The reaction of **6** with RMgX·2HMPA coupled with the recently reported[9] addition of organolithiums to *tert*-alkyl isocyanides now provides a facile technique for the deuterioformylation of the two most common classes of organometallics. Furthermore since formic acid-^{14}C is routinely available, this method allows an easy entry into C-14 labeled aldehydes.

A typical procedure for formylating a Grignard reagent follows. ***N*,4,4-Trimethyl-2-oxazolinium iodide** (**5**) was prepared by stirring **1** (20 g) in 25 ml of methyl iodide for 20 hr and removing unreacted components *in vacuo*. The solid was washed with ether, dried, and purified by precipitation of an acetonitrile solution with ether, producing **2** in 89% yield. The salt, although slightly hygroscopic, could be stored in an inert atmosphere without deterioration.

***o*-Methoxybenzaldehyde.** The Grignard reagent of *o*-bromoanisole (11 mmol) was prepared in THF (15 ml) and treated with dry HMPA (22 mmol). The resulting solution was added dropwise to a stirred suspension of **2** (10 mmol) in THF (30 ml) at room temperature and allowed to stir for 15–16 hr. The reaction mixture was decomposed with ice–water and acidified with 3 *N* hydrochloric acid. The acid solution was extracted with hexane (discarded) and then carefully made alkaline with sodium hydroxide solution (30–40%). The crude oxazolidine **6** was removed by ether extraction[10] and, after concentration, was heated to reflux for 15 min in an aqueous oxalic acid (45 mmol/25 ml) solution. The cooled acid solution was extracted with ether and the extracts were concentrated yielding the aldehyde as a crystalline residue (mp 36–38°).

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(9) H. M. Walborsky and G. E. Niznik, *J. Amer. Chem. Soc.*, **91**, 7778 (1969); H. M. Walborsky, W. H. Morrison, III, and G. E. Niznik, *ibid.*, **92**, 6675 (1970). In the latter study, the magnesium aldimines do not appear to react with Grignard reagents other than aliphatic (sp^3 carbon bonded to magnesium). Thus, this method is limited to formylation of alkyl residues whereas the present technique complements nicely by allowing formylation of aryl, benzyl, alkynyl, allyl, and vinyl Grignard reagents.

(10) If pure oxazolidine is required, final traces of HMPA can be removed by elution of the ethereal solution through silica gel (8–20 mesh).

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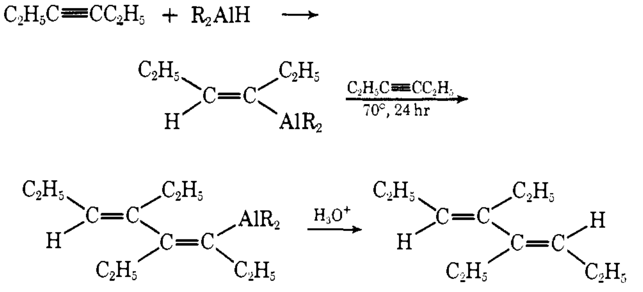
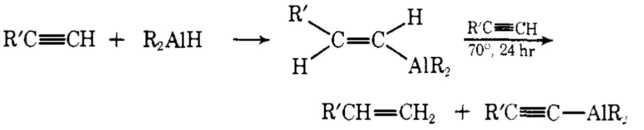
A Novel Stereoselective Synthesis of 1,3-Dienes from Alkynes *via* the Addition of Cuprous Chloride to Vinylalanes[1]

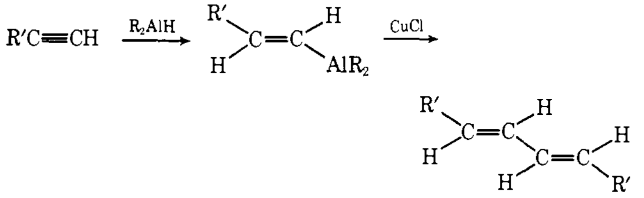
Sir:

An interesting reaction specific to the vinylalanes derived from disubstituted alkynes is their addition to the triple bonds of disubstituted acetylenes to form dienylalanes.[2] These derivatives yield, after hydrolysis, tetrasubstituted trans,trans 1,3-dienes. Thus, hydroalumination of 3-hexyne with diisobutylaluminum hydride in a 2:1 ratio at 70° followed by hydrolysis of the intermediate dienylalane gives 4,5-diethyl-*trans*,-*trans*-3,5-octadiene in high yield.[3] Unfortunately, our endeavours to utilize 1-alkynes for the above dimerization reaction were unsuccessful due to competing metalation of the acetylenes. Likewise, attempts to add the vinylalane derived from 3-hexyne and diisobutylaluminum hydride to 1-hexyne afforded *cis*-3-hexene and diisobutyl(1-hexyn-1-yl)alane.





In exploring alternate routes for the synthesis of dienes from terminal acetylenes *via* the hydroalumination reaction we have now found that terminal vinylalanes, when treated with cuprous chloride in tetrahydrofuran solution, react to give isomerically pure trans,trans 1,3-dienes. Thus, addition at 25° of a 20% molar excess of cuprous chloride to a tetrahydrofuran solution of the vinylalane derived from 1-hexyne and diisobutylaluminum hydride resulted in the precipitation of copper and a 73% isolated yield of *trans,trans*-5,7-dodecadiene.[4] Increasing the size of the alkyl group attached to the triple bond from *n*-butyl to *tert*-butyl had little effect on the yield and stereochemistry of the diene formed. For each of the reactions studied, glpc analysis of the crude reaction mixture revealed that formation of the diene occurred with nearly complete retention of configuration around the carbon–carbon double bond. The results are summarized in Table I.



The facile coupling reaction with cuprous chloride is also applicable to vinylalanes derived from disub-

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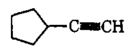
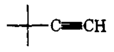
(1) This research was supported by the National Science Foundation through Grant No. GP-9398.

(2) G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960).

(3) G. Zweifel, N. L. Polston, and C. C. Whitney, *J. Amer. Chem. Soc.*, **90**, 6243 (1968).

(4) Glpc examination of the reaction mixtures revealed that coupling products derived from isobutyl–isobutyl or isobutyl–hexenyl dimerization were formed in small amounts.

Table I. Yields of Dienes Derived from Various Alkynes

Alkyne	Hydroalumination temp, °C[a]	Diene	Yield, %[b,c]
$C_4H_9C{\equiv}CH$	50	*trans,trans*-5,7-Dodecadiene	73 (78)
	50	1,4-Dicyclopentyl-*trans,trans*-1,3-butadiene	68 (83)
	25	2,2,7,7-Tetramethyl-*trans*,-*trans*-3,5-octadiene	67 (87)
$C_2H_5C{\equiv}CC_2H_5$	70	4,5-Diethyl-*trans,trans*-3,5-octadiene	71

[a] In each case hydroalumination was carried out with diisobutylaluminum hydride in *n*-hexane for 4 hr. [b] The values in parentheses were obtained by glpc analysis using an internal standard. The other values are isolated yields. [c] The nmr, ir, uv, and mass spectral data were in agreement with the assigned structures.

stituted alkynes. Thus, treatment with cuprous chloride of the monohydroalumination product obtained from 3-hexyne yielded 71% 4,5-diethyl-*trans,trans*-3,5-octadiene. This novel dimerization procedure therefore complements the more time consuming synthesis of tetrasubstituted 1,3-dienes *via* dienylalane intermediates.[2]

The simplicity of the present procedure for the preparation of trans,trans dienes is illustrated by the following example. A dry 250-ml flask equipped with a thermometer, a condenser, a magnetic stirrer, and a side arm capped with a rubber septum was flushed with nitrogen. To the flask, which was kept under a static pressure of nitrogen, was added 8.2 g (0.10 mol) of 1-hexyne, 40 ml of *n*-hexane, and 18.6 ml (0.10 mol) of diisobutylaluminum hydride while maintaining the temperature during the addition at 25–30° by means of a water bath. The solution was stirred at room temperature for 30 min, then heated at 50° for 4 hr. After cooling the reaction mixture to room temperature, the *n*-hexane was removed under reduced pressure and 80 ml of dry tetrahydrofuran was added at 0°. Dry cuprous chloride (12.0 g, 0.12 mol) was added over a period of 10 min while maintaining the temperature between 25 and 35° (water bath). The resultant dark reaction mixture was kept for an additional 50 min at ambient temperature before being poured slowly into a mixture of 5% H_2SO_4 (100 ml) and *n*-pentane (100 ml) which had been precooled in an ice bath.[5] The organic phase was separated, and the aqueous layer was extracted repeatedly with *n*-pentane. The combined extracts (containing some of the black precipitate) were washed with aqueous sodium bicarbonate, then dried over anhydrous magnesium sulfate. Distillation gave 6.05 g (73%) of *trans,trans*-5,7-dodecadiene: bp 76° (3 mm); $n^{25}D$ 1.4635; uv (cyclohexane) 231 (ϵ 31,200), 226 (sh), and 237 mμ (sh).[6]

Although we have not established the nature of the intermediates undergoing dimerization, it is probable that the vinylalanes react with cuprous chloride to give the vinylcopper(I) compounds which then decompose to give the diene products. The formation of the 1,3-dienes by this reaction sequence is reasonable in light of the previously observed thermal decompositions of vinylcopper(I) compounds derived from vinyllithium[7] and vinylmagnesium derivatives[8] to dienes.

It is apparent that the facile conversion of the readily available vinylalanes of defined stereochemistry into other vinylmetallic compounds having different reactivities toward organic and inorganic reagents should be exceedingly useful in organic syntheses. We are currently exploring exchange reactions involving vinylalanes and various metal salts other than cuprous chloride.

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(5) The same isomeric purity of the diene was observed when the reaction mixture was decomposed with water.

(6) The corresponding *cis,cis*-dodecadiene is available by reduction of the appropriate diyne with dialkylboranes [G. Zweifel and N. L. Polston, *J. Amer. Chem. Soc.*, **92**, 4068 (1970)], whereas the cis,trans diene can be prepared from 1-hexyne *via* the hydroboration–iodination reaction (ref 3).

(7) G. M. Whitesides and C. P. Casey, *ibid.*, **88**, 4541 (1966).

(8) T. Kaufmann and W. Sahm, *Angew. Chem., Int. Ed. Engl.*, **6**, 85 (1967).

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Equilibrium Acidities in Dimethyl Sulfoxide

Sir:

The presence of methylsulfinyl carbanion, the conjugate base of dimethyl sulfoxide, in solutions of potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) has been inferred from kinetic data and trapping experiments, but previously it has not been possible to detect this anion spectroscopically in such solutions. The demonstration of the existence and measurement of the concentration of this species are of great importance in understanding the chemistry of solutions of alkoxides in DMSO, a medium widely used in base-catalyzed reactions.[1] We wish to report the direct observation, by means of Raman spectroscopy, of methylsulfinyl carbanion in DMSO.

Corey and Chaykovsky first prepared methylsulfinyl carbanion (dimsyl, $CH_3SOCH_2^-$) and they observed addition of this ion to benzophenone in DMSO.[2] Russell observed similar addition products in basic solutions prepared from potassium *tert*-butoxide in DMSO.[3] Products of $CH_3SOCH_2^-$ reactions in alkoxide solutions have also been found by Walling,[4a] Ledwith,[4b] and Schriesheim[4c] and their coworkers. Kinetic evidence for the presence of $CH_3SOCH_2^-$ has been obtained by the observation of the rapid exchange of the protons of DMSO in the presence of *tert*-butoxide.[5]

None of the above evidence provides much insight, however, into the amount of $CH_3SOCH_2^-$ present in alkoxide solutions in DMSO. Ritchie and Uschold[6,7]

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(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(2) E. J. Corey and M. Chaykovsky: (a) *J. Amer. Chem. Soc.*, **84**, 866 (1962); (b) *ibid.*, **87**, 1345 (1965).

(3) G. A. Russell, E. G. Jantzen, H.-D. Becker, and F. J. Smentowski, *ibid.*, **84**, 2652 (1962); G. A. Russell and H.-D. Becker, *ibid.*, **85**, 3406 (1963); G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

(4) (a) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963); (b) A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964); (c) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965).

(5) J. I. Brauman, N. J. Nelson, and D. C. Kahl, *J. Amer. Chem. Soc.*, **90**, 490 (1968); J. I. Brauman and N. J. Nelson, *ibid.*, **90**, 491 (1968).