Acknowledgments. The author is indebted to R. H. Holm for samples of the complexes investigated. The support of the Research Corporation as well as the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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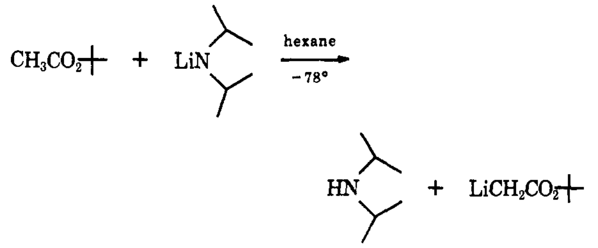
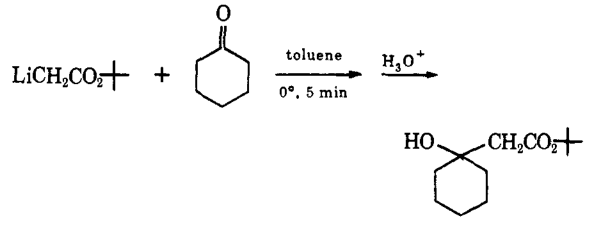
Isolation and Characterization of Lithio *tert*-Butyl Acetate, a Stable Ester Enolate

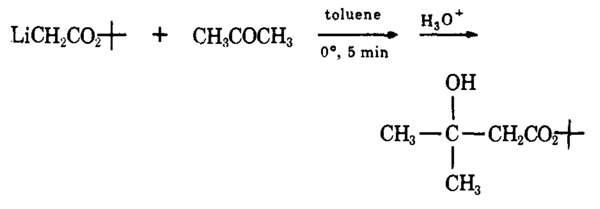
Sir:

Addition of *tert*-butyl acetate to lithium diisopropylamide in hexane furnishes lithio *tert*-butyl acetate as a stable white solid. This ability to isolate a solid ester enolate provides an exceedingly simple method for conducting Reformatsky-type reactions. For example, the following conversions (eq 2 and 3) were obtained in less than 15 min using stoichiometric amounts of lithio *tert*-butyl acetate weighed in air.


(1)


(2)

100% (glpc)

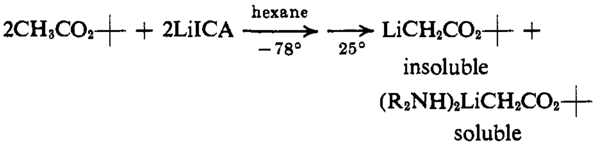

(3)

100% (glpc)

Tetrahydrofuran solutions of a variety of lithium ester enolates may be obtained by reaction of the appropriate ester with lithium *N*-isopropylcyclohexylamide (LiICA).[1] However, attempts to remove the solvent and amine from these solutions even at −78° only yield oily yellow residues containing mostly condensed ester.

LiICA is highly soluble in hydrocarbon solvents, forming 1 *M* solutions in hexane at −78°. It seemed likely that the lower molecular weight ester enolates would be insoluble in such solvents and, accordingly, we attempted to prepare lithio ethyl acetate in hexane. Addition of ethyl acetate to a solution of LiICA in hexane at −78° produces a white precipitate. However, attempts to isolate this material by filtration, even at −78°, result in extensive condensation to form the lithium salt of ethyl acetoacetate.

Addition of *tert*-butyl acetate to hexane solutions of LiICA gives entirely different results. At −78°, the solution remains colorless and no precipitate is formed. When the solution is allowed to reach 25°, a white solid gradually settles out. Filtration produces lithio *tert*-butyl acetate in 50% yield. Recooling to −78° prior to filtration does not increase the yield. Subsequently, we discovered that lithio *tert*-butyl acetate is only slightly soluble in hexane (<0.1 g/100 ml), but is dissolved by hexane solutions containing *N*-isopropylcyclohexylamine. The solubility at 25° is such that 2 mol of the amine dissolves 1 mol of the enolate. Similar results were obtained with other secondary amines, including diisopropylamine and hexamethyldisilazane. Consequently, the 50% yield of enolate is readily explained by the following reaction (eq 4).


(4)

The isolated yield can be made nearly quantitative by choosing the more volatile diisopropylamine, which can be removed by vacuum distillation. Although lithium diisopropylamide is only slightly soluble in hexane at −78°, addition of *tert*-butyl acetate results in immediate dissolution. Evaporation of the solvent and amine at room temperature and reduced pressure produces lithio *tert*-butyl acetate as a white powder in yields of 95–100%.

Solid lithio *tert*-butyl acetate is remarkably stable. Heated under a nitrogen atmosphere, it decomposes only at temperatures higher than 110°. Samples of the enolate have been stored in sealed bottles on the shelf for several months with no change in purity. The solid may be exposed to air for brief periods without extensive hydrolysis. Prolonged exposure results in a gradual decrease in weight, presumably through formation and evaporation of *tert*-butyl acetate, but the solid remains colorless with no evidence of condensation.

Lithio *tert*-butyl acetate forms 1 *M* solutions in benzene or toluene at 25°. These solutions are not stable, but with carefully dried solvents, condensation is less than 5% after 3 hr. The proton nmr spectrum of the benzene solution provides the first clear evidence of an oxygen–lithium bonded structure for an ester enolate I.[2] Two partially resolved doublets are observed at 3.14 and 3.44 ppm (downfield from internal TMS) for the two α hydrogens in the anion. The singlet of the *tert*-butyl grouping appears at 1.56

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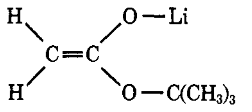
(1) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).

(2) Using ir spectral evidence, Vaughn[3] assigned a zinc–oxygen bonded structure to the Reformatsky reagent obtained from zinc and ethyl bromoisobutyrate in ether–benzene solution. Gaudemar[4] has assigned a range of structures for the reagent obtained from zinc and ethyl bromoacetate in more polar solvents such as tetrahydrofuran or dimethyl sulfoxide.

(3) W. R. Vaughn, S. C. Bernstein, and M. E. Larber, *J. Org. Chem.*, **30**, 1790 (1965).

(4) M. Gaudemar and M. Martin, *C. R. Acad. Sci. Paris, Ser. C*, **267**, 1053 (1968).



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ppm. The infrared spectrum (fluorolube) possesses a band at 1620 cm^{-1}, assigned to the carbon double bond stretch, and has no band in the region from 1675 to 2000 cm^{-1}.

The following procedure describes the preparation of lithio *tert*-butyl acetate. A dry 2-l. round-bottomed flask, equipped with mechanical stirring and mercury relief valve, is flushed with nitrogen and immersed in an ice-water bath. The flask is charged with 1 mol of *n*-butyllithium dissolved in 1.5 l. of hexane and 1 mol (101 g) of diisopropylamine is added over a period of 10 min. The flask is then immersed in a Dry Ice-acetone bath and 1 mol (116 g) of *tert*-butyl acetate is added over a 15-min period. The reaction mixture is stirred an additional 30 min at −78° and then allowed to reach room temperature. Solvent and amine are stripped off with a rotary evaporator. Any yellow color in the solid may be removed by trituration with hexane. The weight of lithio *tert*-butyl acetate obtained is 116 g (95%). Addition of samples to water followed by glpc analysis for *tert*-butyl acetate indicates a purity greater than 98%.

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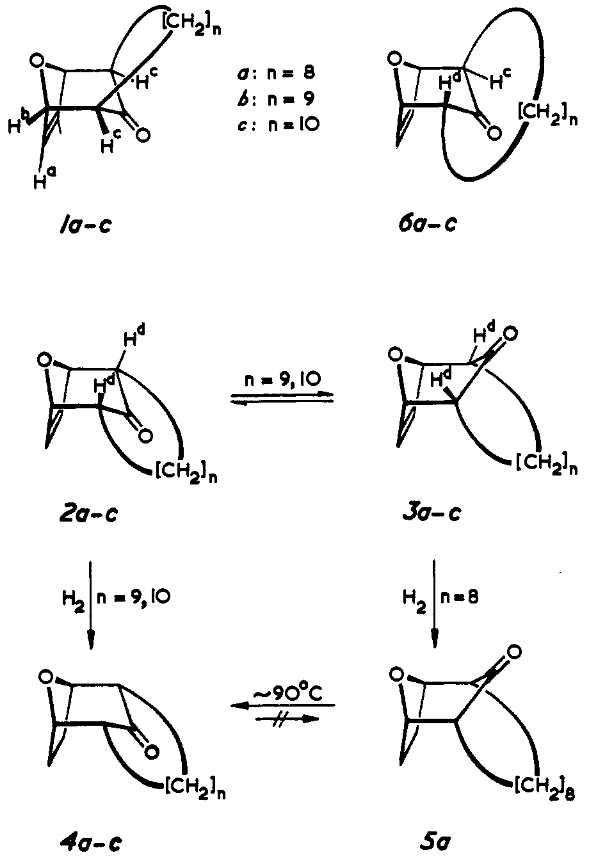
Direct Observation of Chair-Boat Equilibria in Bridged Six-Membered Rings

Sir:

Of the various conformers of saturated six-membered rings the chair is generally by far the most stable.[1] If nonchair populations play some role it is normally the twist form which takes a part, although some of the spectroscopic evidence has been regarded to be still tenuous.[1h] The true, classical boat arrangement usually does not have a finite lifetime, but serves as a transition state for pseudorotation[2] of the twist conformer.

We wish to report the first examples of chair-boat equilibria which exclude the twist conformer and can be frozen out on the nmr time scale. Debromination of 2,12-dibromocyclododecanone[3] with a dry, acid-free zinc-copper couple in the presence of furan[4] yielded two distinct crystalline forms of cycloadducts[5] which after slow (*ca.* 2 days at 25°) crystallization from isooctane could be separated manually. 16-Oxatricyclo[11.2.1.1^{2,12}]heptadec-14-en-17-one of mp 130° was the minor isomer **1b**: nmr (TMS, CCl$_4$) δ a 6.16 (2 H, s), b 4.62 (2 H, s), c 2.16 ppm (2 H, complex); ir (CCl$_4$) ν_{CO} 1703 cm^{-1}; dipole moment 1.7 D.[6]



The nmr spectrum of the major isomer, mp 85°, was temperature dependent (*cf.* Figure 1) and at 0° in CCl$_4$ solution two individual conformers **2b** and **3b** were clearly discernible:[7] nmr (TMS, CCl$_4$) of **2b**, a 6.15 (2 H, s), b 4.76 (2 H, d, J = 3.5 Hz), d 3.32 (2 H, complex); **3b**, a 6.42 (2 H, s), b 4.88 (2 H, d, J = 7.5 Hz), d 2.78 ppm (2 H, complex); dipole moment of **2b** and **3b** 2.4 D; ir (CCl$_4$) 1704 and 1714 cm^{-1}; interestingly in the mull only one band at 1713 cm^{-1} was visible, indicative of the chair conformer **2b**. Further separation of the filtrate yielded **6b**: nmr a 6.12 (2 H, major quartet and two pairs of symmetrical satellites), b 4.56 (2 H, complex), c 2.10 (1 H, complex), d 3.28 (1 H complex); ir (CCl$_4$) ν_{CO} 1713 cm^{-1}.

The assignment of six-membered chair to **1b**, **2b**, and **6b** and of boat to **3b** rests on dipole moment measurements and on nmr comparison with model bicyclic[4] as well as conformationally rigid tricyclic compounds in which the aliphatic chain is shortened to four methylene groups (**1** and **3**, n = 4). Furthermore, the equilibrium

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[1] (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965; (b) M. Hanack, "Conformation Theory," Academic Press, New York, N. Y., 1965; (c) F. G. Riddell, *Quart. Rev.*, *Chem. Soc.*, 21, 364 (1967); (d) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, 4, 39 (1969); (e) J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971); (f) E. L. Eliel, *Angew. Chem.*, *Int. Ed. Engl.*, **11**, 739 (1972); (g) J. E. Anderson, *Fortschr. Chem. Forsch.*, in press; (h) G. M. Kellie and F. G. Riddell, *Top. Stereochem.*, in press.

[2] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7047 (1967).

[3] E. W. Garbisch and J. Wohllebe, *J. Org. Chem.*, **33**, 2157 (1968); *Chem. Commun.*, 306 (1968).

[4] H. M. R. Hoffmann, K. E. Clemens, and R. H. Smithers, *J. Amer. Chem. Soc.*, **94**, 3940 (1972); see also H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc. B*, 57 (1968), and intervening papers.

[5] Elemental analyses and mass spectra were consistent with the structures assigned; the methylene protons of the tricyclics appear uniformly as a broad peak at δ 1.3 ppm in the nmr spectrum.

[6] All dipole moments were determined in solvent benzene; the probable error is ±0.2 D.

[7] For the ketonization of strained meta-bridged *p*-nitrophenols see V. Prelog, *et al.*, *Helv. Chem. Acta*, **30**, 1465 (1947); **31**, 1325 (1948); **33**, 356 (1950). See also D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, **4**, 204 (1971); F. Vögtle, P. Neumann, and M. Zuber, *Chem. Ber.*, **105**, 2955 (1972), and references therein.