moment of 3.15 BM at 27° which falls to 0.8 BM at $-75°$ and rises again to 1.36 BM at $-94°$. Its conductivity is greater than that of the bromide. Nmr measurements confirm that the main species present at $-90°$ is square-planar $Ni(tu)_3I^+$ together with a small amount of octahedral $Ni(tu)_6{}^{2+}$. At room temperature it exists mostly as tetrahedral $Ni(tu)_2I_2$. In all of these complexes there is some displacement of tu by solvent acetone (particularly at high temperatures) which can be conveniently monitored by nmr, but this is not pertinent to the present arguments. A variety of N-substituted thiourea complexes with both coordinating and noncoordinating anions give results which conform to the above pattern.

We believe that the significant generalization from these results is that *under identical conditions* (solvent acetone, $-90°$, excess ligand present) the neutral complexes are tetrahedral ($Ni(tu)_2X_2$), the monopositive ions are square planar ($Ni(tu)_3X^+$), and the dipositive ions are octahedral ($Ni(tu)_6{}^{2+}$). We suggest that the geometry is determined by a competition involving energy gained by forming more or stronger bonds *vs.* energy lost through interelectron repulsion between bonding electrons. Bond energy is maximized in the series octahedral > square planar > tetrahedral. Interelectron repulsion is minimized in the series tetrahedral < square planar < octahedral. Increasing the positive charge on the metal increases bonding energy for either ionic or covalent bonding and this gradually becomes the dominant factor. Competition between d electron repulsion and ligand field stabilization energy is of course the dominant theme in crystal field theory. The role of interelectron repulsion between bonding (and lone pair) electrons in determining molecular geometry has long been advocated.[7] It seems reasonable that similar factors should play a part in the stereochemistry of nickel. It is noteworthy that in cases where there is an equilibrium between square-planar and tetrahedral complexes (*e.g.*, aminotroponeiminates) electron-withdrawing substituents, which will increase the positive charge on the metal, always favor the square-planar form.[8]

Finally we note a pertinent observation concerning the rates of thiourea ligand exchange in these complexes. For the tetrahedral compounds ligand exchange rates decrease in the series $Ni(tu)_2Cl_2 > Ni(tu)_2Br_2 > Ni(tu)_2I_2$. (There is a similar trend in the analogous triphenylphosphine complexes.[9]) For the square-planar complexes $Ni(tu)_3I^+ > Ni(tu)_3Br^+$. All reactions proceed by an associative mechanism and apparently the rates as well as the geometries depend on the metal charge. A plausible supposition is that for the tetrahedral complexes formation of the five-coordinate intermediate is the rate-determining step and this takes place more readily as the positive charge on the metal is increased. For the square-planar complexes the positive charge is sufficient to ensure that formation of the intermediate is rapid and loss of the fifth ligand becomes rate determining, leading to an inversion of the order.

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[7] R. J. Gillespie, *Angew. Chem., Int. Ed. Engl.*, **6**, 819 (1967).

[8] D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963).

[9] E. A. Lalancette and D. R. Eaton, *ibid.*, **86**, 5145 (1964).

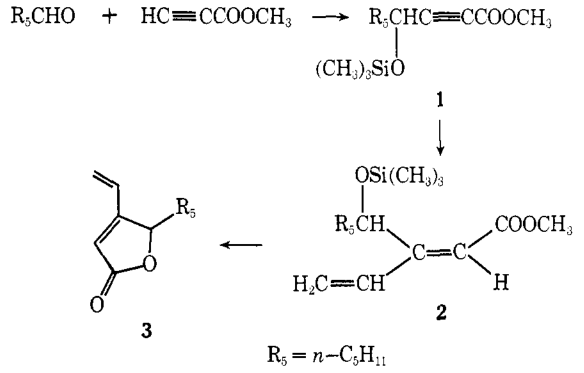
A Method for Stereospecific Synthesis of 1,3- and 1,4-Dienes *via* Organocopper Reagents

Sir:

In connection with the study of a new stereocontrolled approach to the synthesis of prostaglandins, we required a synthesis of a Diels–Alder component of structure **3**. We outline here the solution to this specific problem by a new method and provide evidence of generality by examples of synthesis for a range of 1,3- and 1,4-dienes.

The highly stereospecific cis addition of alkylcopper reagents to α,β-acetylenic carbonyl compounds has previously been described, as has the application of this reaction to the stereospecific synthesis of olefins with di-, tri-, and tetrasubstitution patterns.[1] The extraordinary effectiveness of vinylcopper reagents in conjugate addition processes has also been demonstrated.[2,3] Taken together, these studies form the basis for the method of synthesis of **3** which is summarized in Chart I. Methyl 4-trimethylsiloxy-2-nonynoate (**1**) was prepared in a single step by sequential treatment of methyl propynoate in tetrahydrofuran (THF) (12 ml/g of ester) at $-78°$ with *n*-butyllithium (1 equiv, $-78°$, 1 hr, N_2 atmosphere), hexanal (1 equiv, dissolved in 2 vol of THF, added dropwise at $-78°$ followed by stirring at $-78°$ for 1 hr), and trimethylchlorosilane (1.5 equiv, added at $-78°$: gradual warming to 25° and 1 hr at 25°). Analytically pure **1** was obtained as a colorless liquid from the reaction mixture (71% yield) by concentration under reduced pressure, addition of water, extraction, and distillation:[4] bp 63.5–64.5° (0.07 mm); ir max (neat) 2222, 1720 cm^{-1}. Slow addition (with rapid stirring) of a cold solution of **1** ($-50°$) in THF (1 ml/g of **1**) to a solution of divinylcopperlithium[2] (1.25 equiv, *ca.* 0.4 *M* in THF, $-90°$) followed by stirring at

Chart I



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[1] E. J. Corey and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 1851 (1969).

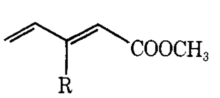
[2] E. J. Corey and R. L. Carney, *ibid.*, **93**, 7318 (1971).

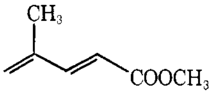
[3] J. Hooz and R. B. Layton, *Can. J. Chem.*, **48**, 1626 (1970).

[4] Satisfactory (a) infrared and nuclear magnetic resonance spectra and (b) high-resolution mass spectrum and/or elemental analysis were obtained for a purified sample of this intermediate.

$-78°$ for 3 hr, cooling again to $-90°$, and quenching with methanol afforded after work-up (addition of aqueous ammonium chloride, vacuum concentration, extraction with ether, and distillation) analytically pure cis adduct **2**:[4] bp 62–63° (0.6 mm); ir max (neat) 1725 cm^{-1} in >90% yield; less than 0.1% of the (*Z*) isomer of **2**[5] as determined by vpc analysis; adduct with maleic anhydride, mp 112°. Exposure of **2** to 0.1% methanolic hydrochloric acid at 25° for 1 hr resulted in cleavage of the trimethylsilyl ether and lactonization to form in high yield the desired lactone **3**,[4] ir max (neat) 1750 cm^{-1}, as a colorless liquid (evaporatively distilled at 80–85° (0.01 mm)).

The reaction of vinylcopper reagents with methyl propynoate and methyl 2-butynoate also proceeded smoothly. In these cases good results were obtained using either 1.1 equiv of the reagent $\hat{V}_2CuLi$ ($\hat{V}$ = vinyl) or 2 equiv of the reagent $\hat{V}Cu$ (from $\hat{V}Li$ or $\hat{V}MgCl$), although the latter generally afforded somewhat higher yields. Thus, addition of methyl 2-butynoate to vinylcopper (generated from 2 equiv of vinyllithium and 2 equiv of cuprous iodide under N_2, $-78°$, 40 min), quenching with methanol at $-78°$, and isolation as indicated above for **2** afforded stereospecifically methyl 3-methyl-*trans*-2,4-pentadienoate (**4**)[4] as a colorless liquid, ir max (neat) 1729, 1654 cm^{-1}, in 74% yield (isolated). Also prepared in a similar manner were **5** (85% yield, identical with an authentic sample[6]) and **6**[4] (isopropenylcopper as reagent, 63% yield).[7]


4, R = CH$_3$
5, R = H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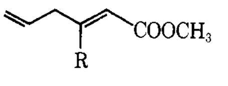
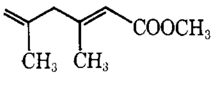
The ready availability of vinylcopper reagents in pure stereoisomeric form, the stereospecificity and directional specificity of the vinylcopper–ynoic ester addition to form 1,3-dienes in a single step, and the importance of such dienes to synthesis as Diels–Alder components all contribute to the proposition that the route to conjugated dienes which is outlined above will prove to be highly useful.

An analogous process for the stereospecific generation of 1,4-dienes starting with allylcopper reagents has also been demonstrated. Thus, reaction of 2 equiv of allylcopper[8] in ether at $-78°$ under N_2 with methyl propynoate for 2 hr followed by the usual work-up gave methyl *trans*-2,5-hexadienoate (**7**)[4] as a colorless liquid: ir max (neat) 1730, 1662, 990, 910 cm^{-1}. Similarly prepared were **8**[4] (70%) and **9**[4] (65%), from methyl 2-butynoate and allylcopper or methallylcopper, respectively.


7, R = H
8, R = CH$_3$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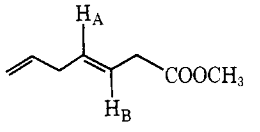
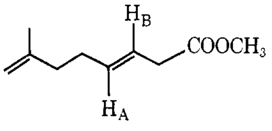
Finally, another and related stereospecific approach to 1,4- and 1,5-dienes was developed based on the addition of copper reagents to 2,4-pentadienoic ester derivatives. Reaction of vinylcopper and methallylcopper at $-78°$ with methyl *trans*-2,4-pentadienoate followed by quenching at $-78°$ with methanol and isolation as outlined above afforded in good yield the *trans*-diene esters **10**[4] and **11**,[4] respectively [ir max (neat) for **10**, 1750, 1640, 990, 910, 972; for **11**, 1750, 1640, 972, 890 cm^{-1}]. In these instances the protonation of the intermediate (allylic) organocopper species occurs specifically α to the ester carbonyl. The assignment of trans geometry about the disubstituted double bond is indicated by the characteristic infrared absorption for **10** and **11** at 977 cm^{-1} and by $J_{H_AH_B}$ = 16 Hz (nmr in presence of Eu(fod)$_3$).


10


11

The examples recorded above illustrate a number of effective stereospecific operations which can be used to good advantage in synthesis. The processes are also quite versatile, since the intermediate organocopper species can be quenched in ways other than by protonation, for example, by alkylation,[1,9,10] halogenation,[1] or oxidative coupling,[11] the latter leading in a very simple way to rather complex polyenes.[12]

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[5] The (*Z*) isomer of **2** was obtained by preparative vpc separation of a mixture of (*E*)- and (*Z*)-**2** which resulted from reaction at 0° after an initial period at $-78°$ (see ref 1).

[6] R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958).

[7] For related reactions of monoalkylcopper with nonconjugated acetylenes, see J. F. Normant and M. Bourgain, *Tetrahedron Lett.*, 2583 (1971).

[8] Prepared from 1 equiv of allylmagnesium chloride and 1 equiv of cuprous iodide in ether at -30 to $-40°$ for 2 hr (deep red color).

[9] E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968).

[10] E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *ibid.*, **89**, 4245 (1967).

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

[12] After the completion of this work a report has appeared describing the addition of bis-*cis*-2-heptenylcopperlithium to ethyl propynoate; see F. Näf and P. Degen, *Helv. Chim. Acta*, **54**, 1939 (1971).

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Photochemical Interconversion of the Geometrical Isomers of Aminoboranes

Sir:

We wish to report that the interconversion of geometrical isomers is a significant primary photoprocess in aminoboranes.[1] This previously undiscerned reaction is of fundamental interest by virtue of its superficial parallels to and mechanistic differences from the corresponding transformation in olefins. It is of practical

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[1] Presented in part by K. G. Hancock, D. A. Dickinson, and A. K. Uriarte at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract ORGN-143.