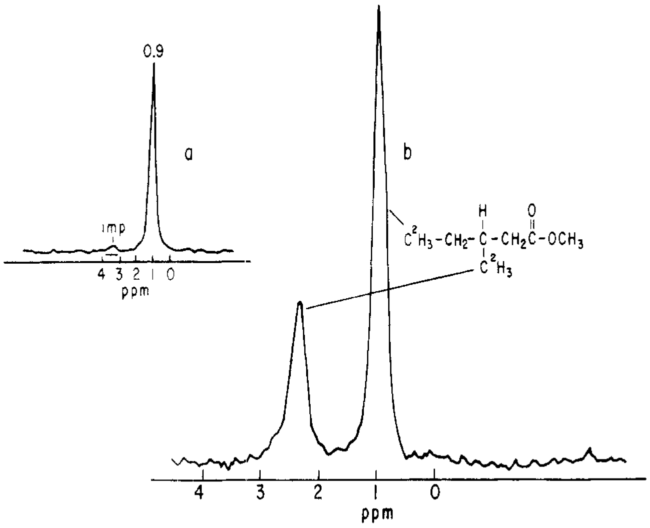

Figure 3. ^2H spectrum of: (a) methyl 3-methylpentanoate, 428 transients, 4.4-s repetition rate, displayed spectral width = 500 Hz, 8K data points; (b) methyl 3-methylpentanoate in the presence of Eu(fod)$_3$ shift reagent, molar ratio of Eu(fod)$_3$/substrate = 0.25, 400 transients, 4.4-s repetition rate, displayed spectral width = 125 Hz. Total ^2H content = 12.6%.

a somewhat broadened spectrum in the presence of Eu(fod)$_3$ because of the increased molecular weight and longer T_1 values of the double coordination site complex. However, the ^2H distribution for three distinct regions along the chain was still evident (Table I).

A full report concerning the catalytic procedures used for the ^2H exchange reactions into various compounds and their analyses by mass spectrometry and ^2H NMR spectroscopy will be the subject of future publications.

References and Notes

(1) For a comprehensive review of the most recent work in ^2H NMR spectroscopy see: H. H. Mantsch, H. Saito, and I. C. P. Smith in "Progress in Nuclear Magnetic Resonance Spectroscopy", J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, London, 1977.
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(10) Federal Research, Science and Education Administration, U.S. Department of Agriculture.

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Cuprates Derived from *endo*-(n + 3)-Bromobicyclo[n.1.0]alkanes and Related Compounds and Their Reaction with β-Iodo Enones. Facile Homo-[1,5]-sigmatropic Hydrogen Migrations Involving *endo*-(n + 3)-(3-Keto-1-cycloalkenyl)bicyclo[n.1.0]alkanes

Summary: The tricyclic compounds **6, 7, 13, 15, 21,** and **26,** efficiently obtained by reaction of the appropriate β-iodo enone (4 or 5) with cuprate reagents derived from *endo*-(n + 3)-bromobicyclo[n.1.0]alkanes and related compounds, undergo facile and, in the case of compounds **21** and **26,** completely site-selective homo-[1,5]-sigmatropic hydrogen migrations to afford, respectively, products **28–33,** inclusive.

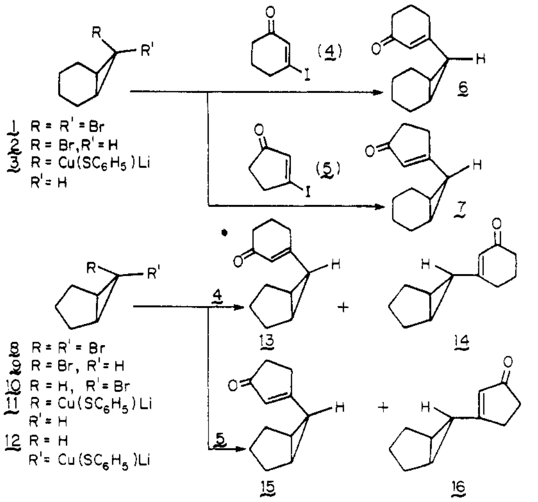
Sir: Recent reports[1–4] have indicated that various lithium cyclopropylcuprates may have considerable potential as reagents in organic synthesis. Our initial work in this area was concerned with the reactions of lithium phenylthio(cyclopropyl)cuprate and lithium phenylthio(2-vinylcyclopropyl)cuprate with β-iodo enones to produce intermediates which could be employed in cyclopentane-[2a] and cycloheptane-type[2b] annelation processes. More recently, we have been engaged in studies concerning the preparation and reactivity of more highly substituted cyclopropylcuprate reagents. We report herein some preliminary results regarding (a) the preparation of cuprate reagents derived from *endo*-(n + 3)-bromobicyclo[n.1.0]alkanes and related compounds, (b) the reaction of these reagents with β-iodo enones, and (c) the thermal sigmatropic rearrangement of the resultant intermediates to produce 2-cycloalken-1-ones which are uniquely functionalized on the β carbon of the α,β-unsaturated ketone system. Apart from the intrinsic interest in this work from a methodological point of view, we feel that the final rearrangement products possess considerable potential as intermediates in projected natural product syntheses.

Reduction of 7,7-dibromonorcarane (1) with Zn–HOAc[5] afforded a mixture of monobromo derivatives in which the endo isomer 2[6,7] predominated (ratio of endo/exo ≈ 10:1). Treatment of 2 with 2 equiv of t-BuLi (ether, −78 °C), dilution of the resultant solution with THF, addition of 1 equiv of C_6H_5SCu,[8] and warming the mixture to −20 °C gave a solution of the cuprate reagent **3.** When the latter was allowed to react (−20 °C, 2 h; 0 °C, 2 h) with each of the β-iodo enones 4[9] and 5,[2a] the corresponding endo enones 6 and 7 were obtained in excellent yields (93 and 83%, respectively, Scheme I).

Treatment of 6,6-dibromobicyclo[3.1.0]hexane (8)[10] with n-Bu_3SnH[11] afforded a 1:1 mixture of the corresponding monobromo derivatives 9 and 10[12] (Scheme I). Conversion of this material into a mixture of the corresponding cuprate reagents **11** and **12,** followed by reaction of the latter with 3-iodo-2-cyclohexen-1-one (4),[9] gave a mixture of compounds **13** (46%) and **14** (48%), which could be separated readily by column chromatography on silica gel. In similar fashion, reaction of the mixture of **11** and **12** with the β-iodo enone 5[2a] produced the epimeric derivatives **15** and **16** (isolated yields 35 and 41%, respectively).

Conversion of the MEM ethers[13] of 2-cyclohexen-1-ol (**17**) and 2-cyclopenten-1-ol (**22**) into the corresponding dibro-

Scheme I



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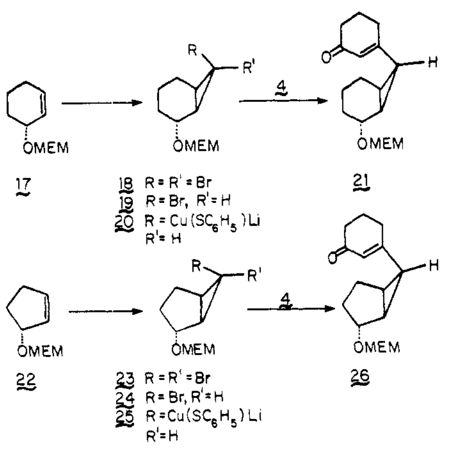
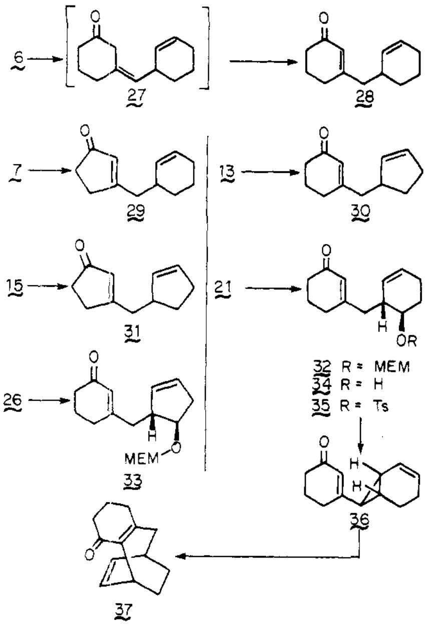
Scheme II



Scheme III



mocyclopropanes **18** and **23** was accomplished (83, 84%, respectively) by standard methodology ($CHBr_3$, NaOH–H_2O–EtOH, $C_6H_5CH_2N^+Et_3Cl^-$; Scheme II).[14,15] Reduction (**18**: Zn, HOAc; **23**: n-Bu_3SnH) of these dibromo compounds, followed by chromatographic purification of the crude products, afforded the pure *endo*-bromides **19** and **24**. The latter substances were transformed into the corresponding cuprate reagents **20** and **25** which, upon reaction with the iodo enone **4**, gave the unsymmetrical tricyclic derivatives **21** and **26** (97 and 62%, respectively).

Although the *endo*-enones **6**, **7**, **13**, **15**, **21**, and **26** were sufficiently stable to withstand purification by distillation under reduced pressure (e.g. **21** was distilled at 150–160 °C, 0.1 mm), each of these compounds rearranged smoothly and cleanly when heated (neat) at temperatures >200 °C (Scheme III). For example, when **6** was heated at 210–215 °C for 10 min, the substituted cyclohexenone **28** was obtained in 95% yield. Clearly, under these conditions, the product **27** initially formed by homo-[1,5]-sigmatropic hydrogen migration[16] isomerized to the more stable conjugated isomer **28**. In similar fashion, enones **7**, **13**, and **15** could be smoothly transformed into the corresponding rearrangement products **29** (98%), **30** (87%), and **31** (90%), respectively.

Thermolysis of the unsymmetrical *endo*-enones **21** and **26** represent especially interesting examples of the present methodology. In each case, the rearrangement process was very clean (**32**, 89%; **33**, 78%), and a careful analysis of each of the crude reaction products (after brief treatment with NaOMe–MeOH[17]) failed to produce evidence for the formation of any other product. At present, the reasons underlying the highly site-selective nature of these homo-[1,5]-sigmatropic hydrogen shifts remains obscure. However, it is clear that these high selectivities could be very useful from a synthetic point of view.

Removal of the MEM group ($ZnBr_2$, CH_2Cl_2)[13] from **32**, followed by tosylation of the resultant alcohol **34**, gave the tosylate **35**. Brief treatment of the latter with 1.2 equiv of t-BuOK in t-BuOH (15 min, room temperature) gave (68% from **34**) the *exo*-enone **36**.[18,19] When a solution of **36** in o-dichlorobenzene (bp 179 °C) was refluxed for 40 h, the tricyclic enone **37** (resulting from Cope rearrangement[20]) was formed in 94% yield.

Work in this area is continuing.

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(15) For steric reasons, dibromocyclopropanation of **17** and **22** would be expected to occur from the side of the molecule opposite the O–MEM group. Independent evidence for the stereochemistry of **18** was obtained as follows. Removal of the MEM group, followed by oxidation of the resultant alcohol A, gave the corresponding ketone. Reduction of the latter afforded an alcohol which was clearly epimeric with A.
(16) For a recent review regarding this type of reaction, see S. W. Spangler, *Chem. Rev.*, **76**, 187 (1976).
(17) In these cases, the initial thermolysis products contained small amounts of the unconjugated ketones (analogous to **27**), which were isomerized to the conjugated isomers by the base treatment.
(18) Compound **36** could also be obtained by reaction of 3-iodo-2-cyclohexen-1-one with the cuprate reagent derived from *exo*-7-bromo-2-norcarene.
(19) The facility with which the transformation of **35** into **36** occurred also provided excellent evidence to support the stereochemical assignment made for compound **17** (see ref 15) and for the subsequent intermediates derived from **17**.
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One-Step Catalytic Synthesis of 2,2,3-Trimethylbutane from Methanol

Summary: Catalytic reaction of methanol in the presence of zinc iodide produces butane and higher hydrocarbons with a high degree of branching and an unexpectedly high triptane (2,2,3-trimethylbutane) content.