Allenic Alcohols from the Reaction of Organolithium Reagents with 4-Alkoxy-2-butyn-1-ols. Addition of Alkyllithiums to 3-Phenylpropargyl Alcohol*

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Butyl- and phenyllithium react with 4-alkoxy-2-butyn-1-ol derivatives to give C2 substituted α-allenic alcohols in an over-all displacement (via a propargylic rearrangement) of the alkoxy group. Allenic alcohols with a tetra-substituted allene group are obtained in yields > 70 %, whereas alcohols with a hydrogen at C4 suffer an over-all 1,4-elimination of LiOH giving alkenynes as by-products (30−40 %). In one case, when the leaving group was a tert-butoxy group, a vinylic organometallic intermediate was indicated in the allene-forming reaction. Butyl- and benzyllithium react with lithium 3-phenylpropargyl alcoholate by addition to the triple bond to give, after hydrolysis, 2-substituted (E)-3-phenyl-2-propen-1-ol derivatives; methyllithium reacts sluggishly. Tetramethylethylenediamine proved to be an essential co-reagent in these latter addition reactions.

It is well-known that organolithium compounds add to isolated carbon-carbon double bonds.[1] They also add readily to conjugated dienes and styrenes. Alkynes, in contrast to alkenes, are generally prone to undergo α-metallation[2] and additions of organolithium compounds to unconjugated carbon-carbon triple bonds are rare.[1] The additions to diarylacetylenes[1,3,4] and poly-ynes,[1] however, proceed smoothly and so does the allene-forming addition of organolithiums to alkenynes.[1]

In several of the above reactions the solvent plays a major role; electron-donating solvents such as ethers and amines favour the addition,

especially the chelate-forming diamine N,N,-N',N'-tetramethylethylenediamine[1] (TMEDA).

Assistance by intramolecular coordination of organolithiums with polar groups in the substrate molecule is also a promoting factor in addition reactions. Neighbouring groups such as ether and amino functions, and, pertinent to the present work, hydroxyl groups facilitate addition.[1,5−7]
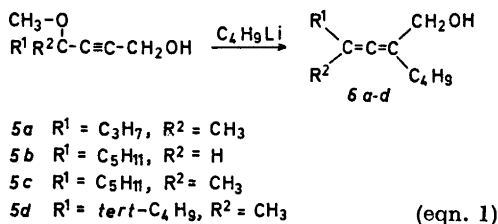
Prior to our preliminary communication[8] the addition reaction of organolithium compounds with propargylic alcohols had not been reported. However, it is known that Grignard reagents add to the triple bond of several acetylenic alcohols when it is relatively proximate to the hydroxyl group.[9] Nearby ether and amino functions also promote this addition.[10]
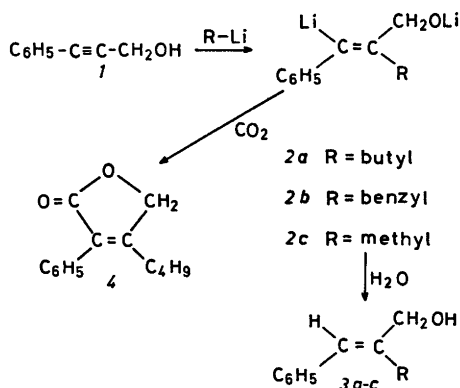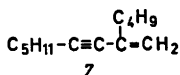

Scheme 1.

We have reported [8] that butyllithium smoothly adds to the triple bond of 3-phenylpropargyl alcoholate (from *1*) in the presence of 0.2 equiv. of TMEDA in an ether-hexane mixture (Scheme 1). Hydrolysis of the organometallic intermediate *2a* gives the cinnamyl alcohol derivative *3a* [11] in 90 % yield and treatment with CO_2 gives the lactone *4* in 77 % yield (GLC). The acetylenic methoxy compounds *5a* and *5b* [12] react with butyllithium (eqn. 1) by an over-all displacement of the methoxy groups to give the allenic alcohols *6a* and *6b* in yields of around 80 and 40 %, respectively. The lower yield of *6b* is caused by its further reaction with butyllithium to the alkenyne *7*, which is formed in 35 % yield.[8] In these two reactions with butyllithium TMEDA has no significant influence

$$CH_3-O$$
$$R^1R^2C-C\equiv C-CH_2OH \xrightarrow{C_4H_9Li}$$

R^1, CH_2OH
$C=C=C$
R^2, C_4H_9
6 a-d

5a $R^1 = C_3H_7$, $R^2 = CH_3$
5b $R^1 = C_5H_{11}$, $R^2 = H$
5c $R^1 = C_5H_{11}$, $R^2 = CH_3$
5d $R^1 = tert-C_4H_9$, $R^2 = CH_3$ (eqn. 1)

on the reaction rate or the formation of minor amounts of by-products.

$$C_4H_9$$
$$C_5H_{11}-C\equiv C-C=CH_2$$
7

The above reactions with organolithium reagents have been studied in more detail and the results are presented here.

RESULTS AND DISCUSSION

3-Phenylpropargyl alcohol and 2-heptyn-1-ol. It has been reported that butyllithium adds to the triple bond of diphenylacetylene to give a stilbene derivative with E configuration,[3] whereas *tert*-butyllithium gives a similar compound with predominant Z configuration.[4] The present 2-butylcinnamyl alcohol *3a* was homogeneous on OV-25 and Carbowax 20 M GLC columns, thus indicating a single geometric isomer. The C1 protons of *3a* appear as a single doublet (J 1.3 Hz) in the ¹H NMR spectrum, further indicating homogeneous stereochemistry. Treatment of the intermediate *2a*
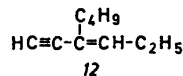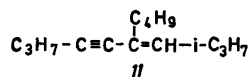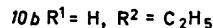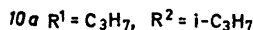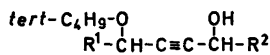
with CO_2 gave the lactone *4* in 77 % yield (GLC), which must arise from the E intermediate *2a*. However, it is not absolutely clear whether this E intermediate is a direct result of the addition of butyllithium or is a product from subsequent isomerization of an initially formed Z intermediate. The stilbene derivatives of Mulvaney [3,4] obviously result from rapid thermodynamic equilibration of the vinylic organometallic intermediates, as it has been shown by other authors [13,14] that vinylic lithium compounds having α-aryl substituents are configurationally instable, especially in the presence of TMEDA.[14] The present E intermediates *2* should therefore also be the result of quick thermodynamic equilibration and it is impossible to make a statement regarding the type of addition (*cis* or *trans*).

Benzyllithium also reacted easily with 3-phenylpropargyl alcoholate under the above conditions (0 – 20 °C) to give the alcohol *3b*, isolated in 70 % yield by preparative TLC. The stereochemistry of the product *3b* was not proved, but its NMR spectrum as well as GLC analysis on an OV-25 column indicated the presence of a single isomer. In contrast to the above reactions, the addition reaction of 3-phenylpropargyl alcohol with methyllithium required 2 equiv. of TMEDA to proceed with a noticeable rate. Work-up and distillation after a reaction time of 30 h at room temperature gave only 15 % of the alcohol *3c* [15] and a heavy residue was left, indicating polymerizing side-reactions. The analogous reaction of methyllithium with 1-methyl-3-phenylallyl alcohol likewise requires enough TMEDA to combine with all the lithium salts present in solution.[6]

The only observed reaction of 2-heptyn-1-ol (*8*) with butyllithium (eqn. 2) in the presence of 0.2 or 1.5 equiv. of TMEDA (reflux 5 h in ether) was, except for some polymerization, proton abstraction at C4; hydrolysis afforded the allenic alcohol *9* [16] (60 % of the volatile products; 40 % starting material).

$$C_4H_9-C\equiv C-CH_2OH \xrightarrow{C_4H_9Li} C_3H_7CH=C=CH-CH_2OH$$
8   *9*

(eqn. 2)
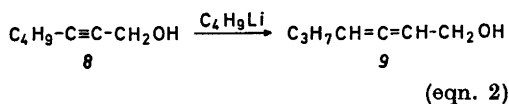
Alkoxy compounds. The reaction of the methoxy compound *5a* according to eqn. 1 seemed a promising route to α-allenic alcohols sub-

$$tert\text{-}C_4H_9\text{-}\underset{|}{O} \qquad \underset{|}{O}H$$
$$R^1\text{-}CH\text{-}C\equiv C\text{-}CH\text{-}R^2$$

10a $R^1 = C_3H_7$, $R^2 = i\text{-}C_3H_7$

10b $R^1 = H$, $R^2 = C_2H_5$

$$\underset{|}{C_4H_9}$$
$$C_3H_7\text{-}C\equiv C\text{-}C\text{-}CH\text{-}i\text{-}C_3H_7$$
$$\textit{11}$$

$$\underset{|}{C_4H_9}$$
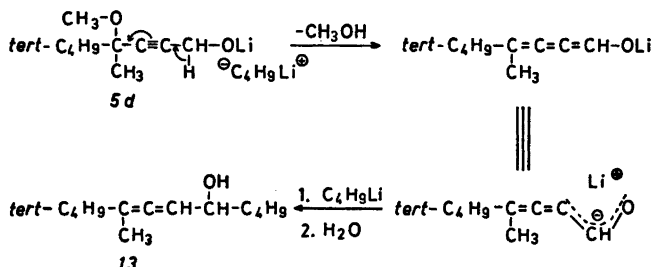$$HC\equiv C\text{-}C\text{=}CH\text{-}C_2H_5$$
$$\textit{12}$$

stituted at C2, which are otherwise obtainable from the reaction of appropriately substituted acetylenic oxiranes with organocuprates,[17] from dihalocyclopropanes and butyllithium, and by other methods.[18] Quite recently another method, in which acetylenic methoxy compounds of the type *5a − d* are treated with a combination of CuI and a Grignard reagent, was reported.[19] The present synthetic method, however, seems to be limited to the preparation of α-allenic alcohols with a tetrasubstituted allene group, because alcohols having one or two C4 hydrogens suffer an over-all loss of LiOH to give alkenynes, *e.g. 7* from *6b*. In the reactions according to eqn. 1 we used 2.5 equiv. of butyllithium, but attempts to raise the yield of *6b* by using only 2 equiv. were disappointing. The 1,4-elimination reaction of *6b* proceeded so rapidly that the ratio of *6b:7* was practically unchanged. We did not try to improve the yield of the alkenyne *7*, since it is well-known that organolithium reagents easily add to such compounds.[1]

When the *tert*-butoxy compound *10a* was allowed to react with butyllithium for 8 h at room temperature, the alkenyne *11* (30 %, GLC) was the only product formed (> 4 %); much of the starting material was recovered unchanged. The allenic alcohol formed from the analogous acetylene *10b* and butyllithium was also quickly consumed to give the corresponding alkenyne *12* (33 %, GLC) as main product.

Other authors have reported that 4-bromo-2,3-butadien-1-ol also undergoes 1,4-elimination to give vinylacetylene when treated with butyllithium.[20] In that case the alcoholate may be thought to undergo a bromine-lithium exchange with subsequent loss of Li_2O. Certain α-allenic alcohols also form minor amounts of alkenynes upon treatment with $LiAlH_4$ in refluxing THF.[12,21] Several other allenic derivatives, such as 2,3-alkadien-1-yl alkyl ethers,[22] likewise undergo facile 1,4-elimination reactions upon basic treatment; this reaction is reversible in the presence of a suitable base.

In the reaction products from *5a, 5c* and *5d* with butyllithium, 8 − 15 % of a compound having a retention time very close to each of the corresponding allenic main products *6* (formed in yields around 80 %) was observed on GLC (OV-25 and Carbowax 20 M). In the case of *5d* this product was isolated by preparative GLC (OV-25) and by comparison with authentic material, prepared according to Claesson *et al.*,[23] identified as the secondary allenic alcohol *13* (Scheme 2). A plausible route to this product is depicted in Scheme 2. The mass spectra (70 eV) of the isomers *6d* and *13* exhibit important differences, for instance the secondary alcohol *13* having β-hydrogens easily loses water (M − 18, 16 %) whereas *6d* does not (< 1 %). The alcohol *6d* has a peak at m/e 154 (20 %), which is lacking for *13*. A possible explanation of this peak is the ion *14*, which could have been formed in a McLafferty

$$CH_3\text{-}O$$
$$tert\text{-}C_4H_9\text{-}\underset{|}{C}\text{-}C\equiv C\text{-}CH\text{-}OLi \xrightarrow{-CH_3OH} tert\text{-}C_4H_9\text{-}\underset{|}{C}\text{=}C\text{=}C\text{=}CH\text{-}OLi$$
$$\underset{CH_3}{|} \quad \underset{H}{|} \quad {}^{\ominus}C_4H_9Li^{\oplus} \qquad\qquad \underset{CH_3}{|}$$
$$\textit{5d}$$

$$\underset{|}{O}H$$
$$tert\text{-}C_4H_9\text{-}\underset{|}{C}\text{=}C\text{=}CH\text{-}CH\text{-}C_4H_9 \xleftarrow[\text{2. } H_2O]{\text{1. } C_4H_9Li} tert\text{-}C_4H_9\text{-}\underset{|}{C}\text{=}C\text{=}C \qquad Li^{\oplus}$$
$$\underset{CH_3}{|} \qquad\qquad\qquad\qquad\qquad \underset{CH_3}{|} \qquad CH$$
$$\textit{13}$$

Scheme 2.

type rearrangement with loss of propene. The corresponding rearrangement of the alcohol *13*, would result in a loss of butene to give *m/e* 140 and this ion is actually present (13 %), while it is small for the isomer *6d*. The other allenic alcohols *6a – c* also exhibit corresponding peaks

14
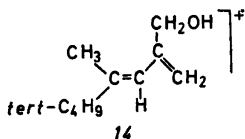
in their spectra [*m/e* 140 (28 %), *m/e* 154 (8 %) and *m/e* 168 (10 %), respectively]. Hydrocarbon McLafferty rearrangements are implicit in the mass spectra of other allenes [24] but have never been proven.

Other organolithium compounds also react with the acetylenic methoxy compounds *5*; phenyllithium with *5c* gave the allenic alcohol *15* in 85 % yield (GLC) accompanied by about 6 % of the allene *6c* from unreacted butyllithium. For the isolation of *15*, the crude material was chromatographed on preparative TLC plates.

15
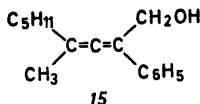
Although methyllithium adds to the double bond of 1-methyl-3-phenylallyl alcohol [6] and to the triple bond of 3-phenylpropargyl alcohol (slowly) in the presence of an excess of TMEDA, this reagent did not affect the acetylene *5c* to give a detectable amount of an allenic alcohol even in the presence of 3 equiv. of TMEDA (20 °C for 3 days). Fortunately, 2-methyl-2,3-alkadien-1-ols are available by other synthetic procedures.[17−19]

The reaction of the acetylene *10b* was undertaken in an attempt to detect a vinylic organometallic intermediate in the formation of the α-allenic alcohol. In analogous formations of α- and β-allenic alcohols from LiAlH₄ reductions we have earlier proved the existence of such vinylic intermediates.[25] Indeed, the existence of the intermediate *16* after 15 h at room temperature was indicated by hydrolysis to compound *17* (19 %; GLC); the stereochemistry of *16* and *17* was not proved. In the case of the

tert-butoxy compound *10a* no intermediate was detected (< 4 %; GLC). The stabilities of similar β-alkoxy vinylic organolithiums have been discussed as well as their application in syntheses.[26]

16 R = Li
17 R = H
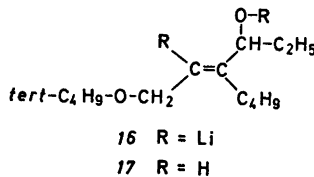
EXPERIMENTAL

General. The general IR and NMR instrumentation has been described.[25] These spectra were routinely recorded and are in full agreement with the proposed structures. Mass spectra were run on an AEI MS-30 spectrometer connected to a Pye 104 gas chromatograph or on a LKB 9000 instrument using the GLC inlet. The ionizing energy was maintained at 70 eV. Correct mass spectral data were obtained for all products.

GLC analyses were run on a Varian 1700 instrument equipped with flame ionization detectors. Columns: 3 m long glass columns packed with 5 % Carbowax 20 M on Chromosorb W (80 – 100 mesh) or 5 % OV-25 on Gas-Chrom Q (100 – 120 mesh). The preparative columns were of aluminium, 300 × 0.96 cm and packed with 20 % Carbowax 20 M, 20 % OV-25 or 20 % SE 30 on Chromosorb W (60 – 80 mesh). "Yield (GLC)" refers to the relative peak areas of the whole reaction mixture in a gas chromatogram run in a temperature range of about 100 °C on an OV-25 column; peak areas were not corrected for detector response. On distillation of several different worked-up reaction mixtures about 10 % of non-volatile residues were obtained, which can be regarded a representative figure for all the present reactions unless otherwise indicated. For preparative TLC 0.5 mm thick layers of silica gel PF on 20 × 20 cm plates were used.

All reactions with Grignard or lithium reagents were performed under nitrogen or argon.

Organolithium reagent used. Butyllithium was either of commercial origin (*ca.* 20 % in hexane) or prepared from butyl bromide and lithium in ether, in the presence of traces of HgBr₂. After complete reaction hexane was added to give a *ca.* 8 % solution of butyllithium. Methyllithium was purchased as a *ca.* 2 M solution in diethyl ether. Phenyllithium and benzyllithium were prepared by warming benzene and toluene respectively, with butyllithium solution and TMEDA under argon.[5]

Addition reactions. General procedure. One equivalent of the propargylic alcohol (1.5 − 3 g) in 30 ml of dry ether was treated with 0.2 equiv. of TMEDA. The mixture was cooled to − 30 °C and 2.5 equiv. of the organolithium reagent were added dropwise while stirring. The reaction mixture was allowed to reach room temperature during 0.5 h. Samples were withdrawn periodically for GLC analysis. The reaction was stopped by adding water, the solution was extracted several times with ether and the combined ethereal extracts were washed with water and dried. The products were isolated by preparative GLC or preparative TLC [for *3b* chloroform was used as eluent, and for *15* a benzene-ether mixture (4:1)] and identified by IR, NMR and MS. The allenic products showed the typical "allene band" at *ca.* 1960 cm⁻¹ which was of low intensity when the allene group was tetrasubstituted.

(E)-*2-Butyl-3-phenyl-2-propen-1-ol (3a)*.[11]
¹H NMR (CDCl₃): δ 7.47 − 7.18 (5 H, m), 6.66 − 6.50 (1 H, m), 4.20 (2 H, d), 2.50 − 2.14 (2 H, m), 1.80 (1 H, s), 1.65 − 1.13 (4 H, m), 0.87 (3 H, t).

(E)-*2-Benzyl-3-phenyl-2-propen-1-ol (3b)*.
¹H NMR (CDCl₃): δ 7.55 − 6.94 (10 H, m), 6.83 − 6.64 (1 H, m), 4.02 (2 H, d), 3.62 (2 H, d), 2.80 (1 H, s).

(E)-*2-Methyl-3-phenyl-2-propen-1-ol (3c)*.[14]
¹H NMR (CDCl₃): δ 7.53 − 7.20 (5 H, m), 6.64 − 6.47 (1 H, m), 4.15 (2 H, d), 2.84 (1 H, s), 1.87 (3 H, d).

4-Methoxy-4-methyl-2-heptyn-1-ol (5a) was prepared as described for similar compounds [23] from 3-(tetrahydro-2-pyranyloxy)propyne [27] (70.0 g; 0.50 mol), 2-pentanone (38.7 g; 0.45 mol) and dimethyl sulfate (100.0 g; 0.79 mol). Yield 70 %. B.p. 66 °C/0.5 mmHg. Found: C 69.0; H 10.2. Calc. for C₉H₁₆O₂: C 69.02; H 10.32.

4-Methoxy-4-methyl-2-nonyn-1-ol (5c). Prepared as above from 3-(tetrahydro-2-pyranyloxy)propyne (22.6 g; 0.16 mol), 2-heptanone (16.8 g; 0.15 mol) and dimethyl sulfate (33.4 g; 0.27 mol). Yield 68 %. B.p. 78 °C/0.1 mmHg. Found: C 71.7; H 10.9. Calc. for C₁₁H₂₀O₂: C 71.70; H 10.94.

4-Methoxy-4,5,5-trimethyl-2-hexyn-1-ol (5d) was prepared according to standard procedures,[16] *i.e.* 16.5 g (0.12 mol) of 3-methoxy-3,4,4-trimethyl-1-pentyne [28] was converted to the corresponding acetylenic Grignard reagent and allowed to react with 4.6 g (0.15 mol) of gaseous formaldehyde. Yield 75 %. B.p. 107 °C/10 mmHg. Found: C 70.6; H 10.6. Calc. for C₁₀H₁₈O₂: C 70.55; H 10.66.

2-Butyl-4,5,5-trimethylhexa-2,3-dien-1-ol (6d). MS, *m/e* (%): 196 (M⁺, 1), 181(1), 179(2), 178(0.5), 167(1), 165(1), 163(2), 155(3), 154(20), 149(3), 140(3), 139(13), 137(3), 135(3), 125(3), 123(10), 121(17), 111(7), 109(9), 107(27), 98(4), 97(8), 96(9), 95(9), 93(14), 91(11), 83(17), 81(20), 80(97), 79(18), 77(11), 69(23), 65(7),

59(7), 58(5), 57(100), 56(9), 55(33), 53(15), 51(4), 44(5), 43(20), 42(4), 41(67), 39(17).

6-tert-Butoxy-2-methyl-4-nonyn-3-ol (10a) was prepared in analogy with similar compounds [23] from 3-*tert*-butoxy-1-hexyne (80.0 g; 0.52 mol) and isobutyraldehyde (33.6 g; 0.47 mol). Yield 66 %. B.p. 87 °C/0.3 mmHg. Found: C 74.0; H 11.6. Calc. for C₁₄H₂₆O₂: C 74.29; H 11.58.

6-tert-Butoxy-4-hexyn-3-ol (10b) was prepared similarly from *tert*-butyl propargyl ether [29] (22.0 g; 0.19 mol) and propionaldehyde (10.6 g; 0.18 mol). Yield 64 %. B.p. 95 °C/2 mmHg. Found: C 70.4; H 10.5. Calc. for C₁₀H₁₈O₂: C 70.55; H 10.66.

8,9,9-Trimethyl-6,7-decadien-5-ol (13) was prepared as described [20] from LiAlH₄ reduction of 8-methoxy-8,9,9-trimethyl-6-decyn-5-ol (9.0 g; 0.04 mol). Yield 73 %. B.p. 76 °C/0.2 mmHg. Found: C 79.4; H 12.2. Calc. for C₁₃H₂₄O: C 79.53; H 12.32. 8-Methoxy-8,9,9-trimethyl-6-decyn-5-ol was prepared from 3-methoxy-3,4,4-trimethyl-1-pentyne (10.0 g; 0.071 mol) and pentanal (5.6 g; 0.065 mol). Yield 77 %. B.p. 85 °C/0.3 mmHg. Found: C 74.7; H 11.6. Calc. for C₁₄H₂₆O₂: C 74.29; H 11.58. MS, *m/e* (%): 196 (M⁺, 1), 181(4), 179(5), 178(16), 163(9), 152(9), 151(2), 149(2), 141(1), 140(13), 139(5), 137(6), 135(5), 122(8), 121(13), 119(3), 112(3), 111(33), 109(4), 107(15), 105(6), 95(7), 94(4), 93(25), 91(12), 85(5), 84(7), 83(6), 81(4), 80(3), 79(18), 78(3), 77(11), 69(14), 68(3), 67(6), 66(5), 65(5), 58(5), 57(100), 56(3), 55(31), 53(8), 51(4), 43(19), 41(47), 39(13).

REFERENCES

1. Wakefield, B. J. *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford 1974, Chapter 7.
2. West, R. and Jones, P. C. *J. Am. Chem. Soc. 91* (1969) 6156.
3. Mulvaney, J. E., Gardlund, Z. G., Gardlund, S. L. and Newton, D. J. *J. Am. Chem. Soc. 88* (1966) 476.
4. Mulvaney, J. E. and Newton, D. J. *J. Org. Chem. 34* (1969) 1936.
5. Crandall, J. K. and Clark, A. C. *Tetrahedron Lett.* (1969) 325; *J. Org. Chem. 37* (1972) 4236.
6. Felkin, H., Swierczewski, G. and Tambuté, A. *Tetrahedron Lett.* (1969) 707.
7. Dimmel, D. R. and Huang, S. *J. Org. Chem. 38* (1973) 2756; Dimmel, D. R. and O'Malley, J. P. *Ibid. 40* (1975) 132.
8. Olsson, L.-I. and Claesson, A. *Tetrahedron Lett.* (1974) 2161.

9. Eisch, J. J. and Merkley, J. H. *J. Organo-metal Chem. 20* (1969) P 27; Richey, H. G. and von Rein, F. W. *Ibid. 20* (1969) P 32.
10. Mornet, R. and Gouin, L. *J. Organometal. Chem. 86* (1975) 57.
11. Mastagli, P. *C. R. Acad. Sci. 205* (1937) 802.
12. Claesson, A. *Acta Chem. Scand. B 29* (1975) 609.
13. Curtin, D. Y. and Koehl, Jr., W. J. *J. Am. Chem. Soc. 84* (1962) 1967.
14. Panek, E. J., Neff, B. L., Chu, H. and Panek, M. G. *J. Am. Chem. Soc. 97* (1975) 3996.
15. Stevens, P. G., Allenby, O. C. W. and DuBois, A. S. *J. Am. Chem. Soc. 62* (1940) 1424.
16. Cowie, J. S., Landor, P. D. and Landor, S. R. *J. Chem. Soc. Perkin Trans. 1* (1973) 720.
17. Ortiz de Montellano, P. R. *Chem. Commun.* (1973) 709; Vermeer, P., Meijer, J., de Graaf, C. and Schreurs, H. *Recl. Trav. Chim. Pays-Bas 93* (1974) 46.
18. Maurin, R. and Bertrand, M. *Bull. Soc. Chim. Fr.* (1972) 2349 and further references therein.
19. Claesson, A., Tämnefors, I. and Olsson, L.-I. *Tetrahedron Lett.* (1975) 1509.
20. Mavrov, M. V., Rodionov, A. P., Prokof'ev, E. P. and Kucherov, V. F. *Zh. Org. Khim. 9* (1973) 658; *J. Org. Chem. USSR 9* (1973) 678.
21. Claesson, A. and Bogentoft, C. *Acta Chem. Scand. 26* (1972) 2540.
22. Mkryan, G. M., Kaplanyan, É. E. and Mndzhoyan, Sh. L. *Zh. Org. Khim. 5,* (1969) 1566; *J. Org. Chem. USSR 5* (1969) 1527.
23. Claesson, A., Olsson, L.-I. and Bogentoft. C. *Acta Chem. Scand. 27* (1973) 2941.
24. Bogentoft, C., Olsson, L.-I. and Claesson, A. *Acta Chem. Scand. B 28* (1974) 163; Polyakova, A. A., Zimina, K. I., Petrov, A.A and Khmel'nitskii, R. A. *Zh. Obshch. Khim. 30* (1960) 2977.
25. Olsson, L.-I., Claesson, A. and Bogentoft,. C. *Acta Chem. Scand. B 28* (1974) 765; Claesson, A. *Acta Universitatis Upsaliensis* (1975) No. 3. p. 10 (Dissertation).
26. Ficini, J. and Depezay, J.-C. *Bull. Soc. Chim. Fr.* (1966) 3878; Idem, *Tetrahedron Lett.* (1969) 4797; Baird, M. S. *Chem. Commun* (1974) 196
27 Henbest, H. B., Jones, E. R. H. and Walls, I. M. S. *J. Chem. Soc.* (1950) 3646.
28. Artsybasheva, Yu. P. and Favorskaya, I. A. *Zh. Obshch. Khim. 28* (1958) 3238.
29. Mantione, R. *Bull. Soc. Chim. Fr.* (1969) 4523.