dergoing very rapid exchange in a process which does not permute CF_3 groups. This result is confirmed by the averaged A_3B_3 pattern [ϕ −74.72 and −75.51, (J = 9.2 Hz)] observed in the ^{19}F NMR spectrum (CF_3 region) of an equimolar mixture of **2**/**4** (−25 °C). The trifluoromethyl groups in **2** exchange at elevated temperatures, with an estimated activation energy $\Delta G^{\ddagger}{}_{54}$ = 17.0 kcal/mol. Noticeable curvature appeared in the plot of ln k vs. $1/T$, and the accuracy of derived activation parameters is thereby reduced. We interpret the nonlinearity to indicate that at least two enantiomerization mechanisms are operating.[15] In contrast to the behavior of **1**, spectra of **2** are solvent dependent, and the exchange rate is sensitive to impurities. Addition of small amounts of HMDS[6] to propionitrile solutions of **2** reduced the CF_3 exchange rate and raised $\Delta G^{\ddagger}{}_{94}$ to ca. 19 kcal/mol.

The observation that the exchange rate of **1** is independent of solvent or added nucleophilic solvent militates against involvement of hexacoordinate silicon.[17] While enantiomerization of **2** cannot be accounted for by simple silicon–oxygen bond breaking steps, rapid exchange of the fluoride ligand may play a role in the itinerary for CF_3 exchange.

Acknowledgment. We thank Dr. G. S. Reddy and W. John for ^{19}F NMR data. Professor J. D. Roberts kindly supplied a copy of DNMR 3 which was adapted for use on our computer by Dr. R. M. Hilmer.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure amplitudes (47 pages). Ordering information is given on any current masthead page.

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(15) Many alternate mechanisms are possible and some may act in concert with pseudorotation. We note two which appear most reasonable: (1) An HF-catalyzed axial–equatorial exchange of the fluorine ligand; (2) axial loss coupled with edge attack on **4** (or equatorial loss coupled with face attack) of the rapidly exchanging fluorine ligand.[16]

(16) The lowest energy pathway for fluoride exchange is believed to involve axial loss and face attack. For calculations on model systems, see Wilhite, D. L.; Spialter, L. *J. Am. Chem. Soc.* **1973**, *95*, 2100. Paybutt, P. *Mol. Phys.* **1975**, *29*, 389.

(17) Such species have been implicated in the racemization of tetracoordinate silicon halides (Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1.) They were believed responsible for axial/equatorial site exchange in pentacoordinate silicon fluorides (Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 3845.)

Alkylation and Oxidative Dimerization of Enolate Anions by Radical Chain Processes[1]

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Received March 20, 1981

The radical chain involving reactions 1–3[2,3] has been termed

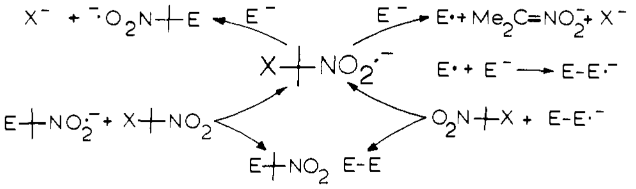
$$RX^{-}\cdot \rightarrow R\cdot + X^{-} \tag{1}$$

$$R\cdot + N^{-} \rightarrow RN^{-}\cdot \tag{2}$$

$$RN^{-}\cdot + RX \rightarrow RX^{-}\cdot + RN \tag{3}$$

$S_{RN}1$.[4] In such substitutions the possibility exists that reactions 1 and 2 may merge and that R· may not be an intermediate. A distinction between a concerted process and the consecutive reactions 1 and 2 can be made on the basis of competitive experiments. When two anions are allowed to compete for a series of substrates containing a common R moiety, the relative reactivities of the anions should be independent of the leaving groups only if free R· is an intermediate. This technique has been employed in aromatic $S_{RN}1$ reactions,[5] and for the reaction of $XCMe_2NO_2$ (X = Cl, NO_2, or p-$MePhSO_2$) with $Me_2C{=}NO_2^-$ and $MeC(CO_2Et)_2^-$ in Me_2SO.[6]

Scheme I. Bimolecular Substitution and Oxidative Dimerization



We now report a second type of competition in the reaction of easily oxidized monoenolate anions (E = $RC(O^-){=}CHR'$) with $XCMe_2NO_2$, leading to coupling (**1** and **2**) and symmetrical dimerization (**3**) products. Our results require that both processes 4 and 5 proceed by free radical chains and that the competition

$$\begin{gathered} E^-Li^+ + XCMe_2NO_2 \xrightarrow{THF} \underset{\mathbf{1}}{ECMe_2NO_2} + X^- \\ \mathbf{1} \xrightarrow{B^-} \underset{\mathbf{2}}{RCOC(R'){=}CMe_2} + NO_2^- \end{gathered} \tag{4}$$

$$2E^-Li^+ + XCMe_2NO_2 \xrightarrow{THF} \underset{\mathbf{3}}{E{-}E} + X^- + Me_2C{=}NO_2^- \tag{5}$$

between these processes is determined by bimolecular reactions of $XCMe_2NO_2^{-}\cdot$ and not by reactions of free $O_2NCMe_2\cdot$.

The competition between (4) and (5) for $E^- = PhC(O^-){=}CHR'$ with 2-chloro-2-nitropropane leads only to **1** and **2** with R′ = H and only to **3** with R′ = Ph. With R′ = Me, Et, or i-Pr both products **1** and **3** are observed. Increasing the steric bulk of R′ or the resonance stabilization of E· favors process 5. In all cases the presence of 5–10 mol % of $(t\text{-}Bu)_2NO\cdot$ prevents the formation of **1**–**3**, and the starting phenone can be recovered. With R′ = Me or i-Pr the ratio **1**/**3** is unaffected by the presence of $Me_2C{=}NO_2Li$ in solvent mixtures of THF–hexane–Me_2SO (or HMPA). For these systems E· is trapped more readily by E^- than by $Me_2C{=}NO_2^-$. This is surprising since the addition step of reaction 6 must be more exothermic than the corresponding step of reaction 7. Apparently E· preferentially reacts with the anion which is the stronger base.[7]

$$E\cdot + Me_2C{=}NO_2^- \xrightarrow{\text{slow}} \mathbf{1}^{-}\cdot \xrightarrow{-e} \mathbf{1} \tag{6}$$

$$E\cdot + E^- \xrightarrow{\text{fast}} \mathbf{3}^{-}\cdot \xrightarrow{-e} \mathbf{3} \tag{7}$$

The ratio **1**/**3** from $E^- = PhC(O^-){=}CHR'$ or $Me_3CC(O^-){=}CH_2$ and $XCMe_2NO_2$ is independent of the concentrations of E^- or $XCMe_2NO_2$ but *depends strongly on the nature of X* with the ratio **1**/**3** decreasing from X = Cl to X = p-$MePhSO_2$ or NO_2 (Table I). A similar effect is observed for cyclohexanone enolate anion where $ClCMe_2NO_2$ yields >80% of the C-alkylation products, but $Me_2C(NO_2)_2$ yields mainly **3**.[8,9]

It is impossible to explain the variation in the ratio **1**/**3** from competition between reactions 8 and 9 or by competition between

$$Me_2\dot{C}{-}NO_2 + E^- \rightarrow ECMe_2NO_2^{-}\cdot \xrightarrow{-e} \mathbf{1} \tag{8}$$

$$Me_2\dot{C}{-}NO_2 + E^- \rightarrow Me_2C{=}NO_2^- + E\cdot \xrightarrow{E^-} \xrightarrow{-e} \mathbf{3} \tag{9}$$

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(1) Electron Transfer Processes. 27. This work was supported by Grant CHE-7823866 from the National Science Foundation.

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(9) In THF–hexane–HMPA (53:34:13) at −35 °C for 1 h, cyclohexanone enolate and $ClCMe_2NO_2$ yield 67% of **1**, 15% of **2**, and 11% of **3**.

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Table I. Yields of $RCOCH(R')CMe_2NO_2$ (**1**), $RCOC(R'){=}CMe_2$ (**2**), $[RCOCH(R')-]_2$ (**3**), and $RCOCH(R')X$ (**4**) from the Reaction of $RC(OLi){=}CHR'$ and $XCMe_2NO_2$ in THF-Hexane (60:40)[a]

R, R'-	X	conditions[b]	yield, %				
			1[c]	**2**[c]	**3**[c]	**4**[c]	(**1** + **2**)/**3**
t-Bu, H	Cl^d	3 h	$0, 0^e$	$72, 6^e$	$<5, 2^e$	$0, 0^e$	>14
t-Bu, H	$NO_2{}^d$	3 h	$0, 0^e, 0^f$	$20, 7,^e 25^f$	$30, 9,^e 27^f$	$15, 16,^e 13^f$	$0.7, 0.9^f$
t-Bu, H	$p\text{-MePhSO}_2{}^d$	3 h	0	28	38	0	1.4
t-Bu, H	$p\text{-MePhSO}_2$	1.5 h, 13 vol % Me_2SO	$0, 0^f$	$45, 29^f$	$10, 6^f$	0	4.5
t-Bu, H	$p\text{-MePhSO}_2{}^d$	1.5 h, 0 °C	25	10	48	0	0.8
Ph, H	Cl^d	1 h, -20 °C, 13 vol % HMPA	0	97	0	0	∞
Ph, Me	Cl	1 h, 0-10 °C	$70, 78,^g 66^h$	$0, 0,^g 0^h$	$23, 19,^g 22^h$	$0, 0,^g 0^h$	$3.0, 4.1,^g 3.0^h$
Ph, Me	Cl	1 h	$48, 0^e$	$0, 0^e$	$37, 0^e$	$0, 0^e$	1.3
Ph, Me	Cl	1 h, 100% THF	50	0	28	0	1.8
Ph, Me	NO_2	1 h	10	0	17	24	0.6
Ph, Me	$p\text{-MePhSO}_2$	1 h	$21, 26,^g 32^{g,h}$	$0, 0,^g 0^{g,h}$	$52, 47^g 54^{g,h}$	$15, 5,^g 5^{g,h}$	$0.6, 0.4,^g 0.55^{g,h}$
Ph, Me	Cl	1 h, 0 °C, 13 vol % HMPA	$76, 52,^f 0^e$	$4, 11,^f 0^e$	$12, 14,^f 0^e$	$0, 0,^f 0^e$	$6.6, 4.0^f$
Ph, Me	Cl	15 min, 0-10 °C, 13 vol % Me_2SO	48	7	11	0	5.0
Ph, Me	Cl	1 h, 35 °C, 13 vol % Me_2SO	28	21	13	0	3.8
Ph, Me	Cl	8 min, 30 °C, K^+ in Me_2SO	0	7	31	0	0.2
Ph, Me	Cl	1 h, 5 °C, HMPA	0	5	31	0	0.2
Ph, Et	Cl	1 h, -10-0 °C, 13 vol % HMPA	73	0	13	0	5.6
Ph, i-Pr	Cl	1 h	$4, 8,^i 0^e$	$0, 0,^i 0^e$	$66, 69,^i 0^e$	$0, 0,^i 0^e$	$0.06, 0.1^i$
Ph, i-Pr	Cl	1 h, 0-10 °C, 13 vol % HMPA	$35, 29,^f 25^h$	$0, 0,^f 0^h$	$42, 42,^f 37^h$	$1.5, 4,^f 7^h$	$0.8, 0.7,^f 0.7^h$
Ph, i-Pr	Cl	1 h, 0 °C, 13 vol % Me_2SO	$24, 0^e$	$0, 0^e$	$32, 0^e$	$8.5, 29^e$	0.8
Ph, i-Pr	Cl	1 h, 10 °C, 38 vol % Me_2SO	$16, 0^e$	$0, 0^e$	$23, 0^e$	$20, 44^e$	0.7
Ph, i-Pr	Cl	1 h, 35 °C, K^+ in Me_2SO	$2, 0^e$	$0, 0^e$	$25, 0^e$	$18, 30^e$	0.05
Ph, i-Pr	Cl	1 h, 5 °C, HMPA	0	0	0	44	- -
Ph, Ph	Cl	3 h, 35 °C	$<2, 0^e$	$0, 0^e$	$66, 0^e$	$0, 0^e$	<0.02

[a] Satisfactory elemental analysis, ^1H NMR spectra and high resolution MS were obtained for all new compounds. The known dimers 3 isolated as the *meso*, *dl* mixtures, or as the pure isomers were demonstrated to be symmetrical dimers by ^1H NMR and my comparison with literature data. [b] Five millimoles of $(i\text{-}Pr)_2NH$ and 5 mL of THF were added to 5 mmol of *n*-BuLi in hexane (3.2 mL) at -40 °C. The solution was warmed to 0 °C, cooled to -20 °C, and the ketone added dropwise to give a solution ~0.5 M in E^-. Additional reagents were added at 0 or 25 °C and the solutions irradiated with a 275-W sunlamp which in the absence of cooling maintained a reaction temperature of 35 °C. Unless otherwise indicated the molar ratio of E^- to $XCMe_2NO_2$ was 1:1. [c] Based on ^1H NMR. For reactions with $E^-/XCMe_2NO_2 = 2$, yields are based on the theoretical formation of 1 mol of product per mol of $XCMe_2NO_2$. With $E^-/XCMe_2NO_2 \leq 1$, yields are based on the theoretical formation of 1 mol of **1**, **2**, or **4** and 0.5 mol of 3 per mol of E^-. [d] Molar ratio $E^-/XCMe_2NO_2 = 2:1$. [e] 0.05 M $(t\text{-}Bu)_2NO\cdot$, 25 °C, no irradiation. [f] 0.15 M $Me_2C{=}NO_2Li$. [g] Diluted 5-fold with THF. [h] Molar ratio $E^-/XCMe_2NO_2 = 1:2$. [i] 0.5 M 12-crown-4-ether.

unimolecular and bimolecular reactions of $XCMe_2NO_2^-\cdot$. However, the effect of X on the ratio **1**/**3** is easily explained if reactions (1) and (2) have merged and competition occurs as shown in Scheme I. Reaction of $XCMe_2NO_2^-\cdot$ with E^- to form $1^-\cdot$ or $E\cdot$ predicts that the ratio **1**/**3** should depend on the structure of X. However, the mechanism by which E^- replaces X at a tetrasubstituted carbon atom is puzzling. Perhaps the formation of **1** and **3** involves a common intermediate distinct form free $O_2NCMe_2\cdot$. Electron transfer from E^- to $XCMe_2NO_2^-\cdot$ would almost certainly be dissociative and the cage intermediate, $|E\cdot\ X^-\ Me_2C{=}NO_2^-|$, is a possibility. Escape of $E\cdot$ from the cage would lead to **3** via reaction 7, while coupling of $E\cdot$ and $Me_2C{=}NO_2^-$ in the cage would lead to $\mathbf{1}^-\cdot$. It appears that as the ease of one-electron donation from the anion increases [e.g., from $MeC(CO_2Et)_2^-$ to $PhC(O^-){=}CHR'$], the chain reaction involved shifts from one involving discrete step, (1)-(3), to a process in which reactions (1) and (2) are no longer distinct.

The competition between reactions 4 and 5 depends upon counterion and solvent (see Table I). For $PhC(OLi){=}CH\text{-}i\text{-}Pr$ the ratio **1**/**3** passes through a maximum as Me_2SO or HMPA is added to the THF-hexane solvent. In 100% Me_2SO or HMPA the ratio **1**/**3** is quite low for secondary enolate anions, perhaps reflecting that free monoenolate anions react with $XCMe_2NO_2^-\cdot$ or $O_2NCMe_2\cdot$ to yield mainly $E\cdot$. As Me_2SO or HMPA is added to the THF-hexane solvent system, the E_2 elimination of HNO_2 from **1** becomes important, particularly at higher temperatures (Table I). With primary enolate anions it is difficult to prevent this reaction, and experiments with these anions were performed by using 2 equiv of E^- to maximize the yield of **2**. In solvents containing Me_2SO or HMPA, chlorine atom or nitro group transfer occurs (reaction 10). Reaction 10 was observed in the

$$E^- + XCMe_2NO_2 \rightarrow \underset{\mathbf{4}}{EX} + Me_2C{=}NO_2^- \qquad (10)$$

presence or absence of radical chain inhibitors, and from inhibited experiments it is clear that **4** is not converted to **3** by an S_N2 displacement.[10]

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(10) The source of $PhCOCH(Me)SO_2PhMe\text{-}p$ mentioned in Table I is not clear, but it may involve the attack of $E\cdot$ on $p\text{-MePhSO}_2^-$.

Bis Heteroannulation. 3. Facile Syntheses of (±)-Ligularone and (±)-Petasalbine

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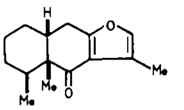
Received March 23, 1981

Ligularone (**1**) and petasalbine (**2**) are furanoeremophilanes isolated from the rhizomes of the *Ligularia* and *Petasites* genus of plants.[1] These same species produce at least 10 other compounds having the basic skeleton of the furanoeremophilanes,[1b]



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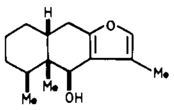

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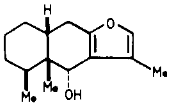

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