On the basis of the VPC analysis of the H_2 produced, quantitative decomposition to H_2 plus CO_2 occurs when formic acid (1 ml) was added to a catalyst solution and heated in a bomb at 110 °C overnight. Since the same solution had been used previously to effect the water gas shift reaction under similar conditions, it is evident that any formate produced during the water gas shift reaction would have decomposed to H_2 plus CO_2. A more quantitative indication of the activity of this system toward formate decomposition is the observation that at 75 °C a catalyst solution prepared from 0.063 g of $Ru_3(CO)_{12}$ (1×10^{-4} mole), 0.44 g of KOH plus 1.0 ml of H_2O in 15 ml of ethoxyethanol in an all-glass apparatus decomposed an added 0.25-ml sample of 77.5% aqueous HCO_2H (5×10^{-3} mol of HCO_2H) with a half-life of ~300 s.

At this stage our comments regarding the possible active ruthenium species in the catalyst system are largely speculative. The active catalyst solution has a color and IR spectrum different from the initial $Ru_3(CO)_{12}$, thus we conclude that this species is not the principal one present. The complexity of the IR spectrum in the carbonyl stretching region (ν_{CO} 2030 (ms), 2014 (s), 1994 (s), 1972 (s), 1952 (s, sh) cm^{-1}) would suggest the presence of polynuclear carbonyl complexes, perhaps anionic and/or hydridic as well, although the alternative explanation would be several simpler metal carbonyl species. The solid residue isolated after low temperature evaporation of the solvent displays the same carbonyl stretching bands with additionally observed bands at 2070 (w) and 1920 (m) cm^{-1}. The reaction of $Ru_3(CO)_{12}$ with potassium hydroxide followed by acidification does yield the hydrido carbonyl species $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$,[12] and anions of such species are produced under similar conditions.[13] Thus these types of clusters are logical candidates as components of the catalyst solutions. Also, the formation of hydrido anionic carbonyl cluster compounds has been noted for the reactions of hydroxide with the iridium cluster $Ir_4(CO)_{12}$. In this case, the species produced have been observed to be active in the reduction of CO to formate.[11]

Continuing work in this laboratory is directed toward a more positive characterization of the active species in the catalyst solution and toward methods of improving the catalyst efficiency and reaction rate by variation of reaction conditions and catalyst composition.

Acknowledgments. C. P. Madhusudhan was a valuable participant in the early stages of this research. Also, Richard M. Lee assisted in the laboratory studies. This work was supported in part by a grant from the United States Energy Research and Development Administration [No. E(04-3)-34] to Robert G. Rinker.

References and Notes

(1) (a) M. M. Taqui Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Academic Press, New York, N.Y., 1974 Chapter 4; (b) J. Falbe, "Carbon Monoxide in Organic Synthesis", Springer Verlag, New York, N.Y., 1970; (c) G. Henrici-Olive and S. Olive, *Transition Met. Chem.* (*Weinheim, Ger.*), 1, 77 (1976).

(2) $\Delta G^\circ = -4.89$ kcal/mol and $\Delta H^\circ = +0.68$ kcal/mol for the reaction $H_2O(l) + CO(g) \rightarrow H_2(g) + CO_2(g)$ according to data taken from F. T. Wall, "Chemical Thermodynamics", 3d ed, W. H. Freeman, San Francisco, Calif., 1974.

(3) (a) C. K. Thomas, "Catalytic Processes and Proven Catalysts", Academic Press, New York, N.Y., 1970; (b) S. Oki, J. Happel, M. Hnatow, Y. Kaneko in "Catalysts", J. Hightower, Ed., American Elsevier, New York, N.Y., 1973, p 173.

(4) Recently, there was a report (R. Petit, 171st National Meeting of the American Chemical Society, April 1976, New York, N.Y.) that $Fe(CO)_5$ in alkaline solution catalyzed the conversion of carbon monoxide and water to hydrogen. However, methanol and formate are also products of this reaction. In addition, ref 1c draws attention to earlier work on the hydrohydroxymethylation of olefins and speculates that the reaction of H_2O plus CO to give H_2 plus CO_2 is prompted by iron carbonyl as part of this reaction scheme.

(5) (a) D. J. Darensbourg and D. Drew, *J. Am. Chem. Soc.*, **98,** 275 (1976); (b) E. L. Muetterties, *Inorg. Chem.*, **4,** 1841 (1965); (c) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Am. Chem. Soc.*, **91,** 1346 (1969); (d) H. D. Kaesz and R. Saillant, *Chem. Rev.*, **72,** 231 (1972).

(6) (a) M. G. Thomas, B. F. Beier, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98,** 1296 (1976); (b) G. D. Mercer, J. S. Shu, T. B. Rauchfuss, and D. M. Roundhill, *ibid.*, **97,** 1967 (1975).

(7) (a) Although the homogeneous catalyst described here appears to have only moderate activity, it is instructive to compare this activity to that of a standard commercial heterogeneous catalyst (Girdler G-3A CO conversion catalyst—principally Fe_3O_4) under similar conditions. An estimate of the activity of the commercial catalyst operated in an isothermal plug flow packed bed reactor ($E_a = 28.3$ kcal/mol) indicates that at 110 °C under 1 atm of CO this catalyst would produce several orders of magnitude less H_2 per gram mole of the catalyst per unit time than does the homogeneous catalyst reported here. (b) The ruthenium based homogeneous catalysis has been examined under a variety of conditions. More rapid conversion to H_2 plus CO_2 was observed when the reaction was carried out under higher CO pressure in a stainless steel bomb equipped with a Teflon liner. Activity was noted both in ethoxyethanol and methanol solvents. For example, a run carried out under 48 atm of CO with a catalyst solution of 0.021 g of $Ru_3(CO)_{12}$, 1.0 g of H_2O, and 0.2 g of KOH in 6 ml of reagent methanol and heated at 110 °C for 96 h led to the formation of 150 mol of H_2 per mole of added $Ru_3(CO)_{12}$ (corrected for H_2 produced under control conditions).

(8) The solutions contained about 5–10% exchangeable ^1H owing to the use of KOH (not KOD) as the source of the base.

(9) In agreement with this conclusion, the IR and NMR spectra of ethoxyethnol solvent (after bulb to bulb low temperature vacuum distillation from the reaction solution) display no features other than those seen in wet ethoxyethanol.

(10) For example, 0.01 mol of $KHCO_3$ in solution of 15 ml of ethoxyethanol plus 1 ml of H_2O evolved the theoretical amount of CO_2 after several hours of heating at 120 °C under 1 atm pressure.

(11) M. Angaletta, L. Malatesta, and G. Caglio, *J. Organomet. Chem.*, **94,** 99 (1975).

(12) B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *Chem. Commun.*, 851 (1966).

(13) J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Am. Chem. Soc.*, **97,** 3947 (1975).

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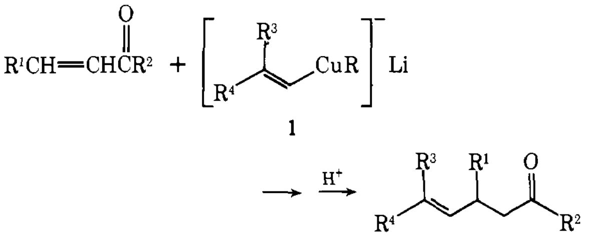
Received July 30, 1976

Conjugate Addition of Vinylcopper Complexes Derived from Addition of Alkylcopper Complexes to Acetylenes. A Stereospecific Synthesis of Trisubstituted Olefins

Sir:

The development of general methods for the stereospecific synthesis of trisubstituted olefins[1] has become a major goal of organic chemists mainly because of the occurrence in nature of many compounds of this class having significant biological activity.[2] Several methods have been reported for the synthesis of simple, nonfunctionalized, trisubstituted olefins,[3] but of greater importance are those methods which afford olefins bearing functional groups which may be employed in further structural transformations.[4] We wish to report a new, convenient, very general, and stereospecific route to functionalized, trisubstituted olefins.

The conjugate addition of vinylcuprates, **1a**, to Michael acceptors such as α,β-unsaturated carbonyl compounds is a commonly used route to disubstituted olefins (e.g., **2a**) bearing various functional groups (eq 1).[5,6] However, this approach has not been practical for the corresponding trisubstituted olefins, **2b**, in the past because the requisite disubstituted vinylcuprates, **1b**, were not as readily available as the monosubstituted species, **1a**. A prospective solution to this problem was provided in recent reports by Normant of a novel reaction (eq 2) in which alkylcopper complexes derived from alkylmagnesium halides undergo addition to simple terminal acetylenes to give disubstituted vinylcopper complexes, **3**.[7] Reactions of **3** with various electrophilic reagents were reported, including reactions with alkyl halides,[7b-h] to produce



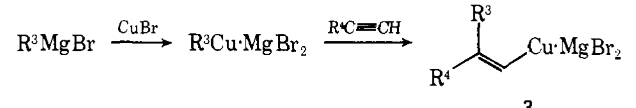
1

2

(1)

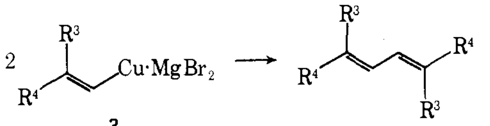
a, $R^3 = H$

b, $R^3 = \text{alkyl}$



3

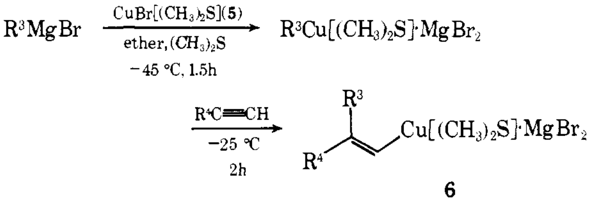
(2)



3

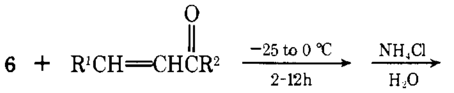
4

(3)

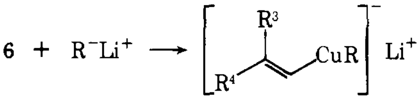


6

(4)



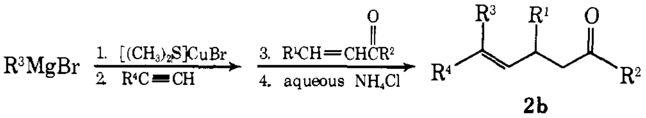
$$\mathbf{6} + R^1CH{=}CH\overset{\overset{O}{\|}}{C}R^2 \xrightarrow[2\text{-}12\text{h}]{-25\text{ to }0\ ^\circ\text{C}} \xrightarrow[H_2O]{NH_4Cl} \mathbf{2b} \quad (5)$$



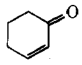
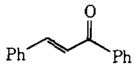
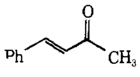
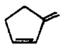
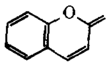
1b

(6)

Table I. Yields of Trisubstituted Olefins



2b

Run	R^3	R^4	$R^1CH{=}CH\overset{\overset{O}{\|}}{C}R$	% yield of olefin (**2b**)[a]
1	C_2H_5	n-C_6H_{13}		70
2	n-C_6H_{13}	C_2H_5		68
3	n-C_4H_9	n-C_6H_{13}		64
4	C_2H_5	n-C_6H_{13}		52
5	C_2H_5	n-C_6H_{13}		(35), 53[b]
6	C_2H_5	n-C_6H_{13}		(10), (30)[b,c]
7	C_2H_5	n-C_6H_{13}		(0), (62)[b,d]

[a] The values in parentheses were determined by GLC. The others are isolated yields. [b] In this run, the intermediate vinylcopper complex was allowed to react with 1-lithio-1-hexyne before the α,β-unsaturated carbonyl compound was added. [c] This conjugated addition was performed at −78 °C for 4 h. [d] This conjugated addition was performed at 0 °C for 60 h.

simple trisubstituted olefins. Consequently, we sought to explore the use of this addition reaction as a source of the disubstituted vinylcopper species, **1b**, required in eq 1.

In our initial efforts to employ the addition reaction (eq 2), varying amounts of 1,3-dienes (**4**) were formed (ca. 5–20% yields) as by-products (eq 3). Coupling of vinylcopper complexes, induced either thermally or by various oxidizing agents, is known to be a very facile process.[7d,e,h,8] The diene was formed whether the cuprous halide was purified by the commonly used precipitation[9] or Soxhlet extraction[6l,10] procedures and even though the reactions were performed under a rigorously maintained inert atmosphere. However, during the course of our work, House reported a method for preparing the dimethyl sulfide-cuprous bromide complex (**5**) in highly pure form, free of contaminants that are believed to promote decomposition of organocopper compounds.[11] We have found that the use of this dimethyl sulfide complex leads to improved yields of the desired vinylcopper complex (**6**, eq 4)[12] accompanied by only trace amounts of the diene (typically 0–3%).[13] When α,β-unsaturated carbonyl compounds are added to the reaction mixture containing **6**, conjugate addition occurs to give the desired trisubstituted olefins (**2b**, eq 5). Some typical results are given in Table I.[14] The reported yields are for the overall route starting with the Grignard reagent and using equimolar quantities of all reactants.[15] Although the yields of **2b** have not yet been optimized, they are quite acceptable in considering that this pathway provides rather complex, trisubstituted olefins in a convenient, *one-flask* procedure using simple, readily available starting materials. In addition to the desired olefin and a trace (0–3%) of the diene, **4**, some of the other components of the product mixtures are small amounts of the 2-alkylolefin ($R^3R^4C{=}CH_2$) and the starting acetylene. The yield of desired product from cyclopenten-3-one (run 6) is relatively low but is typical of many reported conjugate additions of vinyl groups to this substrate.[6l]

In order to improve the yields of **2b**, attempts were made to convert **6** into a mixed cuprate (**1b**) by reaction with various anionic species such as acetylides,[6a] thiolates,[6l] or alkoxides (eq 6)[6l] before the α,β-unsaturated carbonyl compound was added to the reaction mixture.[16] However, when 1-lithio-1-hexyne, for example, is employed, improvements in yield are observed in only a limited number of cases (runs 5–7).[17] Normally, mixed cuprates are prepared by permitting the lithio derivative of the organic group to be transferred to react with the cuprous derivative of the nontransferable group.[6a,l,q,18] In our work, the opposite was attempted but was unsuccessful in improving the efficiency of the desired transfer process in some cases (runs 1–4).[17,19] These results may bear upon the question of the structure of mixed cuprates.[20,21]

To study the stereochemistry of our route, the reactions indicated in runs 1 and 2 were performed. The two products, which were presumably *E*- and *Z*-isomers of each other, were easily separable by GLC (12 ft × ⅛ in. 5% OV-1). Analysis of each reaction mixture by GLC indicated a 99.5:0.5 ratio of the isomers in one case and a 1.0:99.0 ratio of the same isomers in the other. Our route is therefore very highly stereospecific. We have not yet proven the stereochemistry of each product individually, but our assignment as shown in eq 5 is based upon two precedents: (1) Normant has shown that the addition of alkylcopper complexes to acetylenes (eq 2) is cis,[7f,h] and (2) vinylcopper complexes and vinylcuprates retain their stereochemistry during various reactions, including thermal coupling[8] and conjugate addition.[22]

In summary, this work has resulted in a convenient, stereospecific route to trisubstituted olefins. The carbonyl group of the products may be employed in subsequent reactions, such as the Wittig olefin synthesis, for the further elaboration of the carbon skeletons of several important classes of natural products. Work is in progress to optimize the yields of our reactions, to investigate the stereochemistry thoroughly,[23] to study the reaction of the intermediate vinylcopper complex with other electrophilic substrates besides α,β-unsaturated carbonyl compounds,[24] and to apply our route to the synthesis of naturally occurring compounds.

Acknowledgments. We wish to thank Professor Alan B. Levy of this department for many fruitful discussions concerning this work. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Joint Awards Council and University Awards Committee, administered by the Research Foundation of the State University of New York, for support of this research.

References and Notes

(1) For reviews of olefin synthesis see (a) J. Reucroft and P. G. Sammes, *Q. Rev., Chem. Soc.*, **25**, 135 (1971); (b) D. J. Faulkner, *Synthesis*, 175 (1971); (c) A. S. Arora and I. K. Ugi in "Methoden der Organischen Chemie (Houben-Weyl)", Vol. V/Ib, 4th ed, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1972, pp 728–945.

(2) Among the biologically active compounds of this class are insect juvenile hormones. For a synthesis of these compounds and references to several other syntheses see ref 4p.

(3) For recent syntheses of nonfunctionalized, trisubstituted olefins see (a) J. J. Eisch and G. A. Damasevitz, *J. Org. Chem.*, **41**, 2214 (1976); (b) K. Uchida, K. Utimoto, and H. Nozaki, *ibid.*, **41**, 2215 (1976); (c) S. Mageswaran and M. U. S. Sultanbawa, *J. Chem. Soc., Perkin Trans. 1*, 884 (1976); (d) W. Kreiser and H. Wurziger, *Tetrahedron Lett.*, 1669 (1975); (e) A. Pelter, C. Subrahmanyam, R. J. Laub, K. J. Gould, and C. R. Harrison, *ibid.*, 1633 (1975); (f) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263 (1975); (g) H. C. Brown, J.-J. Katz, and B. A. Carlson, *ibid.*, **40**, 813 (1975); (h) P. L. Stotter and R. E. Hornish, *J. Am. Chem. Soc.*, **95**, 4444 (1973); (i) F. Jung, N. K. Sharma, and T. Durst, *ibid.*, **95**, 3420 (1973); (j) G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *ibid.*, **94**, 6560 (1972); (k) W. Adam, J. Baeza, and J.-C. Liu, *ibid.*, **94**, 2000 (1972).

(4) For recent syntheses of functionalized, trisubstituted olefins see (a) G. Eletti-Bianchi, F. Centini, and L. Re, *J. Org. Chem.*, **41**, 1648 (1976); (b) S. W. Pelletier and N. V. Mody, *ibid.*, **41**, 1069 (1976); (c) J. Prejzner, *Rocz. Chem.* **49**, 1953 (1975); (d) O. P. Vig, B. Ram, K. S. Atwal, and S. S. Bari, *J. Indian Chem. Soc.*, **52**, 257 (1975); (e) J. P. McCormick and D. L. Barton, *J. Chem. Soc., Chem. Commun.*, 303 (1975); (f) J. C. Depezay and Y. Le Merrer, *Tetrahedron Lett.*, 3469 (1975); (g) P. L. Stotter and K. A. Hill, *ibid.*, 1679 (1975); (h) B. M. Trost and J. L. Stanton, *J. Am. Chem. Soc.*, **97**, 4018 (1975); (i) J. A. Katzenellenbogen and T. Utawanit, *ibid.*, **96**, 6153 (1974); (j) J. A. Katzenellenbogen and K. J. Christy, *J. Org. Chem.*, **39**, 3315 (1974); (k) M. Julia and J.-M. Paris, *Tetrahedron Lett.*, 3445 (1974); (l) A. Pelter, C. R. Harrison, and D. Kirkpatrick, *ibid.*, 4491 (1973); (m) B. M. Trost and T. N. Salzmann, *J. Am. Chem. Soc.*, **95**, 6840 (1973); (n) H. Takahashi, K. Oshima, H. Yamamoto, and H. Nozaki, *ibid.*, **95**, 5803 (1973); (o) T. A. Bryson, *Tetrahedron Lett.*, 4923 (1973); (p) C. A. Henrick, F. Schaub, and J. B. Siddall, *J. Am. Chem. Soc.*, **94**, 5374 (1972).

(5) For reviews of conjugate addition reactions of organocopper compounds see (a) A. E. Jukes, *Adv. Organomet. Chem.*, **12**, 215 (1974); (b) J. F. Normant, *Synthesis*, 63 (1972); (c) G. H. Posner, *Org. React.*, **19**, 1 (1972); (d) G. Bähr and P. Burba, ref 1c, Vol. XIII/1, 4th ed, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1970, pp 731–761.

(6) For recent examples of conjugate addition reactions of vinylcuprates see (a) G. Stork and M. Isobe, *J. Am. Chem. Soc.*, **97**, 4745 (1975); (b) C. G. Chavdarian and C. H. Heathcock, *ibid.*, **97**, 3822 (1975); (c) C. J. Sih, R. G. Salomon, P. Price, R. Sood, and G. Peruzzotti, *ibid.*, **97**, 857 (1975); (d) C. J. Sih, J. B. Heather, R. Sood, P. Price, G. Peruzzotti, L. F. H. Lee, and S. S. Lee, *ibid.*, **97**, 865 (1975); (e) E. J. Corey and J. W. Suggs, *J. Org. Chem.*, **40**, 2554 (1975); (f) E. J. Corey and R. H. Wollenberg, *ibid.*, **40**, 2265 (1975); (g) R. K. Boeckman and S. M. Silver, *ibid.*, **40**, 1755 (1975); (h) H. O. House, C.-Y. Chu, J. M. Wilkins, and M. J. Umen, *ibid.*, **40**, 1460 (1975); (i) R. K. Boeckman, K. J. Bruza, J. E. Baldwin, and O. W. Lever, *J. Chem. Soc., Chem. Commun.*, 519 (1975); (j) T. Tanaka, S. Kurozumi, T. Toru, M. Kobayashi, S. Miura, and S. Ishimoto, *Tetrahedron Lett.*, 1535 (1975); (k) R. K. Boeckman and K. J. Bruza, *ibid.*, 3365 (1974); (l) G. H. Posner, C. E. Whitten, and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 7788 (1973); (m) E. J. Corey and J. Mann, *ibid.*, **95**, 6832 (1973); (n) H. O. House and M. J. Umen, *J. Org. Chem.*, **38**, 3893 (1973); (o) A. F. Kluge, K. G. Untch, and J. H. Fried, *J. Am. Chem. Soc.*, **94**, 7827, 9256 (1972); (p) F. S. Alvarez, D. Wren, and A. Prince, *ibid.*, **94**, 7823 (1972); (q) E. J. Corey and D. J. Beames, *ibid.*, **94**, 7210 (1972); (r) E. J. Corey, C. U. Kim, R. H. K. Chen, and M. Takeda, *Ibid.*, **94**, 4395 (1972); (s) E. J. Corey and P. L. Fuchs, *ibid.*, **94**, 4014 (1972).

(7) (a) G. Cahiez, D. Bernard, and J. F. Normant, *Synthesis*, 245 (1976); (b) J. F. Normant, A. Commercon, and J. Villieras, *Tetrahedron Lett.*, 1465 (1975); (c) A. Alexakis, J. Normant, and J. Villieras, *J. Organomet. Chem.*, **96**, 471 (1975); (d) J. F. Normant, G. Cahiez, M. Bourgain, C. Chuit, and J. Villieras, *Bull. Soc. Chim. Fr.*, 1656 (1974); (e) J. F. Normant, G. Cahiez, C. Chuit, and J. Villieras, *J. Organomet. Chem.*, 77, 269, 281 (1974); (f) J. F. Normant, G. Cahiez, C. Chuit, and J. Villieras, *Tetrahedron Lett.*, 2407 (1973); (g) J. F. Normant, G. Cahiez, C. Chuit, A. Alexakis, and J. Villieras, *J. Organomet. Chem.*, **40**, C49 (1972); (h) J. F. Normant and M. Bourgain, *Tetrahedron Lett.*, 2583 (1971).

(8) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Am. Chem. Soc.*, **93**, 1379 (1971).

(9) G. B. Kauffman and L. A. Teter, *Inorg. Synth.*, **7**, 9 (1963).

(10) G. H. Posner and J. J. Sterling, *J. Am. Chem. Soc.*, **95**, 3076 (1973), footnote 6.

(11) For the preparation, purification, and some applications of **5**, see ref 6h.

(12) We do not intend to imply any specific structures for the intermediate copper complexes such as **6** involved in this work.

(13) The efficiency of formation of the vinylcopper complexes under various conditions was determined by quenching the reaction mixtures with aqueous ammonium chloride and analyzing the crude products by GLC (6ft × ⅛ in. 5% OV-1, 110–240 °C) to determine the yields of the simple olefin ($R^3R^4C{=}CH_2$) and the diene. At this time, we cannot exclude the possibility that the increased yields of vinylcopper complexes are due to stabilization of these species by the coordination of dimethyl sulfide rather than the absence of impurities that may promote the coupling reaction.

(14) Products from our small-scale reactions were conveniently isolated by bulb-to-bulb distillation and HPLC using a Waters 1 ft × 0.25 in. μ-Porasil column. All products exhibited satisfactory NMR, IR, and mass spectra and microanalytical data.

(15) Unlike many reports in which large excesses of organocopper species are used in various reactions, the yields reported here are very representative of the efficiency of the overall process because of the use of equimolar quantities of all reactants.

(16) The improvement of yields of conjugate addition products upon using cuprates in place of alkylcopper complexes has been noted previously: see ref 5c, p 20.

(17) In further preliminary studies, the use of mixed cuprates has also led to improved yields of desired products from 1-acetylcyclohexene, 1-phenyl-2-buten-1-one, and methyl vinyl ketone but not from ethyl acrylate.

(18) For possible exceptions see Y. Yamamoto, H. Yatagai, A. Sonoda, and S.-I. Murahashi, *J. Chem. Soc., Chem. Commun.*, 452 (1976); D. E. Bergbreiter and G. M. Whitesides, *J. Org. Chem.*, **40**, 779 (1975).

(19) Conjugate additions of vinylcopper complexes have been reported previously (see ref 6r). However, the vinylcopper complexes involved in this earlier work and in our present studies may actually exist as heterocuprates of the type $(R^3R^4C{=}CHCuX)^-M^+$ in which X is halide. Related cuprates have been implicated in conjugate additions: N.-T. Luong-Thi and H. Riviere, *Tetrahedron Lett.*, 1583 (1970). See also ref 5b, p 66, and ref 5c, p 11.

(20) For a discussion of possible structures of mixed cuprates see W. H. Mandeville and G. M. Whitesides, *J. Org. Chem.*, **39**, 400 (1974).

(21) For a recent paper concerned with the structure of lithium dimethylcuprate see R. G. Pearson and C. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976).

(22) (a) F. Näf, P. Degen, and G. Ohloff, *Helv. Chim. Acta*, **55**, 82 (1972); (b) F. Näf and P. Degen, *ibid.*, **54**, 1939 (1971); (c) C. P. Casey and R. A. Boggs, *Tetrahedron Lett.*, 2455 (1971).

(23) One promising approach which has been employed in stereochemical studies of less complex olefins is the measurement of $^{13}C-^{1}H$ NMR coupling constants: (a) U. Vögeli and W. von Philipsborn, *Org. Magn. Reson.*, 7, 617 (1975); (b) J. E. Anderson, *Tetrahedron Lett.*, 4079 (1975).

(24) Preliminary work has shown that **6**, after reaction with 1-lithio-1-hexyne, is alkylated by epoxides to afford trisubstituted olefins bearing a hydroxy group in at least moderate yield.

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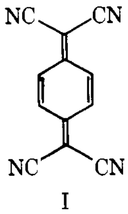
Received August 27, 1976

Peri-Bridged Naphthalenes from 1,8-Dilithionaphthalene

Sir:

In recent years there has been an increasing interest in planar, aromatic compounds containing several sulfur or selenium atoms, largely in connection with the possibly useful electrical, magnetic, and optical properties that charge transfer complexes involving these donor molecules and acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ, I) may have.[1]



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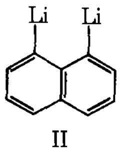

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