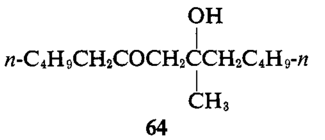
of the enol acetate **58** (mixture containing *ca.* 75% trans and *ca.* 25% cis stereoisomers) to 15 ml of a DME solution containing 51.7 mmol of MeLi and several milligrams of 2,2′-bipyridyl, was added a solution of 25.2 mmol of $ZnCl_2$ in 36.5 ml of Et_2O. The resulting suspension was stirred at 3° for 10 min and then 2.68 g (25.2 mmol) of PhCHO was added, dropwise and with stirring during 1.5 min while the reaction temperature was maintained at -10 to 15°. The reaction mixture was worked up as usual to leave a crude product (5.848 g of pale yellow liquid) containing (tlc and nmr analysis) approximately equal amounts of the stereoisomeric aldol products **60a** and **60b**. Chromatography on acid-washed silicic acid[13] with Et_2O–hexane mixtures as eluents separated in the early fractions 120 mg (2%) of a colorless liquid believed to be the crude aldol product **64**: ir (CCl_4) 3510 (assoc OH) and 1700 cm^{-1} (C=O); nmr (CCl_4)



$$n\text{-}C_4H_9CH_2COCH_2\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}CH_2C_4H_9\text{-}n$$

64

δ 3.4 (1 H, broad, OH), 2.1–2.6 (4 H, m, CH_2CO), and 0.7–1.9 (23 H, m, aliphatic CH); mass spectrum *m/e* (rel intensity) 179 (1), 157 (5), 99 (26), 58 (28), 55 (30), 43 (100), 42 (33), 41 (59), and 39 (38). The later fractions contained, in order of elution, 2.175 g (40%) of the liquid erythro aldol **60b**, 340 mg (6%) of a mixture of stereoisomeric aldol products **60a** and **60b**, and 1.834 g (34%) of the liquid threo aldol **60a**. Short-path distillation afforded the erythro aldol **60b** as a colorless liquid: $n^{25}\text{D}$ 1.5052;[17b] ir (CCl_4) 3610 (free OH), 3490 (assoc OH), and 1705 cm^{-1} (C=O); uv (95% EtOH) series of weak maxima (ϵ 273–318) in the region 240–270 mμ with a maximum at 283 mμ (119); mass spectrum *m/e* (rel intensity) 179 (1), 106 (51), 105 (59), 78 (51), 77 (81), 74 (61), 51 (67), 50 (88), 43 (100), and 41 (77); nmr (CCl_4) δ 7.0–7.3 (5 H, m, aryl CH), 4.66 (1 H, d, J = 6.6 Hz, benzylic CH), 3.42 (1 H broad, OH), 2.5–2.9 (1 H, m, COCH<), and 0.6–1.9 (12 H, m, aliphatic CH with CH_3CO singlet at δ 1.78). In CH_3OD solution the benzylic CH doublet is located at δ 4.77 (J = 7.9 Hz).

Short-path distillation (0.07 mm and 100°) afforded the threo aldol **60a** as a colorless liquid: $n^{25}\text{D}$ 1.5065;[17b] ir (CCl_4) 3610 (free OH), 3480 (assoc OH), and 1710 cm^{-1} (C=O); uv (95% EtOH) series of weak maxima (ϵ 162–261) in the region 240–270 mμ with a maximum at 282 mμ (ϵ 114); mass spectrum *m/e* (rel intensity) 202 (0.4), 154 (3), 106 (40), 105 (58), 78 (58), 77 (91), 74 (57), 51 (70), 50 (84), 43 (100), 42 (65), 41 (75), and 39 (74); nmr (CCl_4) δ 7.1–7.4 (5 H, m, aryl CH), 4.55 (1 H, d of d, J = 8.7 and 4.0 Hz, collapsed to doublet, J = 8.7 Hz, with added D_2O, benzylic CH), 3.56 (1 H, d, J = 4.0 Hz, OH, exchanged with D_2O), 2.5–3.0 (1 H, m, COCH<), 2.04 (3 H, s, CH_3CO), and 0.5–1.5 (9 H, m, aliphatic CH). In CH_3OD solution the benzylic CH doublet is at δ 4.70, J = 9.5 Hz.

The same condensation experiment was repeated with the only modification being the addition of PhCHO to the cold (-10°) solution of the lithium enolate **59** and $ZnCl_2$ over a period of only 5 sec. After this addition, aliquots were removed at regular intervals and quenched by partitioning them between cold (0°) aqueous NH_4Cl and Et_2O. The organic solutions were dried, concentrated, and analyzed using the nmr peaks at δ 1.78 (CH_3CO of the erythro isomer **60b**) and 2.04 (CH_3CO of the threo isomer **60a**) to determine the proportions of aldol stereoisomers present. The proportions of isomers after various reaction times were: 19 sec, 55% **60b** and 45% **60a**; 35 sec, 55% **60b** and 45% **60a**; 65 sec, 51% **60b** and 45% **60a**; 125 sec, 50% **60b** and 50% **60a**; 300 sec, 48% **60b** and 52% **60a**. The reaction was essentially complete in a time less than 19 sec when the first aliquot was removed, and the above data indicate that the composition of the aldol product **60a** + **60b** changed relatively little after 19 sec.

Polylithium Compounds. VII.[1,2] The Tetralithium Compound from 1,3-Pentadiyne and Synthesis of Its Organic and Organometallic Derivatives

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received November 2, 1972

Abstract: 1,3-Pentadiyne reacts with excess *n*-butyllithium complexed with TMEDA to form a perlithiated species, C_5Li_4. With water, C_5Li_4 forms three isomers, 1,3-pentadiyne, 1,4-pentadiyne, and 1,2-pentadien-4-yne; with deuterium oxide, the three corresponding perdeuterated isomers are obtained. C_5Li_4 reacts with dimethyl sulfate to give three permethylated isomers, 6,6-dimethyl-2,4-heptadiyne, 4,4-dimethyl-2,5-heptadiyne, and 2,4-dimethyl-2,3-heptadien-5-yne. Quenching C_5Li_4 with either trimethylchlorosilane, ethyldimethylchlorosilane, or *tert*-butyldimethylchlorosilane yields only the sterically controlled products, tetrakis(organosilyl)-1,2-pentadien-4-ynes. Trimethylchlorogermane reacts with C_5Li_4 to give both 1,1,3,5-tetrakis(trimethylgermyl)-1,2-pentadien-4-yne and 1,5,5,5-tetrakis(trimethylgermyl)-1,3-pentadiyne. From infrared spectroscopy, C_5Li_4 is postulated to have mainly a pentatetraene structure, $Li_2C{=}C{=}C{=}C{=}CLi_2$.

Previous papers in this series have reported that many 1-alkynes bearing α-hydrogen atoms are readily polylithiated by alkyllithiums.[2-5] Propyne, for example, reacts with *n*-butyllithium in hexane to give the tetralithium compound C_3Li_4.[4,5] The present paper reports the preparation of another tetralithium compound, C_5Li_4 (**1**), and some of its organic and organometallic derivatives.

A solution of 1,3-pentadiyne (**2**)[6] in *n*-butane reacts with excess *n*-butyllithium complexed with *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to give a viscous dark brown oil. Treatment of this polylithiated material with excess water under acid conditions leads to a

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(1) This work was supported by the Air Force Office of Scientific Research (NC), Office of Aerospace Research, USAF, Grant No. AF-AFOSR 70-1904.

(2) A preliminary account of a portion of this work has been reported: R. West and T. L. Chwang, *Chem. Commun.*, 813 (1971).

(3) R. West and G. A. Gornowicz, *J. Amer. Chem. Soc.*, **93**, 1720 (1971), and references cited therein.

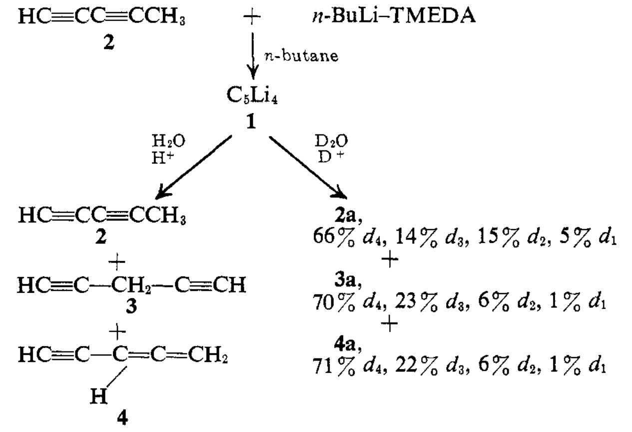
(4) R. West, P. A. Carney, and I. C. Mineo, *ibid.*, **87**, 3788 (1965).

(5) R. West and P. C. Jones, *ibid.*, **91**, 6156 (1969).

(6) 1,3-Pentadiene (2) was prepared by the method of J. L. H. Allan, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1862 (1955).

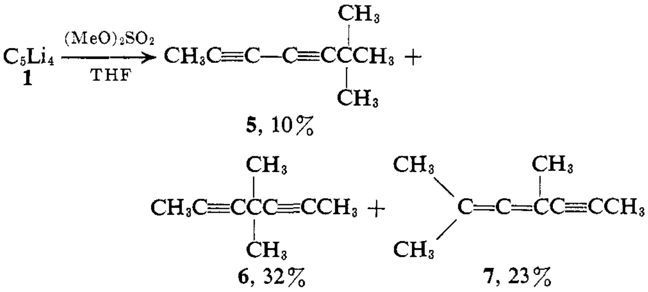
mixture of three isomers, 1,3-pentadiyne (**2**),[7] 1,4-pentadiyne (**3**),[8] and 1,2-pentadien-4-yne (**4**),[9] which were separated by preparative gas chromatography. Quenching the polylithiated species (**1**) with excess D_2O in the presence of DCl yields three deuterated isomers: 1,3-pentadiyne-d_x (**2a**), 1,4-pentadiyne-d_x (**3a**), and 1,2-pentadien-4-yne-d_x (**4a**). The deuterated compounds[10] had gc retention times identical with those of the corresponding undeuterated isomers; each deuterated compound was further identified by its infrared and mass spectra which support the assigned structures. Control experiments showed that **2** did not rearrange or exchange with deuterium under the conditions of the acid work-up. Analysis by mass spectroscopy at low voltage showed that **2a**, **3a**, and **4a** each consisted of about 70% tetradeuterated material, indicating that **1** is mainly a tetralithium species, C_5Li_4. Compounds **2**, **3**, **4**, and their deuterated analogs are all rather unstable. Extensive loss of the products was found to accompany even careful vacuum distillation.

Scheme I



Although **2** reacts with *n*-butyllithium to give predominantly **1** in the presence of TMEDA, with no TMEDA present the reaction yields mainly products arising from addition of *n*-butyllithium across the triple bond of **2**. Increased reactivity of organolithium compounds in the presence of TMEDA was first discovered by Eberhardt;[11d] TMEDA coordination complexes with organolithium reagents are often considerably more reactive in metalation reactions than are organolithium reagents alone.[11] For example, Mulvaney and Newton[11c] have reported that in the absence of TMEDA, diphenylacetylene reacts with organolithium reagents to give addition products only, whereas the use of TMEDA results not only in considerably more rapid addition but in metalation as well. The products obtained in lithiation of **2** may be kinetically controlled. When *n*-butyllithium–TMEDA complex is used as the lithiating agent, the rate of metalation may be much greater than that of addition, so that the predominant products arise from polymetalation.

Treatment of **1** with a solution of dimethyl sulfate in tetrahydrofuran (THF) leads to a mixture of three permethylated isomers: 6,6-dimethyl-2,4-heptadiyne (**5**), 4,4-dimethyl-2,5-heptadiyne (**6**), and 2,4-dimethyl-2,3-heptadien-5-yne (**7**), which were separated by preparative gas chromatography. Compounds **5**[12] and **6**[13] have ir and nmr spectra corresponding to those previously reported. Product **7** exhibits a weak central C≡C stretching band at 2220 cm^{-1}. The allenic antisymmetric stretching at 1950 cm^{-1} is, however, very weak. The latter result might have been anticipated since the antisymmetrical allenic stretching bands around 1900 cm^{-1} for tetraphenyl-,[14] tetramethyl-,[15] and tetraethylallene[15] are all very weak or completely absent. Three singlets at τ 7.77, 7.95, and 7.98 in the relative ratio of 1:1:2 are observed in the nmr spectrum in accordance with the assigned structure **7**. Furthermore, the uv absorption maximum at 218 nm is in good agreement with values reported for the similar dienynes, **4** (211.5 nm in ethanol)[9] and 2-methyl-2,3-heptadien-5-yne (220 nm in *n*-hexane).[16]



When **1** was derivatized with trialkylchlorosilanes, the greatly predominant or exclusive products were the 1,1,3,5-tetrakis(trialkylsilyl)-1,2-pentadien-4-ynes, **8**, **9**, and **10**.[17] Inspection of molecular models shows that tetrasilylated 1,2-dien-4-yne is less crowded sterically than either of the other two possible isomers, 1,3- and 1,4-diynes.

The structures of **8**, **9**, and **10** were assigned on the basis of spectroscopic evidence. All three compounds show very strong ir absorptions in the allenic region, near 1900 cm^{-1}, and a strong absorption in the C≡C stretching region, around 2130 cm^{-1}. In ethanol, compounds **8**, **9**, and **10** exhibit uv high-intensity maxima at 258, 264, and 250 nm, respectively. These values are substantially red shifted compared with those of unsubstituted dienynes, for example, **4** (211.5 nm),[9] **7** (218 nm), and 2-methyl-2,3-heptadien-5-yne (220 nm).[16] This is to be expected since metalloid-substituted π-electron systems frequently show batho-

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(7) The product **2** had identical gc retention time, nmr, ir, and mass spectra with those of the starting material.[6]

(8) The preparation of 1,4-pentadiyne (**3**) has been mentioned, but neither physical properties nor spectral data were reported: F. Serratosa, *Tetrahedron Lett.*, 895 (1964).

(9) E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 341 (1960).

(10) The syntheses of 1,3-pentadiyne-d_4, -d_3, and -d_1 have been reported, but only microwave data were described; see G. A. Heath, L. F. Thomas, E. I. Sherrard, and J. Sheridan, *Discuss. Faraday Soc.*, **19**, 38 (1955).

(11) (a) J. M. Mallan and R. L. Bebb, *Chem. Rev.*, **69**, 693 (1969); (b) J. Klein and E. Gurfinkel, *J. Org. Chem.*, **34**, 3952 (1969); (c) J. E. Mulvaney and D. J. Newton, *ibid.*, **34**, 1936 (1969); (d) G. G. Eberhardt and W. A. Butte, *ibid.*, **29**, 2928 (1964); (e) A. W. Langer, Jr., *Trans. N. Y. Acad. Sci.*, **27**, 741 (1965); A. W. Langer, Jr., U. S. Patent 3,594,396 (1971); (f) A. J. Chalk and T. J. Hoogeboom, *J. Organometal. Chem.*, **11**, 615 (1968), and references cited therein; (g) R. West and P. C. Jones, *J. Amer. Chem. Soc.*, **90**, 2656 (1968).

(12) Yu. I. Porfir'eva, E. S. Turbanova, and A. A. Petrov, *J. Gen. Chem. USSR*, **34**, 4026 (1964).

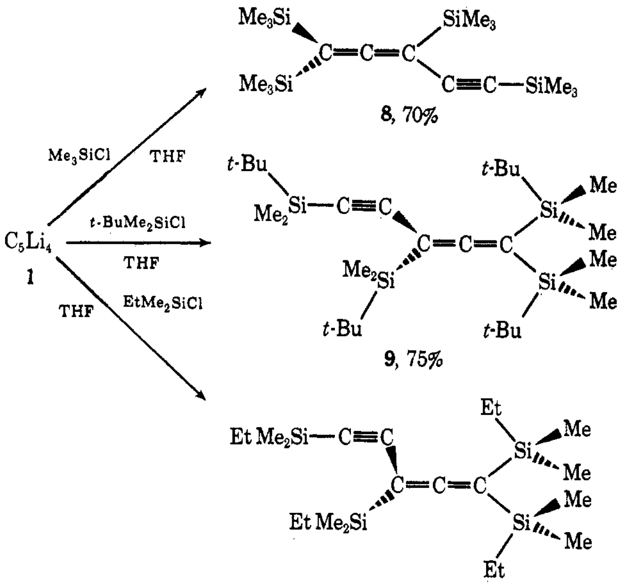
(13) G. D. Gracheva and A. I. Zakharova, *J. Org. Chem. USSR*, **2**, 959 (1966).

(14) J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

(15) Unpublished work by W. Priester and R. West.

(16) L. Skattebøl, *Tetrahedron*, **21**, 1357 (1965).

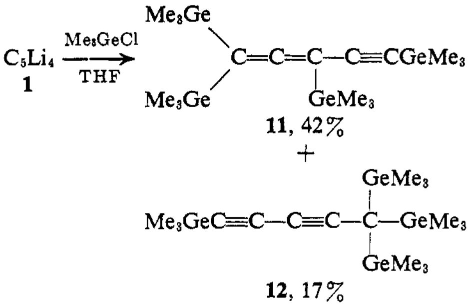
(17) We warmly thank Ms. Kathy Ackerman for synthesizing compound **10**.



chromic shifts of electronic transitions.[18] The proton nmr spectrum of **8** shows three singlets at τ 9.83, 9.85, and 9.88 with the ratio of 2:1:1, in accordance with the assigned structure.

The environments of the two methyl groups on each geminal silicon atom in **9** and **10** are intrinsically diastereotopic, that is, even under conditions of rapid rotation, the two *gem*-methyl groups do not interchange. Indeed, in the silylmethyl region, the proton nmr spectrum of **9** in carbon tetrachloride shows four equal intensity resonances at τ 9.56, 9.59, 9.62, and 9.67. For **10**, the proton nmr spectrum in carbon tetrachloride shows only three closely spaced singlets (τ 9.60, 9.64, and 9.67 with a relative intensity ratio of 2:1:1), but in pyridine four closely spaced resonances with equal intensity (τ 9.66, 9.75, 9.76, and 9.82) are observed. In both compounds **9** and **10** two of these four silylmethyl resonances arise from the different methyl groups on the nongeminal silicon atoms, one acetylenic and the other allenic. The other two result from the pairwise equivalent, diastereotopic methyl groups.

Total chemical shift differences for diastereotopic groups in a molecule depend on the conformer populations as well as on the intrinsic diastereoisomerism.[19] Apparently, the bulkiness of the *t*-butyl groups in **9** alters the conformer populations in such a way as to magnify the total chemical shift difference, so that the diasterotopy is evident in the nmr spectrum even in carbon tetrachloride solution.[20]



Treatment of **1** with trimethylchlorogermane in THF yields the expected product **11** and its interesting isomer **12**. 1,1,3,5-Tetrakis(trimethylgermyl)-1,2-pentadien-4-yne (**11**) and 1,5,5,5-tetrakis(trimethylgermyl)-1,3-pentadiyne (**12**) were identified by their spectroscopic properties. Both **11** and **12** show ir bands in the acetylenic region near 2150 cm^{-1}, as well as absorptions near 1230 cm^{-1} (δ sym $GeCH_3$).[21] **11**, in addition, has a strong C=C=C antisymmetric stretching absorption at 1887 cm^{-1}. Consistent with the assigned structures, **11** exhibits three proton nmr resonances at τ 9.32, 9.35, and 9.41 (1:2:1), whereas **12** shows instead two resonances at τ 9.33 and 9.37 (1:3). Like the silicon compounds, **11** and **12** show bathochromic shifts of ultraviolet maxima compared with unsubstituted compounds. The maximum absorption for **11** falls at 245 nm, and **12** exhibits absorption maxima at 224, 255.5, 270, and 286 nm compared with 227, 236.5, and 249 nm for **2**,[22] and 214, 225, 238, and 253 nm for 6-methyl-2,4-heptadiyne.[16] The polyisotopic nature of germanium is clearly recognizable in the mass spectra of the organogermanes. Ions containing 2, 3, or 4 germanium atoms show distinct characteristic patterns which result from a binomial combination of the basic isotope abundances.[21,23] The calculated abundances and masses for $C_{17}H_{36}Ge_4$ (including ^{13}C contributions) are plotted in Figure 1, along with actual mass and abundance combinations for the ions $(Me_3Ge)_4C_5^+$ of **11** and **12**. The agreement between the calculated spectrum and the actual spectra is very good.[23,24]

The formation of **12** is surprising because although bis(trialkylgermyl)-[25] and bis(triphenylgermyl)-[26,27] methanes have been made, attempts to prepare tris-(trialkylgermyl)-[25] and tris(triphenylgermyl)-[26,27] methanes have been unsuccessful. Thus **12** is apparently the first compound in which three trimethylgermyl groups are bound to the same carbon atom. The germanium–carbon (sp^3-hybridized) bond is about 0.1 Å longer than the corresponding silicon–carbon (sp^3-hybridized) bond.[28,29] The trimethylgermyl groups therefore have lower steric requirement than trialkylsilyl, perhaps just enough so that formation of the diyne **12** can compete with formation of the sterically favored dienyne **11**.

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[18] (a) H. Bock and H. Alt, *Chem. Ber.*, **103**, 1784 (1970), and references cited therein; (b) for a discussion of electronic transitions of group IV organometallic derivatives, see B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969, Chapter IV and Addendum.

[19] K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 24, 28, 32 (1967).

[20] A variable-temperature proton nmr experiment was undertaken to study the effect of conformer populations on the magnitude of the chemical shift nonequivalence for the diastereotopic methyl groups in **9** and **10**. However, compound **9** (in hexachloro-1,3-butadiene) showed no coalescence of silyl methyl resonances even when heated to 150°, while compound **10** (in acetone-d_6) gave an unresolvable broad absorption at −40°.

[21] F. Glockling and K. A. Hooton in "Organometallic Compounds of the Group IV Elements," Part II, Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, pp 68–80.

[22] J. B. Armitage, C. L. Cook, N. Entwistle, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1998 (1952).

[23] A. Carrick and F. Glockling, *J. Chem. Soc. A*, 623 (1966).

[24] The molecular ions are of relatively low intensity compared with other ions in the spectrum, as is also true for the silylated compounds. This phenomena is often observed with alkylated organometallic compounds.[23] We thank Mr. William B. Herdle for writing the computer program.

[25] E. J. Bulten and J. G. Noltes, *Tetrahedron Lett.*, 1443 (1967).

[26] C. A. Kraus and H. S. Nutting, *J. Amer. Chem. Soc.*, **54**, 1622 (1932).

[27] F. B. Smith and C. A. Kraus, *ibid.*, **74**, 1418 (1952).

[28] Values averaged from data compiled by (a) L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 11, M175 (1958); (b) *Chem. Soc., Spec. Publ.*, No. **18**, M67S, S18s (1965).

[29] F. Glockling, "The Chemistry of Germanium," Academic Press, New York, N. Y., 1969, p 13.

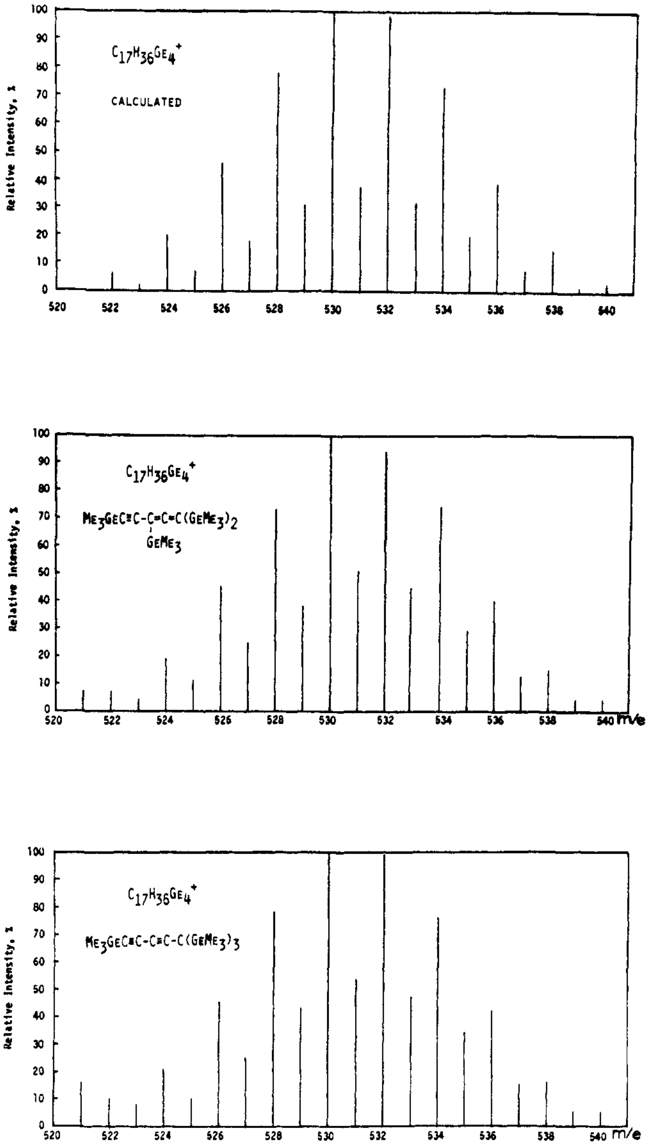


Figure 1. Normalized isotopic abundance patterns for $C_{17}H_{36}Ge_4^+$. Top, calculated; middle, observed for 1,1,3,5-tetrakis(trimethylgermyl)-1,2-pentadien-4-yne; bottom, observed for 1,5,5,5-tetrakis(trimethylgermyl)-1,3-pentadiyne.

Infrared Spectra and Structures of Polylithium Compounds. Product distribution upon derivatization is notoriously unreliable as a guide to the composition of intermediate polylithium species. However, infrared spectroscopy provides some data concerning the structures of poly- and perlithiated compounds. For example, the structure of C_3Li_4 in hexane has been determined by ir to be $Li_2C{=}C{=}CLi_2$ (at least, the major species present must have such an allenic structure).[5]

The dark viscous oil obtained from polylithiation of 1,3-pentadiyne (**2**) with *n*-butyllithium–TMEDA complex shows a strong ir absorption at 1800 cm^{-1}. This band we assign to an allenic stretching mode, shifted to lower energy by lithium substitution.[5] Several weaker unresolvable shoulders are observed at higher frequency (Figure 2), and a very weak absorption is also found at 2050 cm^{-1}. The band at 2050 cm^{-1} could, of course, be due to the incomplete polylithiation and formation of some monolithiated species. It appears that isomerization takes place during polylithiation of **2**, as it does in lithiation of propyne,[5] 2-butyne,[30] and 1-phenylpropynes.[3,31]

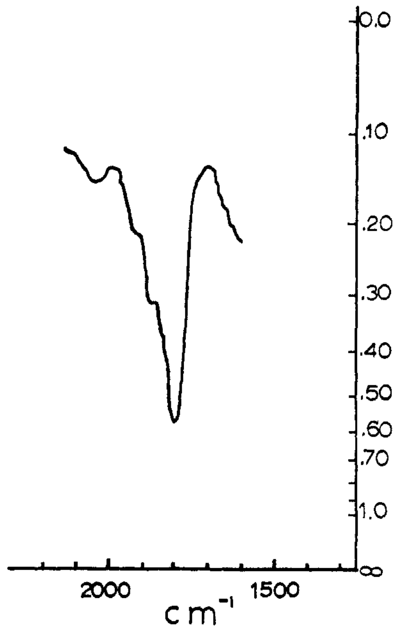


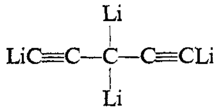
Figure 2. Infrared spectrum of the reaction product of 1,3-pentadiyne with excess *n*-BuLi–TMEDA complex.

Few pentatetraene compounds have been made so far. Kuhn and his coworkers[32] prepared a few tetraaryl-substituted pentatetraenes, and reported the absence of ir absorptions for such a cumulene moiety. Skattebøl[33] claimed the synthesis of a very unstable pentatetraene, 2,6-dimethyl-2,3,4,5-heptatetraene. The compound was not isolated, but a weak ir absorption at 2010 cm^{-1} was reported. The observed strong ir absorption of C_5Li_4 (**1**) at 1800 cm^{-1} is approximately 210 cm^{-1} lower than the reported value for 2,6-dimethyl-2,3,4,5-heptatetraene.[33] Likewise, there is a frequency difference of approximately 290 cm^{-1} between allene and the tetralithioallene, $Li_2C{=}C{=}CLi_2$.[5]

Possible tautomeric structures for **1** are I, II, III, and IV. Relatively strong infrared absorption around

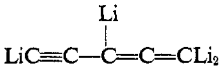
$LiC{\equiv}C{-}C{\equiv}CCLi_3$

I



$$LiC{\equiv}C{-}\overset{Li}{\underset{Li}{C}}{-}C{\equiv}CLi$$

II



$$LiC{\equiv}C{-}\overset{Li}{C}{=}C{=}CLi_2$$

III

$Li_2C{=}C{=}C{=}C{=}CLi_2$

IV

2050 cm^{-1}, characteristic for a 1-lithioacetylenic moiety,[3,5] would be expected for the formal structures I, II, and III. Furthermore, it is hard to account for the strong and relatively broad band at 1800 cm^{-1} for either I or II. From the observed infrared spectrum, IV seems the most likely structure for **1**, with III not fully excluded as a possibility. Of course, a mixture of tautomeric structures may be present in **1**, but the sim-

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(30) T. Ling Chwang, Ph.D. Thesis, University of Wisconsin, 1971.

(31) J. Klein and S. Brenner, *J. Org. Chem.*, **36**, 1319 (1971), and references cited therein.

(32) R. Kuhn, H. Fischer, and H. Fischer, *Chem. Ber.*, **97**, 1760 (1964).

(33) L. Skattebøl, *Tetrahedron Lett.*, 2175 (1965).

plicity of the spectrum suggests that one structure predominates.[34]

Experimental Section

All reactions involving organolithium compounds were carried out in an atmosphere of dry nitrogen. Solutions were usually added by syringe to apparatus which had been flamed and cooled under a nitrogen stream. Ultraviolet spectra were recorded in 95% ethanol on a Cary Model 14 spectrophotometer. Proton nmr spectra were recorded on a Varian A-60 or A-60A spectrometer. Gas chromatographic analysis and separations were made on a Varian Aerograph Model A-705 or 90-P chromatograph with thermal conductivity detectors, or on a Barber Coleman Model 5340 thermal conductivity gas chromatograph. Helium was used as the carrier gas. Mass spectra were obtained using an AEI MS-902 high-resolution mass spectrometer, or a CEC Model 21-103C mass spectrometer equipped with heated inlet. Infrared spectra were recorded on Perkin-Elmer Model 237 or 437 recording spectrometers. Analyses[35] were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

n-Butyllithium in hexane was obtained from Foote Mineral Co. *N,N,N′,N′*-Tetramethylethylenediamine was purchased from Aldrich Chemical Co. and was distilled over sodium hydroxide. 1,4-Dichloro-2-butyne was obtained from Aldrich. Sodium amide was prepared by the published method.[36] 1,3-Pentadiyne was prepared by the method of Allan, Jones, and Whiting.[6,37] Trimethylchlorosilane, Dow Corning Corp., was distilled before use. *tert*-Butyldimethylchlorosilane was prepared by treating dimethyldichlorosilane with an equivalent amount of *tert*-butyllithium.[38] Ethyldimethylchlorosilane was prepared from dimethyldichlorosilane and ethylmagnesium bromide.[38] Dimethyl sulfate, Aldrich Gold Label Quality, was stirred over anhydrous sodium carbonate until neutral to Congo Red paper[39] and then distilled. Deuterium oxide (99.8%), Stohler Isotope Chemicals, was used as obtained. Deuterium chloride was synthesized by the procedure of Brown and Groot,[40] the gas being collected in deuterium oxide. Trimethylchlorogermane, Alfa Ventron, was used as obtained. Tetrahydrofuran was distilled from lithium aluminum hydride prior to use. *n*-Butane gas, Matheson CP Grade, was used as obtained.

General Procedure for Polylithiation of 1,3-Pentadiyne (2). *n*-Butyllithium in *n*-butane or in hexane was placed in a reaction vessel fitted with an air-tight mechanical stirrer (Chesapeake), a condenser containing solid carbon dioxide–acetone mixture, and an addition funnel equipped with a cooling jacket filled with solid carbon dioxide. To the stirred solution, 0.25 molar equiv of TMEDA (N:Li = 1:2) was added dropwise. The complex was allowed to stir for 30 min (1 hr when *n*-butane was used as a solvent) resulting in the formation of a pale yellow solution and a white suspension. With stirring, a measured solution of 1,3-pentadiyne in *n*-butane[37] was then added from the chilled addition funnel over a period of 2–3 hr. At the end of this time, the reaction mixture turned reddish brown with a viscous dark brown oil precipitating. Attempts to induce the oil to crystallize were uniformly unsuccessful.

Derivatization with Water. Using the experimental procedure described above, 153 ml of a solution of 1,3-pentadiyne, 0.087 *M* in *n*-butane[37] (13 mmol of 1,3-pentadiyne), was added to a solution of 0.08 mol of *n*-butyllithium and 2.8 ml (0.02 mol) of TMEDA in 60 ml of *n*-butane. The mixture was stirred at 2–3° for a total of 41 hr. The reaction mixture was then chilled to −25°, and excess concentrated hydrogen chloride (10 ml, 0.12 mol) in 20 ml (1.1 mol) of water was added. The organic layer was separated and dried over magnesium sulfate. Quantitative gas chromatography (25 ft × 3/8 in. 20% SE-30 silicone on 30–60 Chromosorb W column at −10°) showed this solution to contain **2** (10%), **3** (40%), and **4** (20%). The butane solution of these isomers was distilled at 0.1 Torr, collected in a −80° trap, and subsequently separated by preparative gc. **2** was identified by comparing its infrared, ultraviolet, and nmr spectra with that of an authentic sample.[6]

The ir absorptions for **4** are similar to those previously reported.[9] Further proof of structure for **4** was obtained from its spectroscopic data: nmr (CCl_4, external TMS) τ 4.6–5.17 (complex m, 3, allenyl H), 7.23–7.38 (complex m, 1, acetylenic H); accurate mass of the parent ion, 64.03130 (calcd for C_5H_4, 64.03130).

Compound **3** showed the following characteristics: ir (CCl_4) 3305 cm^{-1} (acetylenic C–H), 2135 cm^{-1} ($C\equiv C$), 1420 cm^{-1} (CH_2 flanked by two triple bonds ?);[41] nmr (CCl_3, external TMS) τ 6.91 (t, 2, methylene H), 8.10 (t, 2, acetylenic H), J_{13} = 2.51 Hz; accurate mass of the parent ion, 64.03130 (calcd for C_5H_4, 64.03130).

Derivatization with Deuterium Oxide. **1** as prepared above was cooled to −35° and quenched with 4.5 g (0.12 mol) of concentrated deuterium chloride in 22 g (1.1 mol) of deuterium oxide. The mixture was worked up and separated as described above yielding **2a** (10%), **3a** (25%), and **4a** (19%). The deuterium contents in each isomer given in Scheme I were determined by mass spectroscopy at an ionizing voltage of 12 eV. Under these conditions all the undeuterated isomers gave no P − 1 peaks. Deuterium percentages in Scheme I are corrected for P + 1 contributions from the corresponding undeuterated isomer.

For **2a**, the following characteristics were observed: ir (CCl_4) ν (cm^{-1}) 3320 vw, 2960 s, 2920 s, 2860 m, 2877 m, 2600 m, 2580 vs, 2240 m, 2110 w, 2060 vw, 1470 m, 1460 m, 1380 w, 1250 w, 1030 bw, 970 w, 950 m, 930 w, 615 w, 487 vs, 467 vs; same gc retention time as that of **2**; exact mass, 68.0564 (calcd for C_5D_4, 68.0564).

For **3a**: ir (CCl_4) ν (cm^{-1}) 3320 vw, 3090 vw, 2960 vw, 2920 vw, 2860 vw, 2600 vs, 2140 vw, 2080 vw, 2000 w, 1970 vw, 1720 vw, 1270 m, 1260 w, 1135 s, 1070 w, 1050 m, 985 s, 640 w, 500 vs; same gc retention time as that of **3**; exact mass, 68.0570 (calcd for C_5D_4, 68.0564).

For **4a**: ir (CCl_4) ν (cm^{-1}) 3320 vw, 2960 w, 2930 w, 2860 w, 2590 vs, 2240 w, 2215 vw, 1985 vw, 1928 s, 1720 vw, 1510 vw, 1355 vw, 1342 vw, 1280 s, 1250 vw, 1135 vw, 990 vw, 940 vw, 875 vw, 675 s, 655 m, 565 w, 500 vs, 470 s; identical gc retention time as that of **4**; exact mass, 68.0569 (calcd for C_5D_4, 68.0564).

Derivatization with Dimethyl Sulfate. Using the general polylithiation procedure described above, 145 ml of 0.14 *M* **2** (0.02 mol) in *n*-butane[37] was added to 75 ml of 1.6 *M* *n*-butyllithium (0.12 mol) complexed with 4.6 ml (0.03 mol) of TMEDA. With the solid carbon dioxide–acetone condenser replaced by a water condenser, the reaction mixture was stirred overnight with no heating. With the reaction mixture cooled to −78°, a solution of 16.2 ml (0.17 mol) of dimethyl sulfate in 100 ml of THF was added over a period of 2 hr. After 3 hr of gentle refluxing, a negative Gilman color test I[42] was obtained. Sodium hydroxide (40 g) in 200 ml of water was added and the mixture was heated at reflux for 3 hr to decompose excess dimethyl sulfate. The organic layer was washed with dilute hydrochloric acid to remove excess amines and then washed with water and dried over magnesium sulfate. Crude distillation yielded 4 g of material. **6** (estimated, by gc, to be 0.8 g, 32%) was isolated pure by preparative gc (15 ft × 3/8 in. 20% SE-30 plus 5% $AgNO_3$ on 30–60 Chromosorb W column at 70°), whereas **5** and **7** were separated as one component. Final separation of **5** and **7** was accomplished by preparative gc utilizing 15 ft × 3/8 in. 20% β,β'-oxydipropionitrile on 30–60 Chromosorb W operating at 50°. Gc analysis showed that approximately 0.25 g (10%) of **5** and 0.6 g (23%) of **7** were present. **5**[12] and **6**[13] were characterized by comparing their ir and nmr spectra with those previously reported.

Further structural proof for **5** was obtained from its uv and mass spectrum: uv (95% ethanol) λ_{max} 213 nm (ϵ 284.3), 223 (349), 237 (314.9), 250 (168); accurate mass for the parent ion, 120.0932 (calcd for C_9H_{12}, 120.0939).

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(34) Attempts to record ^{13}C nmr spectrum of **1** in cyclohexane gave no signal.

(35) Due to the instability of some of the ene–yne products in pure form, exact molecular weight determinations of the gc purified products were often used in place of elemental analysis.

(36) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Longmans, London, 1959, p 898.

(37) To avoid decomposition of the 1,3-pentadiyne (**2**), it was always used as a solution in *n*-butane. The *n*-butane extract from preparation of **2**[6] was dried over magnesium sulfate and analyzed by gas chromatography (25 ft × 3/8 in. 20% SE-30 silicone on 30–60 Chromosorb W column at −10°). Calibration was effected using a small sample of chilled, purified 1,3-pentadiyne (**2**). Only a trace (<5%) of lower boiling impurity was evident from gc. In a controlled experiment, no apparent difference in the lithiated infrared spectrum and the derivatization yield was observed when **2** in *n*-butane was crudely distilled prior to use in the lithiation reaction.

(38) P. R. Boudjouk, Ph.D. Dissertation, University of Wisconsin, 1971.

(39) Reference 36, p 804.

(40) H. C. Brown and C. Groot, *J. Amer. Chem. Soc.*, **64**, 2223 (1942).

(41) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, pp 28, 134.

(42) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. I, 3rd ed, Methuen & Co. Ltd., London, 1967, p 31.

Further proof of structure for **6** was obtained from its accurate mass: calcd for the parent ion C_9H_{12}, 120.0939; found, 120.0927.

The spectral properties of **7** were ir (CCl_4) ν (cm^{-1}) 2980 vs, 2940 vs, 2918 vs, 2850 s, 2710 w, 2220 vw, 2040 vw, 1950 vs, 1715 vw, 1440 s, 1370 m, 1360 s, 1345 m, 1220 m, 1180 m, 1114 s, 1067 vs, 1028 m, 930 vw, 620 m, 558 m, 490 m; nmr (CCl_4, external TMS) τ 7.77 (s, 1, acetylenic CH_3), 7.95 (s, 1, allenyl CH_3), 7.98 (s, 2, allenyl CH_3); uv (95% ethanol) λ_{max} 218 nm (ϵ 7333); mass spectrum (70 eV) *m/e* (rel intensity) 121 (7), 120 (73, M^+), 119 (12), 117 (4), 106 (9), 105 (100), 104 (10), 103 (18), 92 (4), 91 (23), 89 (4), 80 (4), 79 (40), 78 (11), 77 (49), 75 (4), 74 (4), 67 (4), 66 (9), 65 (28), 64 (4), 63 (15), 62 (5), 53 (11), 52 (7), 51 (18), 50 (8), 44 (9), 41 (15), 40 (7), 39 (28); accurate mass for the parent ion, 120.0942 (calcd for C_9H_{12}, 120.0939).

Derivatization with Trimethylchlorosilane. Using the general procedure for polylithiation of **2**, 0.01 mol of **2** in 80 ml of *n*-butane[37] was allowed to react with 37.5 ml of 1.6 *M* *n*-butyllithium (0.06 mol) complexed with 2.3 ml (0.015 mol) of TMEDA. The reaction mixture was quenched with 10.9 ml (0.085 mol) of trimethylchlorosilane in 50 ml of THF at −78°. The reaction mixture was then heated at gentle reflux for 3 hr, cooled, and washed with dilute acid (5% HCl) followed by water. The combined aqueous washes were extracted with ether and hexane. The combined organic phase (dried over magnesium sulfate) was concentrated to yield 3.5 g of crude material. Gc analysis (25 ft × $^3/_8$ in. column, 20% QF-1 on 30–60 Chromosorb W at 160°) indicated that approximately 2.5 g (70%) of **8** was present. The pure product **8** was isolated by preparative gc. The characteristic spectral data of **8** were $n^{24}\mathrm{D}$ 1.4818; ir (neat) ν (cm^{-1}) 2960 s, 2910 m, 2130 s, 1980 vs, 1410 w, 1360 w, 1250 vs, 1065 w, 885 vs, 845 vs, 760 s, 695 m, 640 m, 620 m; nmr (CCl_4, TMS) τ 9.83 (s, 2, $SiMe_3$), 9.85 (s, 1, $SiMe_3$), 9.88 (s, 1, $SiMe_3$); uv (95% ethanol) λ_{max} 258 nm (ϵ 18,400); mass spectrum (70 eV) *m/e* (rel intensity) 354 (6), 353 (12), 352 (32, M^+), 337 (7), 266 (11), 265 (23), 264 (84), 250 (4), 249 (10), 191 (4), 165 (5), 155 (15), 141 (6), 125 (4), 109 (4), 97 (15), 83 (10), 75 (7), 74 (15), 73 (100), 59 (7), 45 (29), 43 (5); accurate mass for the parent ion, 352.1883 (calcd for $C_{17}H_{36}{}^{28}Si_4$, 352.1894).

Anal. Calcd for $C_{17}H_{36}Si_4$ (**8**): C, 57.95; H, 10.23; Si, 31.82. Found: C, 58.36; H, 10.51; Si, 31.29.

Derivatization with *tert*-Butyldimethylchlorosilane. A solution of **1** was prepared from 0.01 mol of **2** as described for the trimethylchlorosilane derivatization experiment. The reaction mixture was cooled to −78° and 12.81 g (0.085 mol) of *tert*-butyldimethylchlorosilane in 50 ml of THF was added. After work-up and crude distillation as above, 3.5 g of material was isolated. It was estimated by gc (25 ft × $^3/_8$ in. column, 20% QF-1 on 30–60 Chromosorb W at 240°) that about 2.6 g (75%) of **9** was present in this crude material. Final purification was accomplished by preparative gc. The spectral data of **9** were $n^{24}\mathrm{D}$ 1.4994; ir (neat) ν (cm^{-1}) 2968 vs, 2940 vs, 2900 s, 2868 vs, 2130 s, 1875 vs, 1472 s, 1467 s, 1410 w, 1392 w, 1365 m, 1250 s, 1210 w, 1075 w, 1010 m, 940 m, 870 s, 840 vs, 825 vs, 810 vs, 778 vs, 680 s, 583 s; nmr (CCl_4, external TMS) τ 8.72 (s, 3, *t*-Bu), 8.73 (s, 6, *t*-Bu), 8.82 (s, 3, *t*-Bu), 9.56 (s, 2, SiMe), 9.59 (s, 2, SiMe), 9.62 (s, 2, SiMe), 9.67 (s, 2, SiMe); uv (95% ethanol) λ_{max} 264 nm (ϵ 16,900) nm; mass spectrum (70 eV) *m/e* (rel intensity) 521 (4), 520 (5, M^+), 293 (5), 277 (5), 241 (4), 239 (5), 238 (8), 237 (40), 219 (14), 217 (5), 216 (9), 215 (47), 160 (4), 159 (33), 155 (8), 141 (5), 139 (4), 138 (7), 137 (65), 117 (7), 109 (15), 99 (4), 97 (5), 81 (12), 79 (5), 78 (50), 77 (47), 75 (9), 74 (9), 73 (100), 60 (4), 59 (83), 57 (4), 55 (4), 51 (4), 44 (5), 41 (9), 39 (60); accurate mass for the parent ion, 520.3780 (calcd for $C_{29}H_{60}{}^{28}Si_4$, 520.3772).

Derivatization with Ethyldimethylchlorosilane. A solution of **1** from 0.01 mol of **2** was prepared as in the two previous experiments. The reaction mixture was treated at −78° with a solution of 12.4 g (0.07 mol) of ethyldimethylchlorosilane in 100 ml of THF. After work-up as above, 3.7 g of crude material was obtained. It was estimated by gc (15 ft × $^3/_8$ in. column, 20% SE-30 silicone on 30–60 Chromosorb W at 230°) that about 0.6 g (15%) of **10** was present. The spectral properties of **10** were ir (CCl_4) ν (cm^{-1}) 2960 vs, 2905 vs, 2875 vs, 2800 w, 2120 vs, 1905 vs, 1460 s, 1410 s, 1380 w, 1365 w, 1290 m, 1245 vs, 1060 sb, 1005 vs, 955 vs, 790 vsb, 690 vs, 630 m, 595 s, 535 w, 490 m, 460 m, 385 m, 370 m; nmr (pyridine, TMS) τ 8.60–9.65 (complex m, 20 SiEt), 9.66 (s, 6, SiMe), 9.75 (s, 6, SiMe), 9.76 (s, 6, SiMe), 9.82 (s, 6, SiMe); uv (95% ethanol) λ_{max} 250 nm (ϵ 11,714); mass spectrum (70 eV) *m/e* (rel intensity) 408 (vw, M^+), 338 (5), 337 (13), 336 (31), 324 (4), 323 (8), 322 (22), 307 (4), 293 (5), 236 (4), 235 (10), 234 (31), 222 (5), 221 (13), 220 (37), 208 (5), 207 (10), 206 (20), 205 (6), 196 (6), 192 (11), 191 (9), 179 (5), 178 (5), 177 (6), 169 (5), 165 (6), 163 (5), 161 (6), 155 (5), 147 (5), 141 (7), 133 (6), 127 (5), 123 (5), 111 (6), 109 (6), 97 (11), 95 (5), 91 (5), 88 (6), 87 (78), 85 (5), 83 (11), 81 (6), 77 (6), 75 (5), 73 (30), 71 (6), 70 (5), 69 (10), 67 (7), 59 (100), 57 (35), 56 (20), 55 (28), 45 (9), 44 (98), 43 (20), 42 (11), 41 (28), 39 (12), 38 (12), 36 (38); accurate mass for the parent ion, 408.2511 (calcd for $C_{21}H_{44}{}^{28}Si_4$, 408.2520).

Derivatization with Trimethylchlorogermane. A solution of **1** was prepared from 0.01 mol of **2** as described for the trimethylchlorosilane derivatization. The reaction mixture was treated at −78° with 10.71 g (0.07 mol) of trimethylchlorogermane in 100 ml of THF. After work-up as above, 5.2 g of crude material was obtained. It was estimated by gc (15 ft × $^3/_8$ in. column, 20% SE-30 silicone on 30–60 Chromosorb W at 230°) that about 2.3 g (42%) of **11** and 0.9 g (17%) of **12** were present. The two isomers were separated by preparative gc.

The spectral properties of **11** were ir (CCl_4) ν (cm^{-1}) 2970 m, 2905 m, 2120 m, 1887 vs, 1405 w, 1295 w, 1231 m, 770 sb, 600 s, 565 m, 490 w, 445 w; nmr (CCl_4, external TMS) τ 9.32 (s, 1, Me_3Ge), 9.35 (s, 2, Me_3Ge), 9.41 (s, 1, Me_3Ge); uv (95% ethanol) λ_{max} 245 nm (ϵ 12,974); mass spectrum (70 eV) *m/e* (rel intensity) 536 (6), 535 (5), 534 (12), 533 (7), 532 (15), 531 (8), 530 (16), 529 (6), 528 (12), 527 (4), 526 (8), 524 (4), 517 (4), 418 (4), 416 (5), 415 (4), 414 (6), 413 (4), 412 (5), 410 (4), 404 (9), 403 (7), 402 (23), 401 (15), 400 (40), 399 (20), 398 (45), 397 (18), 396 (36), 395 (9), 394 (20), 393 (4), 392 (8), 387 (5), 385 (9), 384 (4), 383 (10), 382 (4), 381 (8), 379 (5), 296 (4), 295 (4), 286 (4), 285 (4), 284 (13), 283 (9), 282 (19), 281 (8), 280 (17), 279 (6), 278 (8), 276 (4), 271 (4), 269 (7), 267 (8), 265 (9), 263 (4), 221 (4), 207 (4), 166 (4), 165 (4), 139 (5), 137 (5), 121 (26), 120 (5), 119 (100), 118 (24), 117 (74), 115 (54), 105 (4), 104 (6), 102 (4), 100 (4), 91 (5), 89 (10), 87 (8), 84 (5), 81 (4), 69 (4), 57 (4), 55 (4), 44 (7), 41 (5); accurate mass for one of the parent ions, 519.9768 (calcd for $C_{17}H_{36}{}^{70}Ge_4$, 519.9788).

12, isolated by gc, was sublimed *in vacuo* to give white crystals which melted at 130–131.5° (uncorrected). It has the following properties: ir (CCl_4) ν (cm^{-1}) 2970 m, 2910 m, 2810 vw, 2170 vs, 1406 w, 1235 s, 1200 s, 780 sb, 692 m, 595 vs, 570 m, 560 shm, 485 vw, 420 m, 410 m; nmr (CCl_4, external TMS) τ 9.33 (s, 1, $GeMe_3$), 9.37 (s, 3, $GeMe_3$); uv (95% ethanol) λ_{max} 224 nm (ϵ 71,300), 255.5 (685.1), 270 (795.6), 286 (530.4); mass spectrum (70 eV) *m/e* (rel intensity) 534 (8), 533 (6), 532 (14), 531 (9), 530 (19), 529 (10), 528 (19), 527 (8), 526 (14), 525 (5), 524 (8), 517 (5), 515 (7), 514 (4), 511 (5), 415 (4), 413 (4), 404 (13), 403 (9), 402 (35), 401 (21), 400 (59), 399 (28), 398 (67), 297 (25), 396 (55), 395 (12), 394 (32), 393 (6), 392 (12), 387 (9), 386 (5), 385 (15), 384 (7), 383 (16), 382 (6), 381 (13), 379 (8), 311 (4), 309 (5), 307 (4), 284 (4), 282 (6), 281 (5), 280 (5), 279 (5), 269 (4), 267 (4), 251 (4), 249 (4), 207 (5), 179 (4), 177 (4), 139 (4), 121 (22), 119 (100), 118 (23), 117 (75), 115 (55), 105 (6), 104 (5), 89 (6), 87 (5); accurate mass for one of the parent ions, 519.9718 (calcd for $C_{17}H_{36}{}^{70}Ge_4$, 519.9788).

Infrared Spectra of Lithiated 1,3-Pentadiyne (1). The polylithiated 1,3-pentadiyne was prepared as described above. The bulk of *n*-butane plus hexane was removed under partially reduced pressure. Under a stream of nitrogen, the dark brown viscous oil was spread between two sodium chloride plates. The periphery of the plates was then coated with a thin layer of Apiezon N grease. The ir (neat) of the oil is shown in Figure 2.

Reaction of 2 with *n*-Butyllithium without TMEDA, and Subsequent Trimethylsilyl Derivatization. 1,3-Pentadiyne (**2**) (145 ml, 0.14 *M*, 0.02 mol) in *n*-butane[37] was added dropwise into a reaction flask, equipped with a stirrer and a condenser filled with solid carbon dioxide–acetone mixture, containing 75 ml of 1.6 *M* *n*-butyllithium (0.12 mol) in hexane. Another 80 ml of dry hexane was then added. The addition of **2** was completed in about 4 hr. The reaction mixture was allowed to stir at 0° for 4 hr and then to warm slowly to room temperature. Stirring was continued for another 12 hr. The reaction mixture was then quenched with 21.8 ml (0.17 mol) of trimethylchlorosilane in 80 ml of THF at −78°. After the mixture warmed slowly to room temperature, solvents were removed. Distillation of the residue (62–75° (0.05 Torr)) yielded 4.5 g of liquid. Analysis by gc (25 ft × $^3/_8$ in. column, 20% QF-1 on 30–60 Chromosorb W at 185°) yielded the following components.

(A) (24%) ir (neat) ν (cm^{-1}) 2960 s, 2940 msh, 2910 msh, 2860 w, 2120 m, 1580 w, 1450 wb, 1410 vw, 1380 vw, 1250 vs, 1130 vw, 1080 vw, 840 vs, 760 s, 690 m; nmr (CCl_4, external TMS) τ 8.16 (s, 1, CH_3), 8.32–9.54 (complex m, 3, *n*-butyl), 9.84 (s, 3, Me_3Si), 9.88 (s, 3, Me_3Si).

(B) (26%) ir (neat) ν (cm^{-1}) 2960 s, 2940 msh, 2910 msh, 2865 w, 2120 m, 1580 w, 1460 vw, 1410 vw, 1370 vw, 1250 vs, 1130 vw, 1090 vw, 890 msh, 840 vs, 760 s, 690 w, 635 wsh, 620 w; nmr (CCl_4, external TMS) τ 8.04 (s, 1, CH_3), 8.32–9.50 (complex m, 3, *n*-butyl), 9.84 (s, 3, Me_3Si), 9.81 (s, 3, Me_3Si).

(C) (15%), showed ir and nmr spectra identical with those of **8**.

(D) (8%) ir (neat) ν (cm^{-1}) 2960 s, 2940 msh, 2900 msh, 2880 wsh, 2120 m, 1900 vw, 1890 vw, 1610 vw, 1460 vw, 1410 vw, 1260 vw, 1155 w, 1070 w, 840 vs, 760 m, 690 w, 660 vw; nmr (CCl_4, external TMS) τ 8.14 (s, 1, CH_3), 8.32–9.40 (complex m, 3, *n*-butyl), 9.86 (s, 3, Me_3Si), 9.94 (s, 3, Me_3Si).

The C≡C triple bond stretching absorption at 2120 cm^{-1} in A, B, and D is characteristic for $R_3Si—C≡C—$.

A, B, and D are probably isomers of $Me_3SiC≡CC(Me_3Si)=C(C_4H_9)CH_3$; they were not further characterized.

Organometallic Reaction Mechanisms. X. Concerning the Effect of Magnesium Metal Purity and the Method of Preparation of Grignard Reagents on Reaction with Ketones and Nitriles

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Abstract: Reaction rates and product analysis for the addition of methylmagnesium bromide to benzophenone, 2,4-dimethyl-4′-methylmercaptobenzophenone, 2-methylbenzophenone, and benzonitrile have been evaluated. The reaction conditions were such that a large excess of one reagent was employed. In addition, dilute solutions (<0.1 *M*) of Grignard reagent were used to ensure that complications due to associated organomagnesium species would not arise. The Grignard reagents were prepared from several grades of magnesium employing both an excess of magnesium and an excess of methyl bromide. The reaction of methylmagnesium bromide with benzophenone under pseudo-first-order conditions (in excess methylmagnesium bromide) gives rate constants which are dependent on the initial ketone concentration and also gives significant amounts of nonaddition products. These effects are significantly reduced when the purity of the magnesium used to prepare the Grignard reagent is increased. When ultrapure magnesium was used for the preparation of methylmagnesium bromide, the complications described were essentially eliminated and the rate data were found to be consistent with a specific mechanism in which both $(CH_3)_2Mg$ and CH_3MgBr react with ketone in a first-order fashion. Similar results were observed in the reaction of Grignard reagents with benzonitrile. In those cases in which large excesses of 2-methylbenzophenone and benzonitrile were employed, no by-products were detected and the rate constants were found to be independent of the manner in which the Grignard reagent was prepared or of the purity of the magnesium employed.

Mechanisms describing the addition of Grignard reagents to ketone have received much attention in recent years.[1] The experimental technique most often used in these investigations has been kinetics. The kinetic methods employed have been the following: allowing the Grignard reagent and ketone to react in nearly equal ratios,[2a,b] employing a large excess of Grignard reagent,[2c–i] and, more recently, employing a large excess of ketone.[2j,k] The advantage of the latter two methods is that the concentration of the reagent used in excess remains essentially constant throughout the course of the reaction. Thus, the kinetic dependence of the reagent used in excess is eliminated and a direct determination of the order of the reagent used in limited amount is possible. The order of the reagent used in large excess can be determined indirectly from the functional dependence of k_{obsd} on its concentration.

Smith and coworkers[2c–e] have investigated the reaction of methylmagnesium bromide with 2,4-dimethyl-4′-methylmercaptobenzophenone,[2c,d] 4-methylmercaptoacetophenone,[2e] and benzophenone.[2e] The Grignard reagent was prepared from singly sublimed magnesium employing an excess of magnesium turnings. The kinetic method employed involved the use of large excesses of the Grignard reagent. Interpretation of the resultant data was not straightforward. At low concentrations, *ca.* 10^{-5} *M*, of 2,4-dimethyl-4′-methylmercaptobenzophenone and 4-methylmercaptoacetophenone, the pseudo-first-order rate constants showed a dependence on the initial ketone concentration at constant Grignard reagent concentration. At lower ketone concentrations, *i.e.*, higher Grignard reagent to ketone ratios, larger rate constants were observed. The problem could be reduced by adding a small concentration of acetone to the Grignard reagent prior to the kinetic experiment, or by recrystallization of the Grignard reagent. Analysis of the products from the reaction of both 2,4-dimethyl-4′-methylmercaptobenzophenone and 4-methylmercaptoacetophenone with methylmagnesium bromide showed that only addition had occurred. Rate constants obtained from the reaction of methylmagnesium bromide with benzophenone displayed the largest dependence on initial ketone concentration of the three ketones investigated.[2e]

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