could be detected by NMR when high-purity α-pinene ($[\alpha]^{25}_D$ + 51.5°) was used.

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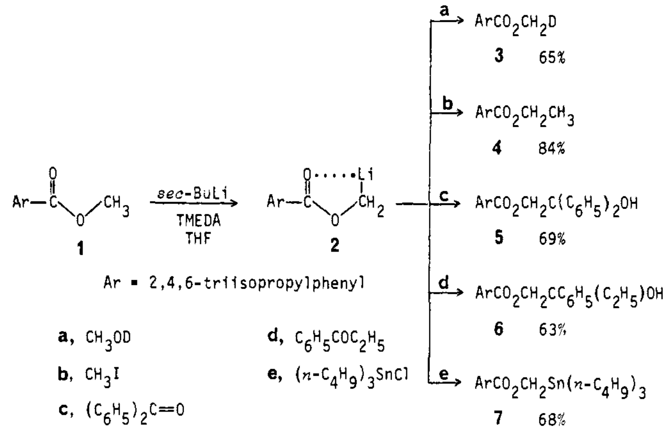
Dipole-Stabilized Carbanions. Direct Lithiation of the Methyl Group of a Methyl Ester

Sir:

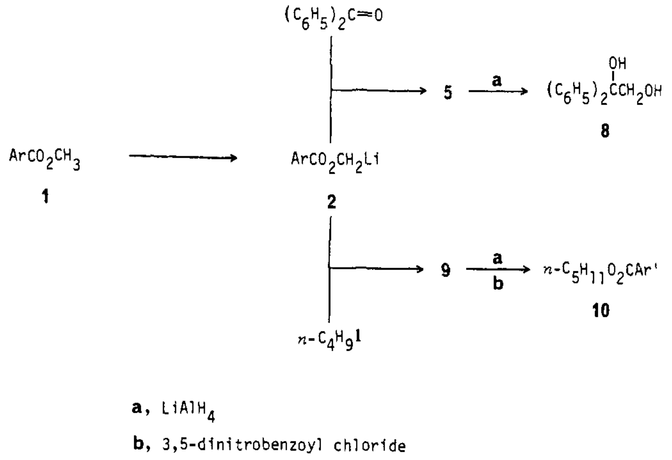
The preparation of synthetically useful α-oxoorganometallics by deprotonation has been reported for allyl and vinyl ethers, cases in which stabilization of the formal carbanion is provided by unsaturation.[1,2] We now wish to report direct metalation of the methyl group of a methyl ester, a case in which stabilization of the carbanion may be attributed in part to the formally positive oxygen of the ester dipole.[3] Since the metalation can be followed by reaction with an electrophile and subsequent cleavage of the substituted ester, the overall sequence provides a method for nucleophilic oxomethylation.

Reaction of methyl 2,4,6-triisopropylbenzoate (**1**) with *sec*-butyllithium/tetramethylethylenediamine (TMEDA) at −75 or −98 °C for 2 to 2.5 h provides **2**. Subsequent addition of an electrophilic trapping agent gives the expected products **3–7** in the yields indicated in Scheme I.[4] Yields have not been optimized.[5]

Scheme I



Scheme II



The formally dipole-stabilized carbanion **2** provides the oxymethylene synthon $LiCH_2OH$.[6] For example, reaction of **2** with benzophenone to give **5** may be followed by reduction with lithium aluminum hydride in tetrahydrofuran to give the diol **8** in 49% yield from **1**. In an alkylation sequence *n*-butyl iodide undergoes reaction with **2** to give *n*-pentyl 2,4,6-triisopropylbenzoate (**9**) which can be reduced with lithium aluminum hydride to 2-pentanol, followed by acylation with 3,5-dinitrobenzoyl chloride to give the known derivative **10** in 61% yield from **1**.

The present results show the ester function to be capable of activating the position α to the bivalent oxygen toward metalation to give a formal dipole-stabilized carbanion.[7] The fact the ester function retains its structure in the face of possible stabilizing rearrangements is also interesting. The α-acyloxy carbanion **2** is analogous to intermediates which have been proposed in the self-condensations of benzyl, allyl, and vinyl benzoate[8] and to carbanions which could be involved in the formation of α-acyloxy carbeneoids on reaction of the α-acyloxychloro ester function with lithium 2,2,6,6-tetramethylpiperidide.[9] The general synthetic utility of **2** and its derivatives,[10] questions about kinetic and thermodynamic acidities, and the role of the metal ion in the formation of such species are being explored.

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References and Notes

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(3) For formation of analogous species from amides and thioesters, see P. Beak and R. Farney, *J. Am. Chem. Soc.*, **95**, 4771 (1973); P. Beak, G. R. Brubaker, and R. F. Farney, *ibid.*, **98**, 3621 (1976); D. Seebach and W. Lubosch, *Angew. Chem., Int. Ed. Engl.*, **15**, 313 (1976); P. Beak, B. G. McKinnie, and D. B. Reitz, *Tetrahedron Lett.*, in press.

(4) Yields are for analytically pure materials. The assigned structures were confirmed by IR, NMR, and mass spectral properties.

(5) Trapping of **2** also took place with benzaldehyde, allyl bromide, cyclohexanone, and cyclopentanone in 40–60% yields as indicated by the NMR of the crude products. Isolation and characterization of these materials has been deferred until optimal conditions are achieved.

(6) For an alternative preparation of this synthon from formaldehyde, see D. Seebach and N. Meyer, *Angew. Chem., Int. Ed. Engl.*, **15**, 438 (1976).

(7) Apparently the activating effect of the ester is sufficient to overcome the usually deactivating effect of oxygen toward α-carbanion formation. For discussions, see F. G. Bordwell, M. Van Der Puy, and N. R. Vanier, *J. Org. Chem.*, **41**, 1885 (1976); D. H. Hunter, Y. Lin, A. L. McIntyre, D. J. Shearing, and M. Zvagulis, *J. Am. Chem. Soc.*, **95**, 8327 (1973), and references cited therein. For general discussions, see E. Buncel, "Carbanions: Mechanistic and Isotopic Aspects", Elsevier, New York, N.Y., 1975, Chapter 2; M. Schlösser, "Struktur und Reaktivität Polar Organometallic", Springer-Verlag, Berlin, 1973, Chapter 2; D. J. Peterson, *Organometal. Chem. Rev.*, **A7**, 295 (1972).

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(10) Reaction of ethyl 2,4,6-triisopropyl benzoate with *sec*-BuLi/TMEDA in THF at −75 °C for 2 h followed by addition of methanol-d_1 gave an 85% recovery of the starting ester with 57% of one methylene proton exchanged for deuterium. The location and extent of deuteration was established by nmr and mass spectral determinations. Extensions of this observation will follow when optimal conditions and functionality for the formation of oxygen dipole-stabilized carbanions have been found.

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