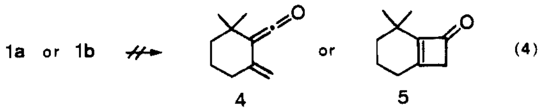
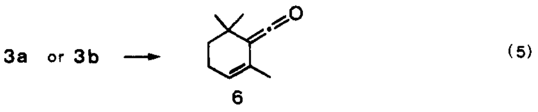
Finally, trapping of the intermediate ketone enolates with acetaldehyde (entry 15) allows regiocontrolled formation of two C,C-bonds in one operation as exemplified in the direct construction of the artemisia ketone skeleton.[15]

The course of the reaction described herein is dependent on substrate structure and leaving group (steric and stereoelectronic factors), metal counterions, and nucleophilic reactivity of the organometallic reagent. In order to elucidate the potential intermediacy of a ketene, we have focused on the reactivity of ester enolates with or without added nucleophile. The *s*-cis *E* dienolates **1a** and **1b** are stabilized by lithium ion complexation,[6] and all experiments directed toward the synthesis and detection of ketene **4** or its valence tautomer **5** starting from either the dienolate **1a** or **1b** have failed (eq 4). Presumably, the COX group of these enolates is twisted out of the allyl $\pi$-system for steric reasons.[4b,16] Therefore it is probable that these ester anions lead to the formation of ketone enolates **2** via species that possess carbanionic character and whose COX groups still retain residual electrophilicity.[4]



Next, in an attempt to trap a putative ketene intermediate by intramolecular [2 + 2] cycloaddition, we heated the enolate (entry 13) with or without added nucleophile; however, no 2-methylene-7,7-dimethylbicyclo[3.1.1]heptan-7-one[17] or derived products thereof were isolated. In addition, the enolates (entries 13 and 14) both undergo acylation reactions and thus do not provide support for a putative ketene intermediate in these cases.[18]

In contrast, the $\alpha$-cyclogeranate enolates **3a** and **3b** are thermally unstable and are converted to ketene **6**[3d] above 10 and −78 °C respectively (eq 5).



In order to account for these observations, we propose the following mechanistic rationale: the nucleophile RM, bonded by complexation or aggregation to the ester enolate, contributes to the weakening of the C–X bond; in a second stage, RM then attacks the COX group to afford the ketone or aldehyde enolate.[19] Only in certain cases is the C–X bond cleaved completely to give rise to an elimination–addition reaction type via a ketene intermediate.[20]

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(14) For recent $\beta$-safranal syntheses, see: Kametani, T.; Suzuki, K.; Kurobe, H.; Nemoto, H. *J. Chem. Soc., Chem. Commun.* **1979**, 1128. Könst, W. M. B.; van der Linde, L. M.; Boelens, H. *Tetrahedron Lett.* **1974**, 3175. For the reduction of ynolates, see: Kowalski, C. J.; Haque, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 1325.

(15) For a related trapping with aldehydes, see ref 3a.

(16) For analogous cases, see ref 6 and: Büchi, G.; Wüest, H. *Helv. Chim. Acta* **1971**, *54*, 1767. MNDO calculations (Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899; 4907) on **1a** (Boschung, A. F., unpublished) further indicate that the carbonyl C has a substantial partial positive charge and that the COX group is not coplanar with the allyl $\pi$-system (dihedral angle between the two planes ≈80°).

(17) Kulkarni, Y. S.; Snider, B. B. *J. Org. Chem.* **1985**, *50*, 2809.

(18) BHT ester enolates possessing H atoms at the $\alpha$-position are reported not to afford ketones when treated with organometallic reagents, possibly because the intermediate ketenes are deprotonated to ynolates.[3a] Indeed, the reaction (entry 13) on *n*-BuLi on the corresponding BHT ester enolate failed to give any of the corresponding butyl ketone.

(19) For a discussion on lithium enolate aggregates, see: Seebach, D. *Proc. R. A. Welch Found. Conf.* **1984**, *27*, 93. For interaction between organolithium compounds and esters or ketones, see: Al-Aseer, M. A.; Allison, B. D.; Smith, S. G. *J. Org. Chem.* **1985**, *50*, 2715. The importance of complexation of organometallic reagents with the substrate which imparts some intramolecular character to the transformation has been recently emphasized; see, e.g., ref 2 and: Laube, T.; Dunitz, J. D.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 1373. Beak, P.; Basha, A.; Kokko, B.; Loo, D. *J. Am. Chem. Soc.* **1986**, *108*, 6016 ("lithium bridging promotes reaction between two species which would normally be considered to repel each other"). Rachon, J.; Goedken, V.; Walborsky, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 7435. Meyers, A. I.; Barner, B. A. *J. Org. Chem.* **1986**, *51*, 120. Corey, E. J.; Naef, R.; Hannon, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 7115. Corey, E. J.; Peterson, R. T. *Tetrahedron Lett.* **1985**, *26*, 5025.

(20) For mechanistic investigations which distinguish between a tetragonal $B_{AC}2$ mechanism and an E1cB pathway, see: Douglas, K. T. *Acc. Chem. Res.* **1986**, *19*, 186. In an intramolecular ester condensation implicating a cumulated enolate, a pathway involving a ketene intermediate is discarded for steric reasons: Corey, E. J., synthesis of $C_{15}$-gingkolide; conference presented at ETH Zürich, 20 March, 1987.

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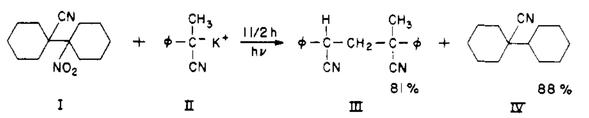
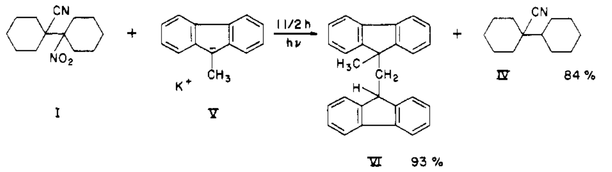
## Carbanions That Function Both as Electron Transfer Agents and as Hydrogen Atom Donors: A New Electron Transfer Chain Reaction[1]

*Summary:* New reactions are described in which carbanions function both as one electron transfer agents and as hydrogen atom donors; a novel feature of these reactions is the generation of a radical anion by hydrogen atom abstraction.

*Sir:* We have discovered a new reaction in which carbanions function both as one electron transfer agents and as hydrogen atom donors. Thus $\beta$-nitro nitrile I reacts completely with $\alpha$-methylbenzyl cyanide anion (II) in $1^1/_2$ h (eq 1).[2] In contrast, the potassium salt of benzyl cyanide under the same conditions does not react at all with $\beta$-nitro nitrile I.



Furthermore, $\beta$-nitro nitrile I when treated with the anion of 9-methylfluorene (V) reacts rapidly as shown in eq 2. On the other hand the potassium salts of fluorene and 9-phenylfluorene fail to react.



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(1) Paper 33 in the series "Substitution Reactions Which Proceed *via* Radical Anion Intermediates". For preceding paper, see: Kornblum, N.; Ackermann, P.; Manthey, J. W.; Musser, M. T.; Pinnick, H. W.; Singaram, S.; Wade, P. A. *J. Org. Chem.*, in press.

(2) This and the other reactions reported here were carried out with exposure to two 110-V, 20-W white fluorescent lights. They proceed at a slightly slower rate if simply exposed to room light.

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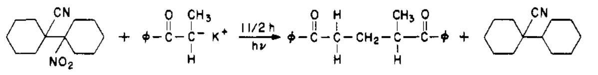
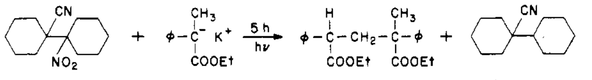
Whereas β-nitro nitrile I and propiophenone anion (VII) react completely in $1^1/_2$ h (eq 3), the anion of acetophenone does not react under the same conditions.

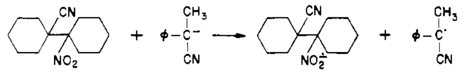

I VII VIII 82% IV 82% (3)

In the same way, the reaction of the anion of α-methylphenylacetic ester (IX) with β-nitro nitrile I is 80–85% complete in 5 h (eq 4); but with anion of the ethyl ester of phenylacetic acid, there is no detectable reaction in 5 h.

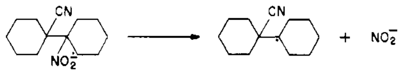

I IX X 71% IV 64% (4)

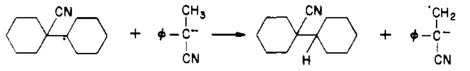
These puzzling results become readily intelligible on the basis of a chain mechanism which is exemplified by eq 5–8.[3]

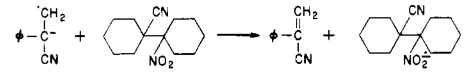
INITIATION


(5)

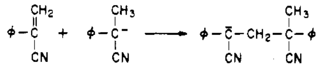
CHAIN PROPAGATION


(6)


(7)


(8)

The α-cyanostyrene then enters into a Michael addition with the starting anion II to give III (eq 9).



$$\phi-\underset{CN}{\overset{CH_2}{\overset{\|}{C}}} + \phi-\underset{CN}{\overset{CH_3}{C^-}} \longrightarrow \phi-\underset{CN}{\bar{C}}-CH_2-\underset{CN}{\overset{CH_3}{C}}-\phi \quad (9)$$

Clearly, the chain sequence of eq 5–8 is not possible with the anions of benzyl cyanide, fluorene, 9-phenylfluorene, acetophenone, and ethyl phenylacetate. presumably, a methyl group is not unique—ethyl and isopropyl, for example, should, in principle, produce the same result although the Michael addition may well prove much slower than for the methyl cases.[4]

The view that these are indeed chain reactions involving free radicals and radical anions is supported by the fact that they are inhibited by 20 mol % of di-*tert*-butyl nitroxide and by *m*-dinitrobenzene. Also, in conformity with the proposed mechanism, the 9-methylfluorene dimer has the structure VI rather than that of the symmetrical dimer. Although β-nitro nitrile I was employed in most of our studies, other β-nitro nitriles exhibit the same behavior.[5] The cyano group is not necessary for these reactions; α-nitrocumene, $C_6H_5C(NO_2)Me_2$, reacts with V in the same way as I, albeit at a much slower rate.

The following is a typical procedure. Under $N_2$, 0.188 g (0.0047 mol) of dry KH was dissolved in 20 mL of dry, degassed $Me_2SO$ and to this solution was added a solution of 9-methylfluorene (0.923 g; 0.0052 mol) in 10 mL of dry, degassed $Me_2SO$. The resulting red solution was transferred via a cannula to a solution of I (0.543 g; 0.0023 mol) in 5 mL of $Me_2SO$. After the reaction mixture was stirred for $1^1/_2$ h under $N_2$ with exposure to two 20-W ordinary fluorescent lights, the resulting red solution was poured into 300 mL of cold $H_2O$ and extracted with diethyl ether. The extracts were washed with $H_2O$ and dried ($MgSO_4$), and the ether was removed. The white solid that remained was flash chromatographed on silica gel by using pentane–chloroform (9:1). This gave 0.873 g of white crystals; mp 175–177 °C. Recrystallization from hexane afforded 0.835 g (93% yield) of VI, mp 175–176 °C (lit.[6] mp 175–176 °C). $^1$H NMR ($CDCl_3$): δ 1.58 (s, 3 H), 2.18 (d, 2 H), 3.12 (t, 1 H), and 6.56–7.82 (complex multiplet, 16 H). MS: *m/e* 358 (20.14), 193 (7.63), 179 (100), and 165 (26.95). These values accord with the published values.[6] When the red reaction solution is quenched with $D_2O$, the product is the 9-deuteriofluorene corresponding to VI. This is clear from the NMR spectrum: the triplet at δ 3.12 vanishes and the doublet at δ 2.18 becomes a singlet. At least 90% of the product is the 9-deuteriofluorene.

Further elution with pentane–chloroform (3:1) gave 0.390 g of a white solid; mp 63–66 °C. Recrystallization from methanol afforded 0.369 g (84% yield) of IV; white crystals, mp 67–68 °C. $^1$H NMR ($CDCl_3$): δ 1.16 (m, 8 H), 1.56–2.10 (complex multiplet, 12 H). IR ($CDCl_3$): 2225 cm$^{-1}$ (CN). Anal. Calcd for $C_{13}H_{21}N$: C, 81.62; H, 11.07; N, 7.32. Found: C, 81.75; H, 11.20; N, 7.29.

**Acknowledgment.** We thank the National Science Foundation, Merck and Co., Inc., and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

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[6] Guthrie, R. D.; Wesley, D. P.; Pendygraft, G. W.; Young, A. T. *J. Am. Chem. Soc.* **1976**, *98*, 5780.

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## Indium in Organic Synthesis: Indium-Mediated Allylation of Carbonyl Compounds

*Summary:* Indium-mediated allylation of a variety of ketones and aldehydes afforded excellent yields of the corresponding homoallylic alcohols under very mild reaction conditions.

*Sir:* There has been growing interest in the use of metallic elements in synthetic chemistry, among which Li,[1] Mg,[1]

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[3] Chain termination presumably results from combination, and disproportionation, of the radicals.

[4] These and other obvious extensions of this new chain sequence are being explored.

[5] All new compounds were characterized by elemental analyses, NMR, IR, and mass spectra.

[1] Katzenellenbogen, J. A.; Lenox, R. S. *J. Org. Chem.* **1973**, *38*, 326.

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[3] Hiyama, T.; Sawahara, M.; Obayashi, M. *Chem. Lett.* **1983**, 1237. Hiyama, T.; Sawahara, M.; Obayashi, M. *Nippon Kagaku Kaishi* **1984**, 1022.