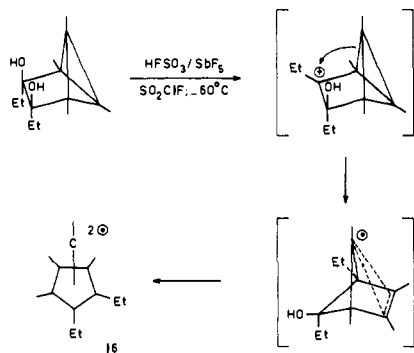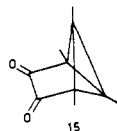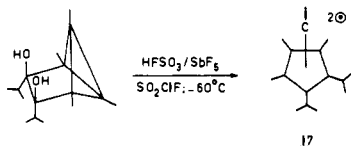Scheme III

groups were obtained in an analogous way when diketone **15** was allowed to react with the appropriate lithium reagent

followed by addition of water. Both ethyl and isopropyl groups were found to be in *basal* positions in the corresponding dications **16** and **17**, respectively, which is rationalized in Scheme III.

Acknowledgment. C.G wishes to thank Montedison S.p.A. Dipartimento di Chimica Organica (Novara-Italia) for a leave of absence.

References and Notes

(1) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973); *J. Am. Chem. Soc.*, **96**, 2208 (1974); *Acc. Chem. Res.*, **8**, 413 (1975).

(2) For reasons of simplicity we have used a representation of the pyramidal dications in the way indicated (the similarity with organometallic chemistry is clear). The positions of the substituents may be indicated as basal (at the five-membered ring) and apical (at the top).

(3) R. F. Heldeweg and H. Hogeveen, *Tetrahedron Lett.*, 1517 (1975).

(4) Reported melting points were determined by the Kofler method and were not corrected. Satisfactory analytical data have been obtained for compounds **2**, **6**, and **11**. NMR spectra were recorded with a Varian XL-100 (^{1}H, 100.1 MHz; ^{13}C, 25.2 MHz) in the case of **7**, **8**, **9**, **10**, **11**, and **13** and with a JEOL C-60 HL.

(5) Mp 53–54 °C (pentane, – 40 °C); IR (Nujol) 3330 (OH stretch), 1655 cm^{-1} (C=C stretch); ^{1}H NMR (CDCl$_3$) δ 4.92 (s, 1 H), 4.66 (s, 1 H), 1.40 (s, 3 H), 1.32 (s, 3 H), 1.20 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H).

(6) All the precursors were prepared starting from crude enone **1** and the corresponding Li reagents. Methyl derivative **2** was purified by crystallization (pentane, –40 °C) and isolated as pure compound in 40% yield. Ethyl derivative **6** was obtained in 20% yield by distillation (60–70 °C (0.9 mmHg)) and subsequent crystallization (pentane, –20 °C). Compound **11** was purified by distillation (20% yield).

(7) Mp 52–53 °C (pentane, –20 °C); IR (Nujol) 3350 (OH stretch), 1655 cm^{-1} (C=C stretch); ^{1}H NMR (CDCl$_3$) δ 4.78 (s, 1 H), 4.60 (s, 1 H), 1.65 (q, J_{CH_3,CH_2} = 7.0 Hz, 2 H), 1.37 (s, 3 H), 1.27 (s, 3 H), 1.07 (s, 3 H), 1.00 (s, 3 H), 0.68 (t, J_{CH_2,CH_3} = 7.0 Hz, 3 H).

(8) ^{1}H NMR (CDCl$_3$) δ 3.32 (s, OCH$_3$), 3.12 (s, OCH$_3$), 1.28 (s), 1.24 (s), 1.16 (s), 1.01 (s), 0.99 (s) (owing to overlapping signals, the ethyl absorptions could not be assigned unambiguously); ^{13}C NMR (CDCl$_3$, proton decoupled) δ 81.3, 80.5, 57.4, 52.1 (OCH$_3$), 51.6 (OCH$_3$), 43.6, 36.9, 31.4, 18.7, 17.2, 15.5, 12.1, 7.9, 6.9, 2.7.

(9) G. A. Olah and E. Namanworth, *J. Am. Chem. Soc.*, **88**, 5328 (1966).

(10) The elemental analysis corresponds to the formula C$_{13}$H$_{22}$O$_2$. The following spectroscopic data are in agreement with the proposed mixture: IR (Nujol) 3200 cm^{-1} (OH stretch); ^{1}H NMR (CDCl$_3$) shows three groups of absorptions centered on δ 4.9 (four peaks disappearing on treatment with D$_3$O$^+$), 1.7, 0.9 (the ratio of the relative area of the downfield group and the combined integral of the latter groups was found to be 1:10); ^{13}C NMR revealing 27 peaks in a proton-decoupled spectrum (CDCl$_3$) δ 143.1, 139.4, 138.1, 104.3, 101.6, 101.4, 101.0, 65.0, 60.9, 60.6, 60.1, 25.2, 18.9, 18.1, 17.1, 16.5, 14.2, 12.7, 11.2, 10.7, 10.5, 10.2, 9.3, 4.7, 3.7, 3.6, 3.0; mass spectrum *m/e* 192 (M$^+$ – H$_2$O). The IR of mixture **9** on heating^{11} at 150 °C showed the following absorptions: 1690, 1650, 1355, 1190, 1090, 1070 cm^{-1} in agreement with those as reported for the cyclopentadienyl ketone by H. N. Junter, W. Schäfer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967).

(11) L. A. Paquette, S. A. Lang Jr., S. K. Porter, and J. Clardy, *Tetrahedron Lett.*,

3137 (1972).

(12) Bp 54–56 °C (0.6 mmHg); IR 3500 (OH stretch), 1650 cm^{-1} (C=C stretch); ^{1}H NMR (CDCl$_3$) δ 4.89 (s, 1 H), 4.65 (s, 1 H), 2.00 (h, $J_{CH_3,CH}$ = 7.0 Hz, 1 H), 1.39 (s, 3 H), 1.29 (s, 3 H), 1.05 (s, 3 H), 1.01 (s, 3 H), 0.97 (d, J_{CH,CH_3} = 7.0 Hz, 3 H), and 0.86 (d, J_{CH,CH_3} = 7.0 Hz, 3 H).

(13) Mp 83.0–84.0 °C (pentane, –20 °C); IR (Nujol) 3600–3500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.52 (q, J_{CH_3,CH_2} = 7.0 Hz, 4 H), 1.32 (s, 3 H), 1.20 (s, 3 H), 1.08 (t, J_{CH_2,CH_3} = 7.0 Hz, 6 H), 1.00 (s, 6 H); mass spectrum exact mass M$^+$ peak calculated at *m/e* 224.178, found *m/e* 224.181.

(14) Mp 83.0–83.5 °C (pentane, –20 °C); IR (Nujol) 3600–3500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.10 (h, $J_{CH_3,CH}$ = 7.0 Hz, 2 H), 1.32 (s, 3 H), 1.22 (s, 3 H), 1.12 (d, J_{CH,CH_3} = 7.0 Hz, 6 H), 1.05 (s, 6 H), 1.04 (d, J_{CH,CH_3} = 7.0 Hz, 6 H); mass spectrum exact mass M$^+$ peak calculated at *m/e* 252.209, found *m/e* 252.211.

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Organolithium Substitution at a Bicyclo[1.1.0]butane Bridgehead Position. Evidence for a Bicyclo[1.1.0]but-1(3)-ene as a Reaction Intermediate

Sir:

The intriguing molecule bicyclo[1.1.0]but-1(3)-ene has so far only been known to theorists; calculations^1 suggest that it represents a local minimum on the C$_4$H$_4$ potential energy hypersurface. We now wish to report preliminary experimental evidence for the fleeting existence of a species containing such a skeletal unit in the reaction of 1-chlorotricyclo-[4.1.0.0^{2,7}]heptane (**1a**)^2 with organolithium derivatives.

Addition of **1a** to an ether solution of 3 equiv of *n*-butyllithium at room temperature produced, after aqueous workup, an 87% isolated yield of 1-*n*-butyltricyclo[4.1.0.0^{2,7}]heptane (**2a**) in a practically instantaneous reaction. Structure proof for **2a** rests on its mass spectrum and its ^{1}H NMR, the latter showing, in addition to the expected signals for the side chain, the same pattern for the framework protons as the parent hydrocarbon tricyclo[4.1.0.0^{2,7}]heptane (**1c**).^{3}


	X	R
a	Cl	CH$_2$(CH$_2$)$_2$CH$_3$
b	Br	CH(CH$_3$)C$_2$H$_5$
c	H	C(CH$_3$)$_3$
d	Li	C$_6$H$_5$
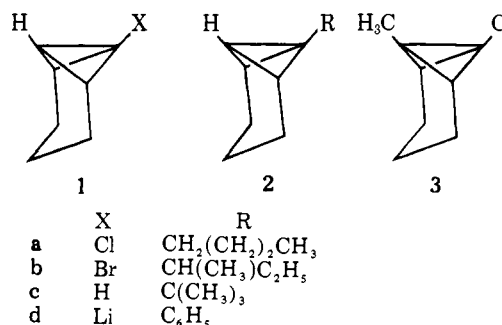
The derivatives **2b–2d** were prepared under similar conditions;^{4} the NMR spectra of **2c**^{5} and **2d**^{6} were identical with those reported in the literature.

We consider three mechanistic pathways as possible routes to the products: (I) direct coupling between the organolithium compound and **1a**; (II) halogen–metal exchange between **1a** and the organolithium derivative forming **1d** and the corresponding chloride, followed by a coupling reaction between these components (in the case of **2d** dehydrobenzene could be involved); (III) elimination of hydrogen chloride from **1a** by the organometallic reagent with the formation of a bicyclo[1.1.0]but-1(3)-ene derivative and addition of the organolithium compound to the strained double bond. The following observations provide arguments against the mechanisms I and II. (a) When 1-chloro-7-methyltricyclo[4.1.0.0^{2,7}]heptane (**3**)^2 was added to a threefold excess of *n*-butyllithium in ether and kept for 15 h at 20 °C, on aqueous workup, **3** was

isolated unchanged. This shows that direct coupling as well as chlorine–lithium exchange are insignificant processes and that the absence of a proton at C-7 prevents the substitution reaction to take place. (b) 1-Bromotricyclo[4.1.0.0^{2,7}]heptane (1b)[7] and n-butyllithium in ether led (via 1d) to the parent hydrocarbon 1c as the main product indicating lithium–bromine exchange in this case to be fast and the possible consecutive coupling between 1d and n-butyl bromide, however, under the applied conditions (15 min at 20 °C), to be an inefficient process.[8] As alkyl chlorides need longer reaction times to couple successfully with organolithium compounds than the corresponding alkyl bromides,[9] this result further excludes that the derivatives 2 were produced via route II. (c) When 1a and n-butyllithium were quickly mixed and the mixture was quenched with D$_2$O after reaction times of 30, 90, and 150 s at 20 °C, 1-n-butyltricyclo[4.1.0.0^{2,7}]heptane-7-d was obtained, in each case with a deuterium content >96%.[10] The bridgehead metalation of the parent hydrocarbon 1c with n-butyllithium in ether has been shown to occur rather slowly.[11]; Therefore, the introduction of the lithium to the bicyclo-[1.1.0]butane unit must have taken place not at the stage of the final product 2a with the excess of the organometallic base but at an earlier step of the reaction sequence.

Mechanisms I and II are inconsistent with these results; however, all our observations are in accord with III which is outlined in Scheme I.

Scheme I
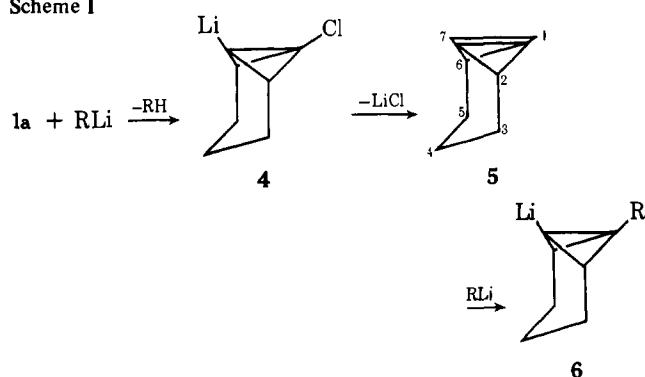
The chlorine atom in 1a should enhance the acidity of the proton at C-7 and accelerate the metalation reaction[12,13] to 4. The consecutive β elimination of lithium chloride from 4 leads to tricyclo[4.1.0.0^{2,7}]hept-1(7)-ene (5) as a reaction intermediate. This highly strained hydrocarbon adds, as expected, the organolithium reagent with the formation of 6.[14]

The three-carbon bridge in 5 connecting C-2 and C-6 causes the bicyclo[1.1.0]but-1(3)-ene unit to take a bent structure. It is interesting to note that this might not introduce additional strain into the molecule; calculations predict nonplanarity for the parent olefin.[1]

The proposed scheme for the substitution reaction implies that the carbon atoms 1 and 7 become chemically equivalent on their way from 1a to 6.[15] Experiments to test this consequence are in progress. Also, attempts are underway to trap the proposed intermediate 5 with further suitable reagents.

References and Notes

(1) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).
(2) From the corresponding 1-lithiotricyclo[4.1.0.0^{2,7}]heptane and p-toluenesulfonyl chloride. Details will be reported elsewhere.
(3) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).
(4) Ether solutions of 1a were added to 3 equiv of the halide-free solution of the organolithium compound in ether. The isolated yields (not optimized)

were 30% for 2b, 30% for 2c (reaction at −40 °C), 62% for 2d.
(5) L. A. Paquette and G. Zon, *J. Am. Chem. Soc.*, **96**, 203 (1974).
(6) K. Fujita, T. Nakamura, K. Matsui, and T. Shono, *Tetrahedron Lett.*, 2441 (1975).
(7) From 1d and p-toluenesulfonyl bromide. Details will be reported elsewhere.
(8) This corresponds to an observation of Paquette who found that 1d and isopropyl bromide did not give a tricyclo[4.1.0.0^{2,7}]heptane derivative.[5]
(9) K. Ziegler and H. Colonius, *Justus Liebigs Ann. Chem.*, **479**, 135 (1930).
(10) These results were obtained from the mass spectra of the final products. Also, the spectra indicated that after a reaction time of 150 s 1a was totally consumed.
(11) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 2022 (1963). The authors found that n-butyllithium and 1c at 25 °C in ether and in concentrations of 1 mol/L needed 3 h to reach the half reaction point for the formation of 1d.
(12) A related effect has been observed in the ortho metalation of the halobenzenes: R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York and London, 1967, p 9 ff.
(13) This is further indicated by the fact that 1a and an excess of 1d led to bis(1-tricyclo[4.1.0.0^{2,7}]heptyl) as the major product. Details will be reported elsewhere.
(14) Organolithium compounds are known to add to cyclopropene: J. G. Welch and R. M. Magid, *J. Am. Chem. Soc.*, **89**, 5300 (1967).
(15) This is only true if the conformational change of the three-carbon bridge in 5 is fast compared with the addition of the organolithium reagent to the double bond.

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Synthesis of β,γ-Unsaturated Esters. Direct Generation of Ester Dienolates from β-Keto Ester Tosylhydrazone Trianions

Sir:

An excellent and frequently used procedure for the ketone → olefin (1 → 6) transformation is the Shapiro reaction.[1] The ketone 1 is converted to its tosylhydrazone derivative (2) which, in turn, is allowed to react with ≥2 equiv of strong base (CH$_3$Li, LiNR$_2$) to yield ultimately olefin 6 via the successive intermediacy of tosylhydrazone dianion (3), vinyldiazinyl anion (4), and vinyllithium (5).[2]

1, X = O
2, X = NNHSO$_2$C$_7$H$_7$
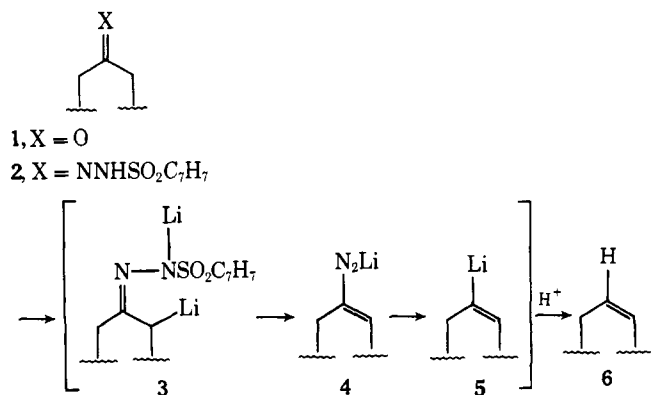
In connection with one of our programs, we are evaluating the synthetic potential of deprotonation reactions of more highly functionalized tosylhydrazones.[3] We are pleased to report that reaction[4] of a series of β-keto ester tosylhydrazones 7–18 with 3.1 equiv of lithium diisopropylamide[5] (LDA) in tetrahydrofuran at −78 °C, followed by warming to room temperature (4–24 h), quenching with ammonium chloride, and distillation, provides an exceptionally convenient synthesis of β,γ-unsaturated esters 19–30 (Table I).

The penultimate intermediate in this unsaturated ester synthesis is presumed to be a dienolate, which undergoes kinetic protonation α to the ester moiety; thus, the simple expedient of quenching the reaction mixture with various electro-