, the relative reactivities at 25° of $MeC(CO_2Et)_2^-$ and $Me_2C{=}NO_2^-$ (k_m/k_n) in Me_2SO/K^+, (2.2.2)-cryptand toward the $Me_2\dot{C}NO_2$ are 10:1 but in the presence of 1M Li^+ the values of k_m/k_n are ~0.5 in Me_2SO, 4.0 in DMF and >70 in THF. In Me_2SO or DMF we are observing the effects of preferential ion pairing and the value of k_m/k_n reflects reaction occurring via the free anion and the ion-paired species. The observed values of k_m/k_n are thus a function of the Li^+ concentration. Since malonate ions are better complexing agents than nitronate anions towards Li^+, we are observing the competition of $Me_2\dot{C}NO_2$ for malonate anions more highly complexed with Li^+ than are the nitronate ions. In THF both anions are highly ion-paired and we see that as ion-paired species the value of k_m/k_n is larger (>70) than for the free ion ($k_m/k_n = 10$). Ion pairing apparently decreases the reactivity of both anions and increases the selectivity in the attack by $Me_2\dot{C}NO_2$.

With more easily oxidized carbanions such as the anions of Fig. 1, little or no substitution is observed in the reaction with $XCMe_2NO_2$.[12,13] Here, the major reaction is one of oxidative dimerization (reaction 4) with further reaction of $Me_2C{=}NO_2^-$ with $XCMe_2NO_2$ to yield $O_2NCMe_2CMe_2NO_2$ via the chain sequence of reactions (1)–(3).

$$2R{:}^- + XCMe_2NO_2 \longrightarrow R\text{–}R + X^- + Me_2C{=}NO_2^-. \qquad (4)$$

One interpretation of these results is that the anions of Fig. 1 prefer to react with $Me_2\dot{C}NO_2$ by electron transfer (reaction 4a) rather than by addition (reaction 2a).

$$Me_2\dot{C}NO_2 + R{:}^- \longrightarrow \begin{cases} Me_2C{=}NO_2^- + R\cdot & (4a) \\ Me_2C(NO_2)R^{\cdot -}. & (2a) \end{cases}$$

The oxidative dimer can be formed by coupling of two radicals in a non-chain reaction, or possibly by a chain sequence in which an alkyl radical is trapped by the alkyl anion (reactions 5–7).

$$R\cdot + R^- \longrightarrow R\text{–}R^{\cdot -} \qquad (5)$$

$$R\text{–}R^{\cdot -} + XCMe_2NO_2 \longrightarrow R\text{–}R + XCMe_2NO_2^{\cdot -} \qquad (6)$$

$$XCMe_2NO_2^{\cdot -} + R^- \longrightarrow R\cdot + X^- + Me_2C{=}NO_2^-. \qquad (7)$$

The rapidity with which the anions of Fig. 1 react with $XCMe_2NO_2$ has hindered kinetic investigation which might have better defined the process in which $R{:}^-$ is oxidized to $R\cdot$ and in which $R\cdot$ is converted to R–R. The absence of significant amounts of the cross coupling (or substitution) products, $RCMe_2NO_2$, in these reactions is noteworthy. It does seem that the common feature of the anions of Fig. 1 is that they have a low oxidation potential because of the formation of a resonance stabilized free radical R·. Thus, when the less easily oxidized $AlkC{\equiv}C{:}^-$ is employed, reaction (4) is no longer observed and the coupling product ($AlkC{\equiv}CCMe_2NO_2$) is formed in good yield in a process which proceeds rapidly

Table 1. Relative reactivity of M = MeC(CO$_2$Et)$^-$ and N = Me$_2$C=NO$_2^-$ towards Me$_2\dot{C}$NO$_2$ generated from XCMe$_2$NO$_2\cdot^-$

Solvent and Counter-ion	k_m/k_n		
	Cl-CMe$_2$NO$_2$	O$_2$NCMe$_2$NO$_2$	p-MePhSO$_2$CMe$_2$NO$_2$
K$^+$, [2.2.2]-cryptand, THF	0.4	---	---
K$^+$, [2.2.2]-cryptand, THF-Me$_2$SO (90:10)	1.7	---	---
K$^+$, [2.2.2]-cryptand, Me$_2$SO	12	---	10
0.1 M Li$^+$, Me$_2$SO	0.15	0.19	---
0.2 M Li$^+$, HMPA	0.22	---	---
0.2 M Li$^+$, Me$_2$SO	0.26	0.24	0.22
0.5 M Li$^+$, Me$_2$SO	0.30[a]	---	0.28
1 M Li$^+$, Me$_2$SO	0.47	0.41	0.44[b,c]
0.2 M Li$^+$, DMF	1.3	0.7	1.0
1.6 M Li$^+$, DMF	4.5[b]	---	4.1
0.2 M Li$^+$, THF	>70	---	---
0.2 M Li$^+$, 12-crown-4, THF	20		
0.2 M Li$^+$, THF-DMF (90:10)	18		
0.2 M Li$^+$, THF-DMF (50:50)	1.9		

[a] The values of k_m/k_n were 0.31 with 0.25 M ClCMe$_2$NO$_2$ and 0.29 with 0.10 M ClCMe$_2$NO$_2$

[b] Same relative reactivity observed for M$^-$ = N$^-$ = 1.2[Li]$_{Total}$ and for M$^-$Li$^+$ = N$^-$Li$^+$ = 0.1 M with excess LiI added.

[c] Values of k_m/k_n were 0.41, 0.45, 0.47 with p-MePhSO$_2$CMe$_2$NO$_2$ = 0.5, 0.1 and 0.05 M, respectively.

at −78°.[12] The fact that either Me$_2$C(NO$_2$)$_2$ or ClCMe$_2$NO$_2$ can be employed, strongly suggests that a radical chain reaction is involved.

The reaction of AlkC ≡ C:$^-$ with ClCMe$_2$NO$_2$ shows dramatic effects of solvent and counter ion.[12] Working with M$^+$/Me$_2$SO or Na$^+$/NH$_3$ none of the coupling product is observed whereas with Li$^+$/THF or Mg^{++}/hexane the coupling product is observed. We now recognize a number of similar reactions with mono-enolate anions (E$^-$) wherein coupling to yield ECMe$_2$NO$_2$ is observed only in a non-polar solvent such as THF with a counter-ion such as Li$^+$.[14] Furthermore, with secondary mono-enolate anions the reaction with XCMe$_2$NO$_2$ forms both the oxidative dimerization product (E–E + Me$_2$C=NO$_2^-$ + X$^-$) and the coupling product (E–CMe$_2$NO$_2$ + X$^-$) and from an analysis of the competition between reactions (8 and 9), we deduce that substitution follows reactions (10 and 3) rather than reactions (1–3) while dimerization occurs by reactions (5–7) (R$^-$ = E$^-$).[15] With the mono-enolate anions reactions (1 and 2) have merged into a single reaction (reaction 10). Competition between reactions (10 and 7) determines whether the coupling or dimerization product will be formed as shown in Scheme 1.

$$XCMe_2NO_2 + E^- \left\{ \begin{array}{ll} \longrightarrow \underset{\textbf{C}}{ECMe_2NO_2 + X^-} & (8) \\ \longrightarrow \underset{\textbf{D}}{E\text{–}E + Me_2C{=}NO_2^- + X^-} & (9) \end{array} \right.$$

$$XCMe_2NO_2\cdot^- + E^- \longrightarrow ECMe_2NO_2\cdot^- + X^- \quad (10)$$

Table 2 presents evidence that in the reaction of PhC(OLi)=CHMe or PhC(OLi)=CHPr-i with ClCMe$_2$NO$_2$ that both reaction (8 and 9) are free radical chain processes which are completely inhibited by the presence of (t-Bu)$_2$NO·. Table 2 also shows that the coupling product (**C**) is formed in THF-hexane (60:40) or THF-hexane–Me$_2$SO or HMPA (53:34:13) in the presence of Li$^+$ as the counter ion but is not a significant product in Me$_2$SO/K$^+$ where the product of oxidative dimerization (**D**) is the predominant product. The ratio of **C**/**D** for PhC(OLi)=CHPr-i increases from 0.06 in THF-hexane (60:40) to ~1 when 20 vol% (based on THF) of Me$_2$SO or HMPA is added. The reaction of PhC(OLi)=CHMe is less dependent upon solvent but with both substrates little coupling product is formed in

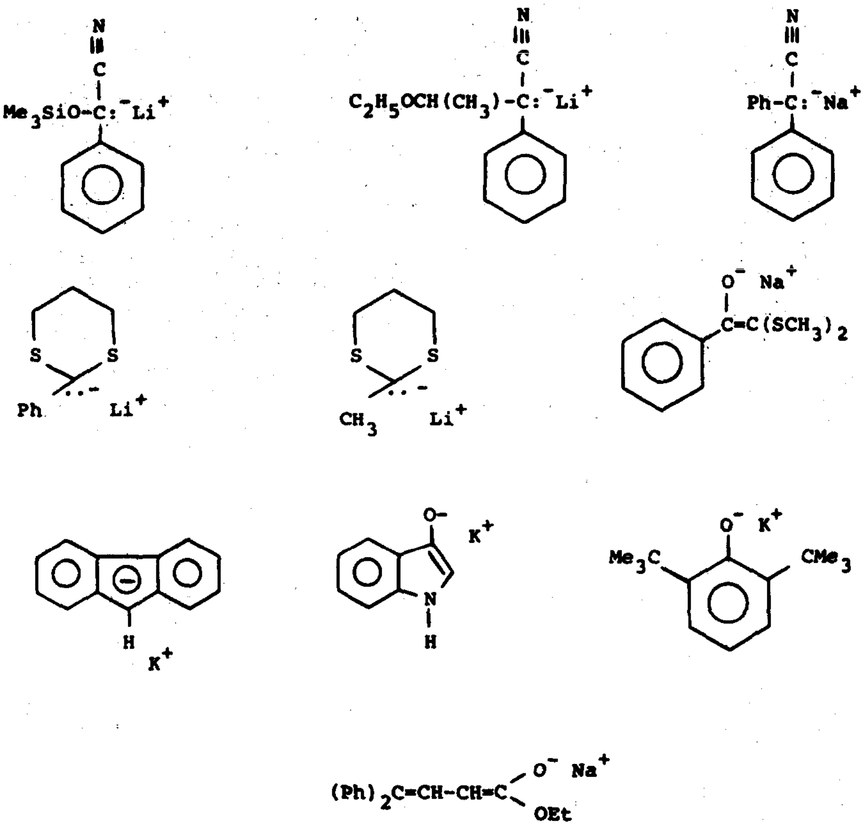
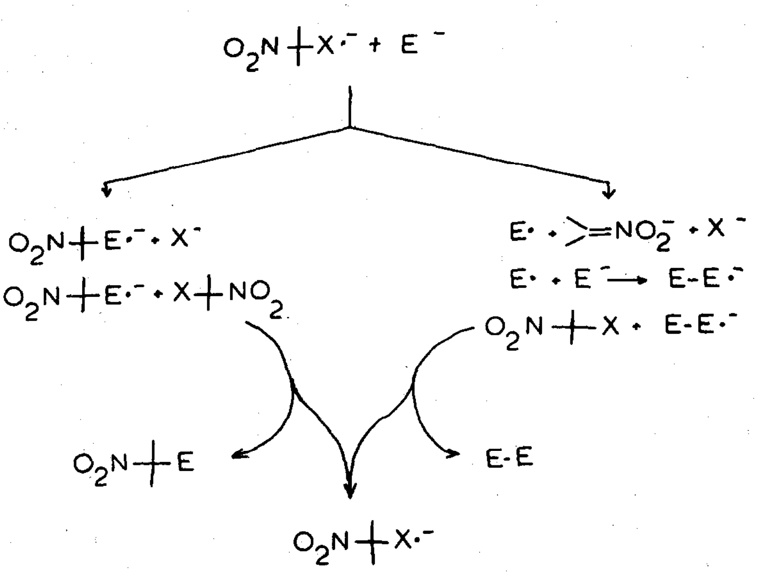


Fig. 1. Anions which react with $XCMe_2NO_2$ to yield products of oxidative dimerization.



Scheme 1. Substitution and oxidative dimerization mechanism (bimolecular).

100% Me_2SO or HMPA as solvents. It appears that tight E^-Li^+ ion pairs (present in THF) have a greater tendency to react with $XCMe_2NO_2$ to give substitution than the looser E^- ion pairs (present in Me_2SO or HMPA) which react predominantly by electron transfer to give dimerization products (E–E) derived from the enolate radical.

As $Me_2SO \cdot$ or HMPA is added to the THF–hexane (60:40) solvent, chlorine atom transfer (reaction 11, $X = Cl$) occurs for $PhC(OLi)=CHPr\text{-}i$. However, reaction (12) can be excluded as a source of the oxidative

$$E^- + XCMe_2NO_2 \longrightarrow E\text{–}X + Me_2C{=}NO_2^- \quad (11)$$

$$E\text{–}X + E^- \longrightarrow E\text{–}E + X^- \quad (12)$$

dimerization product since the presenct of $(t\text{-}Bu)_2NO\cdot$ completely prevents the formation of E–E but appears to have no effect on the formation of $PhC(=O)CH(Cl)Pr\text{-}i$ by nucleophilic attack on chlorine.

Experiments with added $Me_2C{=}NO_2^-$ (Table 2) exclude reaction (13) as a source of **C**. The ratio of **C**/**D** is unaffected by the presence of

$$E\cdot + \begin{array}{l} Me_2C{=}NO_2^- \longrightarrow ECMe_2NO_2\cdot^- \xrightarrow{-e} C \qquad (13) \\ E^- \longrightarrow EE\cdot^- \xrightarrow{-e} D \qquad (14) \end{array}$$

$Me_2C{=}NO_2^-$ or by the concentration of either E^- or $ClCMe_2NO_2$. It thus appears that once $E\cdot$ has been formed it reacts more readily with E^-Li^+ than with $Me_2C{=}NO_2^-Li^+$. Ion pairing probably has a large effect on the reactivity of the anions but it certainly appears that the preference of reaction (14) over reaction (13) is contrathermodynamic in that the formation of $ECMe_2NO_2\cdot^-$ is a more exothermic process than the formation of $EE\cdot^-$. The enolate radical reacts with the anion which is the stronger base (E^-). A similar observation has been made for the reaction of Me radicals with triarylmethide ions.[16]

The data of Table 2 require that some intermediate in the radical chain process undergoes competitive reactions of the same kinetic order with E^- to yield eventually products **C** and **D**. Competitive reactions 4a and 2a of the 2-nitro-2-propyl radicals with E^- would fulfill this requirement. However, as shown in Table 3 the ratio of **C**/**D** depends strongly upon the leaving group. For $PhC(OLi){=}CHMe$ the ratio of **C**/**D** in THF-hexane (60:40) decreases from 1.3 with $X = Cl$ to 0.5 with $X = NO_2$ or p-$MePhSO_2$. The reactions are still free radical chain processes and the ratio of **C**/**D** is uneffected by the presence of $Me_2C{=}NO_2^-$ and independent of the concentrations of $XCMe_2NO_2$ or E^-. We conclude that the leaving group X is still present in the intermediate whose reactions channel E^- to either the coupling or dimerization product. Reaction of $XCMe_2NO_2\cdot^-$ with E^- appears to be the point at which this competition is established.

$$XCMe_2NO_2\cdot^- + E^- \begin{array}{l} \xrightarrow{k_s} X^- + ECMe_2NO_2\cdot^- \xrightarrow{-e} C \\ \xrightarrow{k_{et}} X^- + Me_2C{=}NO_2^- + E\cdot \xrightarrow[-e]{E^-} D \end{array}$$

Perhaps both reactions proceed *via* a common iter-

Table 2. Reaction of $ClCMe_2NO_2$ with $PhC(OLi){=}CHR$ in THF-hexane (60:40)[a]

R	Conditions[b]	Products (%)			C/D
		$PhCOCH(R)CMe_2NO_2$	$PhCOC(R){=}CMe_2$	$[PhCOCH(R)\!-\!]_2$	
H	-20°, 13 vol % HMPA	0	49	0	∞
Me	32°	48	0	37	1.3
Me	35°, 100% THF	50	0	28	1.8
Me	25°, dark, 4 hr, 0.05 M $(t\text{-}Bu)_2NO\cdot$	0	0	0	---
Me	0-10°	70	0	23	3.0
Me	0-10°, diluted 5-fold with THF	78	0	19	4.1
Me	0-10°, 2 eq. $ClCMe_2NO_2$	66	0	22	3.0
Me	0°, 13 vol % HMPA	76	4	12	6.6
Me	0°, 13 vol % HMPA, 0.05 M $(t\text{-}Bu)_2NO\cdot$	0	0	0	---
Me	0°, 13 vol % HMPA, 0.15 M $Me_2C{=}NO_2Li$	52	11	14	4.0
Me	35°, 13 vol % Me_2SO	28	21	13	3.8
Me	0-10°, 0.25 h, 13 vol % Me_2SO	48	7	11	5.0
Me	0-10°, 0.25 h, 38 vol % Me_2SO	17	24	12	3.3
Me	30°, 8 m, K^+, 100% Me_2SO	0	7	31	0.22
i-Pr	35°	4	0	66	0.06
i-Pr	25°, dark	4	0	68	0.06
i-Pr	25°, 0.05 M $(t\text{-}Bu)_2NO\cdot$	0	0	0	---
i-Pr	35°, 0.5 M 12-crown-4-ether	8	0	69	0.12
i-Pr	0°, 13 vol % Me_2SO	24	(8.5)[c]	32	0.75
i-Pr	0°, 13 vol % Me_2SO, 0.05 M $(t\text{-}Bu)_2NO\cdot$	0	(29)[c]	0	---
i-Pr	35°, 0.5 h, 13 vol % Me_2SO	25	(5)[c]	25	1.0

Table 2. (*Contd*)

R	Conditions[b]	Products (%)			C/D
		$PhCOCH(R)CMe_2NO_2$	$PhCOC(R)=CMe_2$	$[PhCOCH(R)-]_2$	
i-Pr	0-30°, 13 vol % HMPA	35	(1.5)[c]	42	0.83
i-Pr	0-30°, 13 vol % HMPA, 0.15 M $Me_2C=NO_2Li$	29	(4)[c]	42	0.69
i-Pr	0-10°, 13 vol % HMPA, 2 eq. $ClCMe_2NO_2$	25	(7)[c]	37	0.68
i-Pr	0-10°, diluted 5-fold with THF:HMPA (80:20)	28	(17)[c]	26	1.1
i-Pr	10°, 38 vol % Me_2SO	16	(20)[c]	23	0.70
i-Pr	10°, 38 vol % Me_2SO, 0.05 M $(t\text{-}Bu)_2NO\cdot$	0	(44)[c]	0	---
i-Pr	35°, K^+, 100% Me_2SO	2	(18)[c]	25	0.05
iPr	25°, K^+, 100% Me_2SO, 0.05 M, $(t\text{-}Bu)_2NO\cdot$	0	(30)[c]	0	---
i-Pr	5°, 100% HMPA	0	(35)[c]	0	---
i-Pr	0-10°, 13 vol % DMF	21	(4)[c]	31	0.68
i-Pr	0-10°, 13 vol % pyridine	16.5	(<2)[c]	71	0.23
i-Pr	0-10°, 13 vol % TMEDA	7	(<1)[c]	60	0.12
Et	-10-0°, 13 vol % HMPA	73	---	13	5.6
Ph	35°, 3 h (24 h)	<2	0	66(82)	<0.01
Ph	35°, 3 h, 0.05 M $(t\text{-}Bu)_2NO\cdot$	0	0	0	---

[a] n-BuLi in hexane (5 mmol, 3.2 mL) was reacted with 5 - 5.5 mmol of $(i\text{-}Pr)_2NH$ in 5 mL THF at -50°. The solution was warmed to 0° and then cooled to -30° and the ketone added dropwise to give a reaction mixture ~0.5 M in enolate anion. Additional co-solvent, 1 eq of $ClCMe_2NO_2$ and other added reagents were added at 0° or 25°.

[b] Unless otherwise indicated reactions were performed for 1 h with irradiation from a 275-W sunlamp. Dark reactions were performed in ordinary laboratory lighting.

[c] $PhCOCH(Cl)Pr\text{-}i$. [d] >90% of $PhCOCH_2Ph$ recovered.

mediate. For example, electron transfer from E^- to $XCME_2NO_2\cdot^-$ might form in a cage,

$$|X^-Me_2C=NO_2^-E\cdot|.$$

Collapse in the cage of E· and $Me_2C=NO_2^-$ would lead to $ECMe_2NO_2\cdot^-$ while escape from the cage would yield E· which can be trapped by E^- to yield the dimerization product.

The reaction of an enolate anion with $XCMe_2NO_2\cdot^-$ seems unlikely from electrostatic considerations. However, it may be that this electrostatic repulsion is overcome by easily oxidized anions and that the second electron may be added to $XCMe_2NO_2$ more readily than the first. The second reduction of $XCMe_2NO_2$ would almost certainly be dissociative and lead to the formation of two stable anions. The reaction of $XCMe_2NO_2\cdot^-$ with E^- may be analogous to an electrochemical reduction in which the second electron transfer occurs more readily than the first, e.g. the reduction of many *p*-benzoquinones. The effect of the counterion certainly cannot be ignored since we are dealing with highly ion-paired species in THF/Li^+.

Reactions of $RC(OLi)=CH_2$ (R = *t*-Bu, Ph or *t*-BuO) with $XCMe_2NO_2$ are summarized in Table 4. Now $ClCMe_2NO_2$ in THF:hexane (60:40) leads only to the coupling product. However, with $t\text{-}BuC(OLi)=CH_2$ the product of oxidative dimerization becomes important when the oxidant is $Me_2C(NO_2)_2$ or $p\text{-}MePhSO_2CMe_2NO_2$. With these oxidants, nitro group transfer (reaction 11, $X = NO_2$) becomes important for $t\text{-}BuC(OLi)=CH_2$ or $t\text{-}BuOC(OLi) = CH_2$, but it was also observed for $PhC(OLi)=CHCH_3$ (Table 3). The nitro group transfer is not inhibited by the presence of $(t\text{-}Bu)_2NO\cdot$ and in the presence of $(t\text{-}Bu)_2NO\cdot$ the α-nitro ketone is not converted to **D**. Nitro group transfer is not a requirement for the formation of **D**. Thus, $PhC(OLi)=CHMe$ reacts with $p\text{-}MePhSO_2CMe_2NO_2$ (Table 3) to yield large amounts of **D** without formation of the α-nitro ketone or $p\text{-}MePhSO_2CMe_2H$ which is observed when nitro transfer from $p\text{-}MePhSO_2CMe_2NO_2$ occurs (e.g. see Table 4). Propio-

Table 3. Reaction of PhC(OLi)=CHMe with XCMe$_2$NO$_2$ in THF:hexane (60:40) at 35°[a]

X	Products (%)			C/D
	PhCOCH(Me)CMe$_2$NO$_2$	[PhCOCH(Me)$-$]$_2$	PhCOCH(Me)X	
Cl	48	37	0	1.3
NO$_2$	10	17	24	0.59
p-MePhSO$_2$	20.5	52	15	0.39
p-MePhSO$_2$[b]	26	47	5	0.55
p-MePhSO$_2$[b,c]	32	54	5	0.59

[a] See footnotes *a* and *b* of Table 1 for conditions.

[b] Diluted 5-fold with THF.

[c] 3 eq. *p*-MePhSO$_2$CMe$_2$NO$_2$ employed.

Table 4. Reaction of 2 equivalents of RC(OLi)=CH$_2$ with 1 equivalent of XCMe$_2$NO$_2$ in THF-hexane (60:40)[a]

R	X	Conditions[b]	Product (%)[c]		
			RCOCH=CMe$_2$	[RCOCH$_2$-]$_2$	Other
t-Bu	Cl	3 h	72	5	
t-Bu	Cl	25°, 19 h, 10% (*t*-Bu)$_2$NO·	6	2	
t-Bu	NO$_2$	3 h	20	30	*t*-BuCOCH$_2$NO$_2$, 15
t-Bu	NO$_2$	3 h, 1 eq Me$_2$C=NO$_2$Li	25	27	*t*-BuCOCH$_2$NO$_2$, 13
t-Bu	NO$_2$	25°, 20 h, 10% (*t*-Bu)$_2$NO·	7	9	*t*-BuCOCH$_2$NO$_2$, 16
t-Bu	*p*-MePhSO$_2$	3 h	28	38	
t-Bu	*p*-MePhSO$_2$	0°, 1.5 h	10 + 25[d]	48	
t-Bu	*p*-MePhSO$_2$[e]	1.5 h, 13 vol % Me$_2$SO	45	10	(O$_2$NCMe$_2$$-$)$_2$, 5
t-Bu	*p*-MePhSO$_2$[e]	1.5 h, 13 vol % Me$_2$SO 1 eq Me$_2$C=NO$_2$Li	29	6	(O$_2$NCMe$_2$$-$)$_2$, 39
t-Bu	*p*-MePhSO$_2$	25°, O$_2$	2	3	
Ph	Cl	-20°, 13% HMPA	97	0	PhCOCH$_3$, 90
t-BuO	Cl	-30° to 25°, 1.5 h	89	0	
t-BuO	NO$_2$	1.5 h	0	0	*t*-BuOC(=O)CH$_2$NO$_2$, 62
t-BuO	*p*-MePhSO$_2$	1.5 h	7	0	*t*-BuOC(=O)CH$_2$NO$_2$, 33 *p*-MePhSO$_2$CMe$_2$H, 58 *p*-MePhSO$_2$CMe$_2$NO$_2$, 37

[a] See footnote *a*, Table 1.

[b] Unless otherwise indicated reactions were irradiated for 1 h with a 275-W sunlamp which maintained a temperature of 35°C.

[c] Based on a theoretical yield of 1 equivalent.

[d] *t*-BuCOCH$_2$CMe$_2$NO$_2$.

phenone enolate does yield significant amounts of $PhCOCH(CH_3)SO_2PhMe$-*p* (Table 3), perhaps from reaction of E· with *p*-$MePhSO_2^-$.

Elimination of the elements of HNO_2 from **C** (a *β*-nitro ketone) becomes more important at higher temperatures and when polar cosolvents are added to the THF-hexane (60:40) solvent. The E_2 elimination is also more important for the coupling products formed from 1°-enolate anions than 2°-enolates. Because of this, the reactions of Table 4 were performed with two equivalents of the enolate anion and yields are based on the expectations of reaction (15).

$$\begin{array}{l}
RC(O^-)\!=\!CH_2 + XCMe_2NO_2 \longrightarrow RC(\!=\!O)CH_2CMe_2NO_2 + X^- \\
RC(O^-)\!=\!CH_2 + RC(\!=\!O)CH_2CMe_2NO_2 \longrightarrow RCOCH_3 + RCOCH\!=\!CMe_2 + NO_2^- \\
\hline
2RC(O^-)\!=\!CH_2 + XCMe_2NO_2 \longrightarrow RCOCH_3 + RCOCH\!=\!CMe_2 + X^- + NO_2^-
\end{array} \tag{15}$$

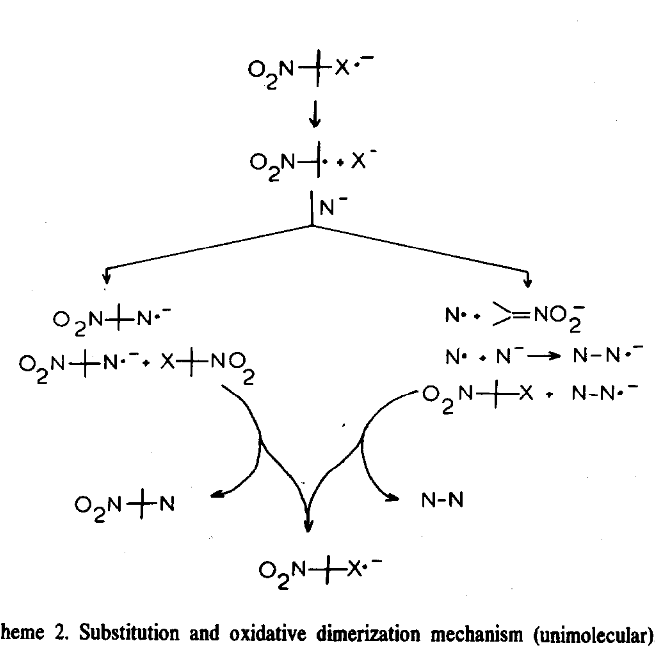
The variation of k_s/k_{et} with the structure of E^- seems to be quite logical. As the structure of R in PhC(OLi)=CHR is varied from R = H to Me, i-Pr or Ph the ratio of k_s/k_{et} for $ClCMe_2NO_2$ in THF-hexane (60:40) varies from ∞(R = H) to 0(R = Ph). The value of k_s/k_{et} is larger for R = Me than for R = i-Pr indicating that steric hindrance favors electron transfer over substitution. However, the major structural effect seems to be the stability of E· formed by electron transfer which of course increases in the series PhC(=O)ĊHR from R = H to R = alkyl to R = Ph. With t-BuC(OLi)=CH_2 either the k_s or k_{et} process can occur with appropriate oxidants, but with t-BuOC(OLi)=CH_2 only the k_s process is observed with reaction (11) an important side reaction.

Other mono-enolate anions show a similar effect of products on the structure of $XCMe_2NO_2\cdot^-$. Thus, cyclohexanone in THF-hexane-HMPA (53:34:13) yields 85% of the coupling product at −20° with $ClCMe_2NO_2$ but with $Me_2C(NO_2)_2$ oxidative dimerization is the major reaction pathway.

The reactions of Scheme 1 are not exclusive of the radical chain process depicted in reactions (1)–(3). It is possible that in certain cases substitution and dimerization can be occurring in competitive bimolecular (Scheme 1) and unimolecular (Scheme 2) reactions of the intermediate $XCMe_2NO_2\cdot^-$. In such cases the partitioning of the reaction according to the two Schemes should be a function of the concentration of the nucleophile with high concentrations favoring Scheme 1 and low concentrations favoring Scheme 2. It does appear that as the ability of the nucleophile to donate an electron increases that the course of the reaction changes from that depicted in Scheme 2 to the reaction of Scheme 1.

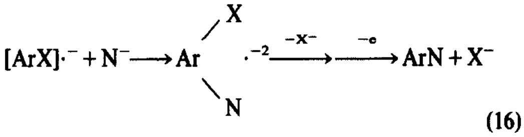
In the present work if reactions with X = Cl, O_2N, *p*-$MePhSO_2$ all proceed by the same chain mechanism, this must be the one depicted in Scheme 1. On the other hand, it is possible that with X = Cl the reactions follow Scheme 2 involving a free 2-nitro-2-propyl radical but with X = O_2N or *p*-$MePhSO_2$ the reactions follow Scheme 1 without the intervention of a free 2-nitro-2-propyl radical. The explanation that the sequences of both Schemes 1 and 2 are both present for all leaving groups seems untenable since competition between Scheme 1 and Scheme 2 should depend on E^- concentration. However, the ratio **C**/**D** was independent of $[E^-]$ for both X = Cl and X = *p*-$MePhSO_2$. Of course both schemes cannot lead to the same ratio of **C**/**D** since otherwise there would be no effect of X on **C**/**D**.

Bimolecular reactions of aromatic radical anions leading to substitution products have been mentioned in the past, but often without direct experimental support. Shein has suggested that substitution reactions of *p*-



Scheme 2. Substitution and oxidative dimerization mechanism (unimolecular).

dinitrobenzene,[17] *p*-nitrochlorobenzene,[18] or 2,4-dinitrochlorobenzene[19] involve reaction (16). It has been demonstrated by Abe and Ikegami that



$$[ArX]\cdot^- + N^- \longrightarrow Ar(X)(N)\cdot^{-2} \xrightarrow{-X^-} \xrightarrow{-e} ArN + X^- \quad (16)$$

displacement of nitrite ion by hydroxide ion from *o*- or *p*-dinitrobenzene is kinetically controlled by the attack of hydroxide ion on the dinitrobenzene radical anion.[20] It has also been recently demonstrated that mercaptide nucleophiles attack dopasemiquinone more readily than the free quinone and that this has considerable biochemical importance.[21] It thus appears that in both aromatic and aliphatic chemistry, the bimolecular interaction between a nucleophile and a radical anion can occur. In view of this conclusion it seems appropriate to be cautious in assigning the $S_{RN}1$ mechanism (i.e. reactions 1–3) to all aromatic substitution processes proceeding *via* a radical chain sequence.[22] Only when competitive substitution reactions yield products consistent with known reactivities of the aromatic radicals can these processes be accepted as established.

With mono-enolate anions we have seen reactions (1 and 2) merge in the reactions of 2-substituted-2-nitropropanes. It is possible to consider reactions (3 and 1) also merging into a single step, i.e. dissociative electron transfer. This is a possibility in the free radical chain substitution reactions of organomercury halides (Cl, Br, I) with nitronate anions, reaction (17).[23]

$$RHgX\cdot^- + Me_2C{=}NO_2^- \xrightarrow{h\nu} RCMe_2NO_2 + Hg^0 + X^- \quad (17)$$

For this reaction the chain sequence can be written as reactions (1′–3′). However, there is as yet no evidence for the intermediacy

$$RHgX\cdot^- \longrightarrow R\cdot + Hg^0 + X^- \quad (1')$$

$$R\cdot + Me_2C{=}NO_2^- \longrightarrow RCMe_2NO_2\cdot^- \quad (2')$$

$$RCMe_2NO_2\cdot^- + RHgX \longrightarrow RHgX\cdot^- + RCMe_2NO_2 \quad (3')$$

of $RHgX\cdot^-$. The intermediacy of the free alkyl radical in this substitution process is easily demonstrated by using the Δ^5-hexenyl-mercury halide. Only cyclized products are isolated and the ratio of cyclopentylcarbinyl to cyclohexyl product of 96/4 is in excellent agreement with other reactions of the Δ^5-hexenyl radical (Scheme 3).[24]

CONCLUSION

Free radical chain processes involving attack of nucleophiles upon radical anions in a bimolecular process are important for nucleophiles which easily loose one electron. Such processes are involved in the reaction of $XCMe_2NO_2$ where X = Cl, NO_2 or *p*-$MePhSO_2$ with 1°- or 2°-monoenolate anions such as $PhC(OLi){=}CHR$ with R = Me or i-Pr, $t\text{-}BuC(OLi){=}CH_2$ or cycloalkanone enolate anions. Such processes may be fairly widespread in organic chemistry. Radical chain substitutions involving nucleophilic attack may also proceed without the intervention of the substrate radical anion if electron transfer is a dissociative process.

EXPERIMENTAL

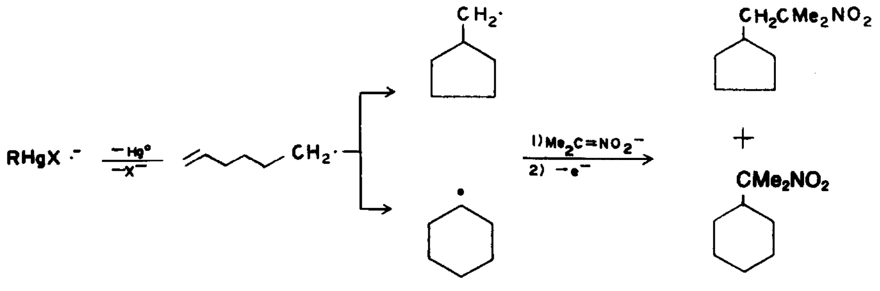
2-Chloro-2-nitropropane,[25] 2,2-dinitropropane,[26] and 2-(*p*-tolylsulfonyl)-2-nitropropane[27] were prepared by literature procedure, Lithium *t*-butoxide prepared from clean lithium wire and *tert*-butyl alcohol under nitrogen was >95% pure by titration. Commercial samples of lithium iodide, *n*-butyllithium, diisopropylamine, potassium *tert*-butoxide, [2.2.2]-cryptand and 12-crown-4 ether were employed. Solvents were dried and fractionally distilled from calcium hydride and stored over molecular sieves under nitrogen.

Competitive alkylation of lithium diethyl methylmalonate and lithium 2-nitropropane were performed by the addition of 5 mmol of diethyl methylmalonate and 5 mmol of 2-nitropropane to a well stirred solution of 11 mmol of lithium *tert*-butoxide in 45 mL of solvent under nitrogen. After 10 m the solution was irradiated with a 250-W sunlamp at 60 cm and a deoxygenated solution of the 2-substituted-2-nitropropane (5 mmol in 5 mL of solvent) added. After 90 m the solution was poured into water and the resulting mixture repeatedly extracted with ether or benzene. The organic extract was washed, dried over $MgSO_4$, the solvent evaporated under reduced pressure and the residue analyzed by integrated PMR spectra using weighed amounts of DMF or phthalide as references. Relative values of k_m/k_n were calculated by means of the equation,

$$k_m/k_n = \log(1\text{-fractional yield } O_2NCMe_2C(Me)(CO_2Et)_2) / \log(1\text{-fractional yield } O_2NCMe_2CMe_2NO_2).$$

Competitive experiments utilizing K^+, [2.2.2]-cryptand were performed by the addition of 0.80 mmol of potassium *tert*-butoxide in 2 mL of solvent under nitrogen with stirring to a solution of 0.80 mmol of [2.2.2]-cryptand in 3.6 mL of solvent followed by the addition of 1.6 mL of a 0.25M solution in diethyl methylmalonate and 2-nitropropane. After 10 m, sunlamp irradiation was commenced and 1.6 mL of a 0.25M solution of the 2-substituted-2-nitropropane added. After 90 m the reaction mixture was analyzed as described above.

Reactions of lithium enolates with 2-substituted-2-nitropropanes in THF-hexane-cosolvent systems were performed in a 25 mL 3-necked flask equipped with a magnetical stirring bar, thermometer and two rubber septa which were wrapped and sealed with Panefilm. A moderate stream of nitrogen was passed through the flask via hypodermic needles in the septa for 10–15 m. Tetrahydrofuran (5 mL) and 5.2 mmoles (5% excess) of



Scheme 3.

diisopropylamine, cyclohexylisopropylamine or hexamethyldisilazane were added by syringe and the flask cooled to −70°. 3.3 mL of 1.55M *n*-butyllithium in hexane (5.1 mmoles, 2–3% excess) was added by syringe to the magnetically stirred solution. The flask was kept at −60° for 3–5 m, allowed to warm to ~ −10°, and then cooled again. The lithium enolates were generated by a careful, dropwise addition (5–10 m) of the ketones by syringe to the well-stirred solution at −40° to −30° (the enolate anion of *tert*-butyl acetate was generated at −78°). The cooling bath was removed and the enolate solution was allowed to stir for 10–15 m. After that time additional cosolvents, reagents or inhibitors were added. The 2-substituted-2-nitropropane (5 mmol) or its solution in THF was injected and the reaction conducted with a 275-W sunlamp 20–30 cm from the reaction flask.

For reactions of lithium enolates with 2-substituted-2-nitropropanes in pure THF or HMPA, the lithium enolate in THF-hexane was prepared as described. The flask was attached to a vacuum pump and the solvents were slowly evaporated at −30–0° to yield the lithium enolate as a white solid. The flask was filled with nitrogen and 10 mL of pure THF or HMPA were added. When the lithium enolate had dissolved, 5 mmoles of the 2-substituted-2-nitropropane or its solution in THF or HMPA was injected.

Reactions of potassium enolates with 2-chloro-2-nitropropane in pure Me_2SO were performed by adding potassium hydride (2–3 g of a 23.6% dispersion in mineral oil) to a dried, 3-necked flask under nitrogen. The oil was removed by 4–5 washings with dry pentane under nitrogen. The oil in pentane was removed with a syringe from the solid potassium hydride after which 15–20 mL of Me_2SO was added under nitrogen. About 1 hr of stirring produced a clear, yellow-green solution of potassium dimsylate (0.5 M). The exact concentration of the base was established by titration of an aliquot. The potassium dimsylate solution (5 mmoles) was transferred to the reaction flask under nitrogen and 5 mmoles of the carbonyl compound added dropwise to the well stirred base at room temperature. The potassium enolate solution was allowed to stir for another 5–10 min before 5 mmoles of 2-chloro-2-nitropropane was injected.

Analysis of the products of enolate anion reactions was performed by pouring the reaction mixtures into a separatory funnel containing 80–100 mL of water or brine and 30–40 mL of ether. The organic layer was separated and the water layer extracted two times with 15 mL of ether. The combined ether layers were washed once with 20–25 mL of 0.25 *N* hydrochloric acid to remove the amine. For the reactions with 2,2-dinitropropane or 2-nitro-2-*p*-tolylsulfonylpropane, the water layer was additionally neutralized with diluted hydrochloric acid and then extracted again with ether to extract α-nitroketones or α-nitroesters. The organic layers were washed once with 100 mL water and dried with anhydrous magnesium sulfate. The solvents were partially evaporated and the mixture was preliminarily analysed by gas chromatography. The rest of the solvent was vacuum evaporated, and a weighed amount of phthalide as an internal standard added. PMR spectra (60 MHz) of the crude mixture was taken in deuterochloroform (1% TMS). The yields of the products were calculated from the integrated product and standard signals of this mixture after the reaction products had been isolated by distillation and identified by ^{1}H NMR, IR, and MS spectra.

The following oxidative dimerization products were isolated and identified: 2,2,7,7-tetramethyl-3,6-octanedione (from pinacolone); b.p. 107–110° (10 torr); ^{1}H NMR ($CDCl_3$) $\delta = 1.18$ (s, 18*H*), 2.78 (s, 4H); IR (neat) 1703 cm^{-1} (lit.[28,29] b.p. 106–107° (10 torr); ^{1}H NMR δ 1.2, 2.8; IR 1706 cm^{-1}): 2,3-dimethyl-1,4-diphenyl-1,4-butanedione (from propiophenone); b.p. 153–160 (0.1 torr); m.p. 67° (meso), 80–82° (racemic); ^{1}H NMR (CCl_4) $\delta = 1.18$ (*d*, 6*H*, $J = 6.8$ Hz), 3.82 (m, 2H), 7.39 (m, 6H), 7.83 (m, 4H); IR ($CHCl_3$) 1683 cm^{-1} (lit.[20] m.p. 67° (meso), 86–87° (racemic); ^{1}H NMR ($CDCl_3$) $\delta = 1.27$, 3.75, 7.2–8.0; IR (KBr) = 1680 cm^{-1}): 2,3-diethyl-1,4-diphenyl-1,4-butanedione (from butyrophenone); b.p. 156–165 (0.1 torr); m.p. 68–68°, 87–92°; ^{1}H NMR ($CDCl_3$) $\delta = 0.78$ (t, 6H, $J = 7.5$ Hz), 1.70 (m, 4H), 3.95 (m, 2H), 7.37 (m, 6H), 7.81 (m, 4H); IR ($CHCl_3$) 1682 cm^{-1} (lit.[31] ^{1}H NMR $\delta = 0.7$–1.3 (m, 6H), 1.6–2.1 (m, 4H) 4.05 and 5.55 (q and t, 2H), 6.9–8.0 (m, 10H); IR (neat) 1680 cm^{-1}): 2,3-disopropyl-1,2-diphenyl-1,4-butanedione (from isovalerophenone); b.p. 158–164° (0.2 torr); ^{1}H NMR ($CDCl_3$), $\delta = 0.85$ (d, 6H, $J = 11$ Hz), 1.02 (d, 6H, $J = 11$ Hz), 2.22 (m, 2H), 4.31 (m, 2H), 7.26–7.58 (m, 6H), 7.83–8.20 (m, 4H); IR ($CHCl_3$) 1680 cm^{-1}; MS (70 ev), m/e = 322.19233 (1.9%), 225 (2%), 203 (3%), 162 (4%), 161 (5%), 160 (5.7%), 145 (5%), 1299 (5%), 105 (100%), 77 (47%); calc. for $C_{22}H_{26}O_2$, 322.1933: 1,2,3,4-tetraphenyl-1,4-butanedione; m.p. 148–154°; ^{1}H NMR ($CDCl_3$) $\delta = 5.40$ (s, 2H), 7.07 (s, 10H), 7.41 (m, 6H), 7.92 (m, 4H); IR ($CHCl_3$) 1678 cm^{-1}; MS. (70 ev) m/e = 390.16336 (< 1%), 389 (1%), 371 (1%), 285 (2.4%), 269 (1.3%), 268 (4.5%), 179 (2.9%), 122 (1.5%), 165 (46.7%), 78 (100%), 77 (99.8%); M.W. calc. for $C_{28}H_{22}O_2$, 390.1620 (lit.[32,33] m.p. 159–160°, 256–257°; IR, 1667 cm^{-1}).

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