



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

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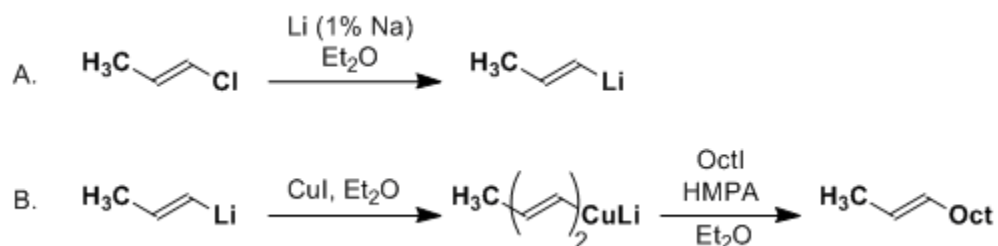
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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**PREPARATION OF ALKENES BY REACTION OF LITHIUM  
DIPROPENYL CUPRATES WITH ALKYL HALIDES:  
(E)-2-UNDECENE**

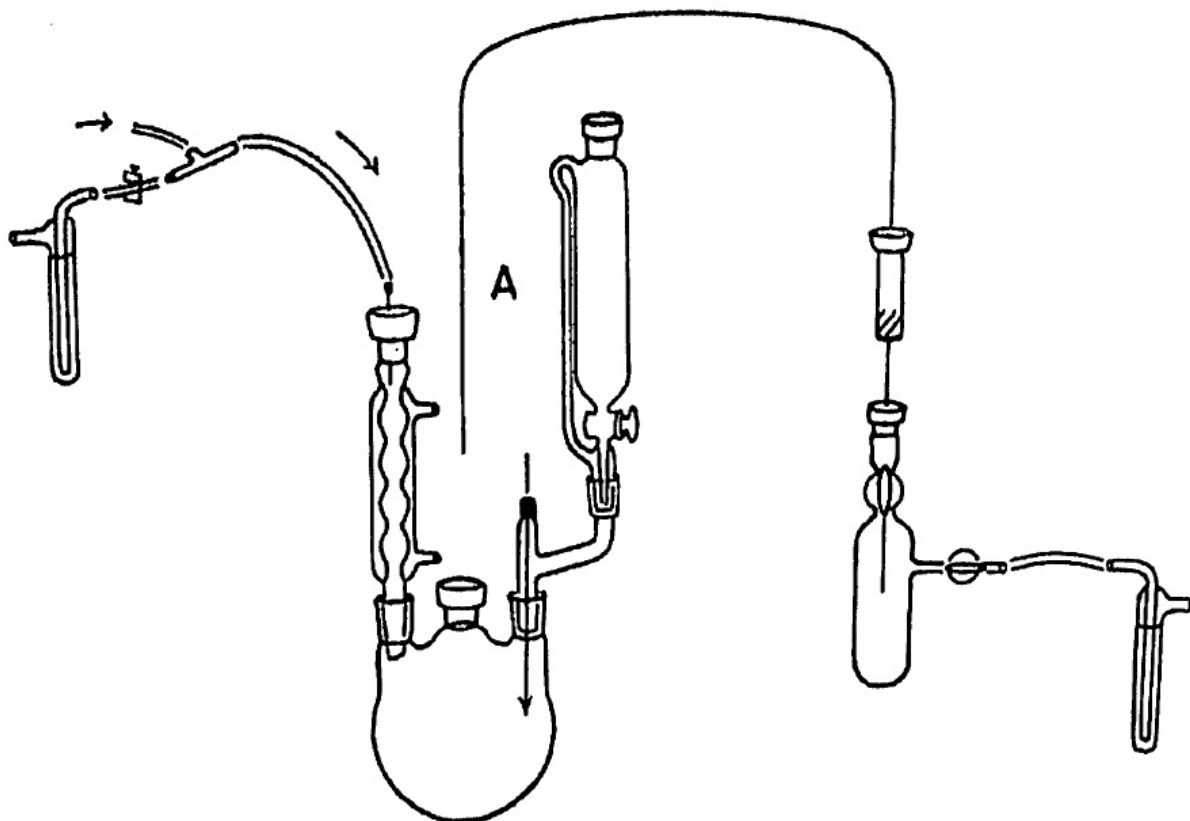


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## 1. Procedure

*Caution! Lithium dispersion is highly reactive. Although it may be handled safely in air when covered with mineral oil, it will spark and ignite organic vapors on contact with water. When clean, it is pyrophoric and may occasionally ignite spontaneously on contact with air. Manipulation of lithium dispersion should be carried out behind a safety shield with the protection of rubber gloves. Particular caution should be taken during disposal of the excess lithium remaining after preparation and filtration of the propenyllithium (Note 1). Hexamethylphosphoric triamide (HMPA) vapors have been reported to cause cancer in rats [J. A. Zapp, Jr., *Science*, **190**, 422 (1975)]. Hence, all operations with HMPA should be performed in a good hood, and care should be taken to keep liquid HMPA off the skin.*

A. *1-Propenyllithium.* A dry (Note 2), 500-ml., three-necked, round-bottomed flask equipped with a Teflon®-covered magnetic stirring bar, a 200-ml. pressure-equalizing dropping funnel, an efficient reflux condenser, and an immersion thermometer is capped with serum stoppers (Note 3) and flushed with argon (Note 4). Lithium dispersion (Note 5), [22.4 g. of a 50% w/w suspension in Amsco, 11.2 g. (1.6 g.-atoms) of lithium] (Note 6), is rapidly weighed in air and transferred to the flask. The apparatus is flushed again with argon for approximately 10 minutes, and then maintained under a static pressure of the inert gas (Note 7).



The lithium is washed three times by transferring approximately 60-ml. portions of anhydrous ether (Note 8) into the flask through a No-Air stopper by forced siphon through a stainless steel cannula (Note 9), stirring the resulting suspension of lithium briefly, allowing the suspension to separate, and finally withdrawing the major part of the ether by forced siphon through a cannula. After separating the last washings, 250 ml. of anhydrous ether is transferred into the flask (see diagram), and a solution of 35 g. (0.46 mole) of (*E*)-1-chloropropene (Note 10) in 120 ml. of anhydrous ether is transferred into the dropping funnel through a cannula. The reaction mixture is cooled in an acetone bath maintained at approximately  $-10^{\circ}$  by periodic addition of dry ice, and the surface of the lithium cleaned by injecting approximately 150  $\mu\text{l}$ . of 1,2-dibromoethane through the serum stopper into the vigorously stirred lithium suspension (Note 11). The chloropropene solution is added to the lithium suspension over a 2-hour period, while the internal temperature of the reaction mixture is maintained at  $10^{\circ} \pm 5^{\circ}$ . It is important to control the temperature in this range throughout the addition (Note 12). A precipitate begins to form. The reaction mixture is allowed to stir for 30 minutes at room temperature, and stirring is stopped. The precipitate is allowed to settle, and the solution is transferred by a large-gauge cannula through a glass wool pad into a storage bottle in the manner illustrated in the diagram (Note 13). The precipitate is washed once with 20 ml. of anhydrous ether, and this solution is transferred to the storage bottle through the filter. Gilman titration<sup>3</sup> of the resulting solution using aqueous 0.10*N* hydrochloric acid and 1,2-dibromoethane typically indicates that the concentration of total base is 1.29*N* and the concentration of residual base is 0.25*N* (Note 14). The reagent can be stored at  $-20^{\circ}$  for more than one week without isomerization or attack on ether, but should be titrated routinely before use.

B. (*E*)-2-Undecene. A dry (Note 2), 500-ml., three-necked, round-bottomed flask equipped with a thermometer, a 200-ml. pressure-equalizing dropping funnel capped with a No-Air stopper, a gas-inlet tube, and a Teflon®-covered magnetic stirring bar is charged with 12.58 g. (0.066 mole) of copper(I) iodide (Note 15). The apparatus is flushed with argon. Under a static argon pressure of 2–3 cm. of Nujol, 80 ml. of anhydrous ether is added, and the resulting suspension is immersed in an acetone-dry ice bath at  $-78^{\circ}$ . Through a cannula 132 ml. of an ethereal 1.04*M* (0.137 mole) solution of (*E*)-1-propenyllithium is

transferred into the dropping funnel and added dropwise to the cold, stirred suspension of copper(I) iodide over 45–50 minutes. The reaction mixture is allowed to warm to  $-35^{\circ}$  over approximately 1 hour (Note 16). At  $-35^{\circ}$ , 44 ml. of hexamethylphosphoric triamide (approximately 3.75 equivalents per equivalent of lithium dipropenylcuprate) is added slowly to the reaction mixture from the dropping funnel, which has been previously rinsed with 20 ml. of ether (Note 17). A white precipitate forms almost immediately (Note 18). After approximately 10 minutes, 15.84 g. (12 ml., 0.066 mole) of 1-iodooctane is added from the dropping funnel over 10 minutes (Note 19), while the reaction temperature is maintained at  $-35^{\circ}$ . The funnel is rinsed with 20 ml. of ether. The resulting mixture is allowed to warm to a temperature between  $-5^{\circ}$  and  $0^{\circ}$  over 45 minutes (Note 20). The entire reaction mixture is then poured into 400 ml. of aqueous saturated ammonium chloride and filtered through fritted glass. The precipitate on the filter is washed with 30 ml. of pentane. The organic layer is separated, and the aqueous phase extracted with four 80-ml. portions of pentane. The combined organic layers are washed once with 40 ml. of aqueous saturated ammonium chloride and once with 20 ml. of aqueous sodium chloride and dried over anhydrous magnesium sulfate. The resulting solution is concentrated by distillation at atmospheric pressure through a 12-cm. Vigreux column, and the residue is distilled at reduced pressure through the same column, yielding 9.2–9.4 g. (90–93%) of (*E*)-2-undecene, b.p.  $88^{\circ}$  (17 mm.),  $n^{25}_D$  1.4276 (Note 21).

## 2. Notes

1. Lithium dispersion can be safely destroyed by carefully adding it in small portions to a large excess of technical *tert*-butyl alcohol in a metal pan. If too much lithium is added at one time, the reaction with the *tert*-butyl alcohol can become very vigorous. Under these circumstances, a fire can be avoided by covering the pan with a second, larger metal pan or with an asbestos sheet.

2. The glassware was dried in an oven at  $120^{\circ}$  for 2 hours and assembled quickly while still hot. It is possible and occasionally desirable in humid climates to dry the apparatus after assembly by heating its accessible parts with a low flame from a Meaker burner while flushing it with a stream of argon, but this operation is normally unnecessary.

3. The serum stoppers used were “sleeve serum stopples,” manufactured by the Bittner Corporation, 181 Hudson St., New York, N.Y., 10013; they were obtained from V.W.R. Scientific. The checkers used rubber serum stoppers obtained from Fisher Scientific Company.

4. Argon, available from Matheson Gas Products, was used without drying. *Caution! Nitrogen can NOT be used as a substitute for argon in preparation of organolithium reagents, since lithium metal reacts rapidly with nitrogen.* Argon and nitrogen can be used interchangeably in subsequent steps. Inert gases are delivered to the reaction vessel through Tygon® or polyethylene tubing, whichever is more convenient.

5. Lithium dispersion containing 1% sodium, so-called “high-sodium” lithium dispersion, suspended in Amsco (a mineral oil) was obtained from Foote Mineral Company. Lithium containing smaller amounts of sodium is not usable in this procedure. This lithium dispersion separates slowly on standing. Before weighing samples of the dispersion, it is stirred briefly to produce a reasonably homogeneous suspension. The checkers used lithium dispersion 50% w/w in cyclohexane obtained from Matheson Coleman and Bell.

6. Experiments carried out using a smaller excess (1.2 g.-atoms) of lithium gave results indistinguishable from those obtained using the procedure outlined here. Nevertheless, because lithium suspension in Amsco is inhomogeneous, an excess of lithium is preferred.

7. A slight positive pressure of argon was maintained in the vessel throughout the reaction with an argon line connected to both a bubbler containing Nujol and a hypodermic needle that had been inserted through the serum stopper covering the reflux condenser, as illustrated in the diagram.

8. Mallinckrodt anhydrous diethyl ether was purified by refluxing with calcium hydride under nitrogen for at least 2 hours and distilling under nitrogen immediately before use. For use in the preparation of the propenyllithium, approximately 650 ml. of ether should be collected in a dry 1-l. graduated flask capped with a serum stopper.

9. Cannulae are fabricated on special order from stainless steel hypodermic needle stock by Popper and Sons Company, 290 Park Avenue, South, New York, N.Y., 10010. Approximately 30-cm. long cannulae made from 15 and 20 gauge stock were used in this preparation.

10. Pure (*E*)-1-chloropropene was obtained by careful distillation of a mixture of (*E*)- and (*Z*)-1-chloropropene (available from Columbia Organic Chemicals Company Inc.) using a Nester-Faust Teflon® annular spinning band column [(*Z*)-1-chloropropene has b.p. 33°; (*E*)-1-chloropropene has b.p. 37°]. Small quantities of powdered sodium bicarbonate and hydroquinone (1,4-benzenediol) placed in the distillation flask inhibit acid-catalyzed isomerization and polymerization. Gas chromatographic analysis of the material used in these experiments on a 4-m., 15% 1,2,3-tris(2-cynoethoxy)propane (TCEP) on Chromosorb P column, operated at room temperature, typically indicated that it had isomeric purity >99.9%. (*E*)-1-Chloropropene is stable for several months at room temperature, but it should be stored in a cool place.

11. Purification of 1,2-dibromoethane was accomplished by passing a small quantity rapidly through a 5-cm. column of alumina. Addition of 1,2-dibromoethane to the lithium dispersion is accompanied by visible evolution of ethylene (ethene).

12. If the internal temperature is too low the reaction stops; therefore the mixture should not be cooled excessively. A buildup of unreacted (*E*)-1-chloropropene in the reaction flask can result in an uncontrollable exotherm when the reaction temperature again increases.

13. The transfer of filtration were accomplished by inserting the cannula (label A in the diagram) through the serum stopper on the center neck of the reaction flask and to the bottom of the flask to avoid transferring the unreacted lithium dispersion floating at the top of the solution. The pressure used in the forced siphon was controlled with the stopcock on the Nujol bubbler attached to the inlet gas line. A convenient filter was constructed by packing glass wool, previously dried in an oven, into a 20-ml. Luer-lock® syringe barrel, fitted with a 20-cm. 15-gauge needle. The syringe barrel was capped with a serum stopper, flushed with argon, and washed with approximately 30 ml. of anhydrous ether. A large-diameter (15 gauge) cannula should be used to transfer the organolithium reagent solution from the flask to the filter, since smaller gauge cannulae are frequently plugged by solid particles. The storage bottle is usually a Schlenk tube fitted with Teflon® stopcocks. The lithium reagent can also be stored for 2 or 3 days in a flask fitted with a serum stopper, provided that puncture holes through the stopper are sealed with Apiezon Q or some equivalent material.

14. After this titration, the isomeric purity of the organolithium reagent can be assayed by adding approximately 4 ml. of pentane to the dibromoethane-water mixture, separating the organic layer, drying over anhydrous magnesium sulfate, filtering, and analyzing by gas chromatography at room temperature. Less than 1% of unreacted (*E*)-1-chloropropene was present; the (*E*)-1-bromopropene was accompanied by approximately 3.5% of (*Z*)-1-bromopropene.

15. Commercial copper(I) iodide (purchased from Fisher Scientific Company) was purified by the published procedure.<sup>4a</sup> The very pale yellow powder obtained was collected by suction filtration on a fritted glass filter, then triturated on the filter in succession with four 100-ml. portions of distilled water, four 80-ml. portions of reagent-grade acetone, and four 80-ml. portions of anhydrous ether. The copper(I) iodide was powdered, transferred into a round-bottomed flask fitted with a connecting tube with a stopcock, dried overnight under vacuum (0.6 mm.) at room temperature, and heated at 90° under the same vacuum for 4 hours. After cooling, nitrogen was introduced. When copper(I) iodide was needed, it was weighed, powdered, and transferred rapidly in air without special precautions. *Each time the flask is opened to remove a sample of copper(I) iodide, the air introduced should be removed by evacuating the flask under vacuum and refilling it with nitrogen through a two-way stopcock several times.* If this precaution is observed, the copper(I) iodide can be stored without change for several months; if air is allowed to remain in the flask, the copper(I) iodide deteriorates.<sup>4b</sup>

16. Occasionally a colorless solution was obtained at approximately -50°. In most cases the reaction mixture contained a small quantity of fine suspended black powder (presumably copper metal). Examination of the reaction mixture at this stage by hydrolysis of a sample at -35° and gas chromatographic

analysis demonstrated the presence of approximately 10% of 2,4-hexadienes [predominately the (*E*), (*E*)-isomer].

17. Hexamethylphosphoric triamide, supplied by Fisher Scientific Company, was purified by distillation from sodium (approximately 6 g. per 500 ml.). The boiling point was 69 ° (1 mm.). In place of hexamethylphosphoric triamide, tetrahydrofuran can be used, and 120 ml. of this solvent was slowly added over 30 minutes through a stainless steel cannula. Mallinckrodt analytical-reagent tetrahydrofuran was purified by distillation from a dark purple solution of disodium benzophenone dianion under nitrogen before use. The checkers used only hexamethylphosphoric triamide (*see p. 103 for warning*).

18. A major part of this precipitate was apparently crystallized hexamethylphosphoric triamide, presumably containing lithium halide.

19. 1-Iodooctane (purchased from Eastman Organic Chemicals) was purified by distillation, b.p. 57 ° (0.7 mm.), and stored at 0 ° in the dark.

20. The reaction is complete within 30 minutes if the temperature of the bath is maintained between -30 ° and -25 °.

21. Gas chromatographic analyses for isomeric purity were carried out using a TCEP column (Note 10) at 70 °; these analyses typically indicated an isomeric composition of 96% (*E*)- and 4% (*Z*)-2-undecene. Examination of the crude product before distillation showed the presence of approximately 10% 2,4-hexadienes (Note 16). (*E*)-2-Undecene has a shorter retention time than (*Z*)-2-undecene on the column used here. Spectral properties of the (*E*)-isomer are as follows; infrared (neat)  $\text{cm}^{-1}$ : 3020 weak inflection, 2960 medium, 2935 very strong, 2865 strong, 1560 weak, 1455 medium, 1380 weak, 975 medium-strong; proton magnetic resonance (carbon tetrachloride)  $\delta$ , multiplicity, number of protons, assignment: 0.9 (multiplet, 3, allylic  $\text{CH}_3$ ), 1.3 (broad singlet, 12, 6 x  $\text{CH}_2$ ), 1.6 (multiplet, 3,  $\text{CH}_3$ ), 1.9 (multiplet, 2, allylic  $\text{CH}_2$ ), 5.35 (multiplet, 2,  $\text{CH}=\text{CH}$ ).

### 3. Discussion

This procedure illustrates the stereospecific preparation of a lithium vinylcuprate and its utilization in the stereospecific synthesis of an (*E*)-alkene by coupling with an organic halide. Similar results have been obtained with lithium di-(*Z*)-propenylcuprate, prepared from (*Z*)-1-bromopropene,<sup>3</sup> and such procedures can be used to prepare alkenes from (*Z*)- and (*E*)-vinylic halides.<sup>5</sup> These coupling procedures seem widely applicable in reactions involving primary alkyl halides or tosylates. Using the conditions described above, yields are variable but generally lower when applied to secondary halides (35%), where elimination becomes an important side reaction, and to aryl halides (25%), where metal-halogen exchange may become important.<sup>6,7</sup> No systematic effort has been made to minimize these side reactions. Vinylcuprates are useful in other stereospecific alkene syntheses involving copper(I), particularly those based on conjugate addition to  $\alpha,\beta$ -unsaturated ketones.<sup>8,9</sup>

Two equivalents of the 1-propenyl group are used in this procedure for each equivalent of alkyl halide. Although the fate of the second propenyl group has not been investigated in detail, it presumably appears as 1-propenylcopper(I) and its decomposition products; similar behavior is observed in the conjugate addition reaction, in which only one of the two alkyl groups of a lithium dialkylcuprate is normally utilized, the second appearing, at least in part, as an alkylcopper(I) compound. The procedure described here is designed to minimize the production of 2,4-hexadiene from thermal decomposition of 1-propenylcopper(I). In other preparations, this precaution may be unnecessary.

The choice of solvent in these couplings is dictated in part by convenience. Ether containing several equivalents of hexamethylphosphoric triamide per equivalent of organometallic reagent and tetrahydrofuran or tetrahydrofuran-ether mixtures usually give comparable yields of products; pure ether and ether-hydrocarbon mixtures are inferior. The ether-hexamethylphosphoric triamide solvent system seems easiest to work up since partitioning of the organic phase against water can be used to remove most of the inorganic salts and the hexamethylphosphoric triamide present at the conclusion of the reaction.

The most important alternative to this coupling procedure involves the reaction of organolithium reagents with organic halides (Table 1).<sup>10</sup> A similar coupling reaction of organomagnesium reagents in tetra-hydrofuran or in hexamethylphosphoric triamide has been reported.<sup>11</sup> Procedures using pure organolithium reagents are potentially capable of higher yields of products based on the organolithium reagent, since all of the organolithium moieties present in solution are available for reaction; further, they avoid thermally unstable organocopper(I) intermediates. However procedures based on lithium divinylcuprates are compatible with a wider range of functional groups present in the organic halide.

TABLE I

YIELDS OF (*E*)-2-UNDECENE PREPARED FROM 1 EQUIVALENT OF THE INDICATED SUBSTRATES BY REACTION EITHER WITH 1 EQUIVALENT OF LITHIUM DIPROPENYLcupRATE OR 1 EQUIVALENT OF PROPENYLlITHIUM

Substrate	Reaction with R <sub>2</sub> CuLi				Reaction with RLi			
	Yield (%) <sup>a</sup>	Time (hours)	Temperature (°C)	Solvent	Yield (%) <sup>a</sup>	Time (hours)	Temperature (°C)	Solvent
1-Iodoctane	100	0.75	-30 to -20	Ether + 4 equivalents HMPA	76	0.25	-35	Et <sub>2</sub> O + 4 equivalents HMPA
	100	0.75	-30 to -25	THF	100	1.7	+25	THF or DME
	73	18	+25	Et <sub>2</sub> O	7	23	+25	Et <sub>2</sub> O
1-Bromooctane	100	3	-30 to +5	Et <sub>2</sub> O + 4 equivalents HMPA	100	3.5	+25	THF
1-Chlorooctane <sup>1</sup>	80	48	+25	Et <sub>2</sub> O + 4 equivalents HMPA	50	70	+25	DME
1-Tosyloctane	95	2.5	-10	Et <sub>2</sub> O + THF <sup>c</sup>	0	48	+25	THF

<sup>a</sup> Yields determined by gas chromatography (Note 20). Preparative scale yields are usually approximately 10% lower.

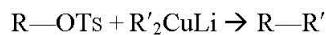
<sup>b</sup> Unreacted chloride remains at the end of the reaction (with R<sub>2</sub>CuLi: 15%, with RLi: 40%); 1.5 equivalents of R<sub>2</sub>CuLi per equivalent of chloride gives 95% (*E*)-2-undecene after 5 days at 25°.

<sup>c</sup> A volume of THF equal to that of the ether present was added after formation of the cuprate was complete. THF: tetrahydrofuran; HMPA: hexamethylphosphoric triamide; Et<sub>2</sub>O: diethyl ether; DME: 1,2-dimethoxyethane.

The general procedure described here is applicable to the preparation and use of many lithium dialkylcuprates derived from the thermally less stable *primary* alkyllithium reagents, although the solutions of intermediate organocopper compounds are usually highly colored and may contain suspended copper metal or organocopper compounds. Applications involving *secondary* organolithium reagents frequently fail as a result of thermal decomposition of the intermediate alkylcopper(I) compounds; these reactions may require the presence of stabilizing phosphine ligands in solution, although the work-up of reaction mixtures containing phosphines is normally more difficult than that described here. Several examples shown in Table II illustrate reaction of primary and secondary tosylates with various organocuprates, using diethyl ether as solvent.

TABLE II<sup>12</sup>

REACTIONS OF PRIMARY AND SECONDARY TOSYLATES WITH ORGANOCUPRATES



R	R'	Equivs of Cuprate	Temperature (°)	Time (hours)	R—R' Yield (%)
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> —	CH <sub>3</sub> —	2	0	1	95
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>2</sub> —	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH(CH <sub>3</sub> )—	5	-15	16	85
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH(CH <sub>3</sub> )—	CH <sub>3</sub> —	2	-20	4	87
(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> —	C <sub>6</sub> H <sub>5</sub> —	3	25	72	80
<i>c</i> -C <sub>5</sub> H <sub>9</sub> —	CH <sub>3</sub> —	2	0	5	65
<i>c</i> -C <sub>6</sub> H <sub>11</sub> —	CH <sub>3</sub> —	2	0	5	20

#### 4. References and Notes

1. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. This work was supported in part by grants from the National Science Foundation and the International Copper Research Association, Inc.
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