Observation on the Synthesis of Allenes by Homologation of Alk-1-ynes

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An investigation is reported on the homologation of alk-1-ynes to allenes by the cuprous bromide-catalyzed reaction with formaldehyde and di-isopropylamine, including extension to an aromatic acetylene and a diacetylene. Optimization of yields was studied. A mechanism is proposed involving an intermediate hydrido-cuprate species derived from a 1 : 1 Mannich base–cuprous bromide π-complex. The mechanism is supported by labelling experiments and observed substituent effects.

Allenes have recently received considerable attention owing to the discovery of interesting biological properties,[1,2] as well as to the development of improved synthetic methods. Among the latter are several useful multi-step procedures for homologation of alk-1-ynes to terminal allenes.[3–7]

Recently, a relatively simple one-pot method of homologation was reported, consisting of the cuprous bromide-catalyzed reaction of an alk-1-yne (1) with formaldehyde and di-isopropylamine in refluxing dioxane to give the corresponding allene homologue (2).[8] In the initial example, an allenyl-substituted steroid was obtained in 31% yield. Subsequently the application of this method to the synthesis of eight alkyl- and α-functionalized alkyl-allenes in 26—97% yields was reported, indicating considerable generality.[9] More recently a mechanism for the conversion has been proposed,[10] but it does not account for the necessary metal salt catalysis.

$$RC{\equiv}CH + H_2C{=}O + Pr^i{}_2NH \longrightarrow RCH{=}C{=}CH_2$$
(1) (2)

In connection with our ongoing interest in the synthesis of biologically active allenes,[2,8,11] we have studied this reaction further and have deduced a mechanism which accounts for the catalysis. A modification of the previous procedure, employing a larger excess of formaldehyde and di-isopropylamine, gave better yields, as determined by either distillation or chromatographic isolation or by quantitative gas chromatographic (g.c.) analysis. The conversions were nearly free of side-products, as far as could be determined by g.c. or isolation; gas chromatography–mass spectroscopic (g.c.–m.s.) studies indicated the presence of small amounts of the diynes (3), expected from Glaser oxidative coupling[12] (due to presence of oxygen) and of varying amounts of the Mannich base (4) derived from starting materials.

$$RC{\equiv}C{-}C{\equiv}CR \qquad RC{\equiv}C{-}CH{-}NPr^i{}_2$$
(3) (4)

It was also observed that coloured precipitates separated from the mixture during the reaction. These precipitates were green in the case of alkylacetylenes, reddish brown from α-hydroxyacetylenes, and bright yellow from the reaction of phenylacetylene. Analysis of the precipitate isolated in the latter reaction is compatible with the structure, PhC≡C–Cu·CuBr. The others appeared to be mainly cuprous bromide, apparently complexed with an as yet unknown by-product.

† Deceased on 3 September 1981.

Table. Synthesis of allenes (2) from acetylenes (1)

No.	R	Reaction time (h)	Yields (%) G.c.	Isolation
a	$Me(CH_2)_4CH(OH)$	2	73,[a] 97 [b]	62
b	$(CH_2)_4C(OH)$	4	89,[a] 50 [b]	50
c	$Me_2C(OH)$	2.5		45
d	PhCH(OH) [b]	1.5	67	
e	$Me(CH_2)_7$	7	90, 65 [b]	
f	$Me(CH_2)_5$ [b]	5	26	
g	$(CH_2)_5CH^-$	7	65	
h	$Me(CH_2)_4CH(OAc)^-$ [b]	6	41	
i	$O(CH_2)_4CH^-O^-CH_2$	5	46	
j	$-(CH_2)_5-$	7	6 [c] + 16 [d]	
k	$HOCH_2(CH_2)_3$ [b]	23	26	
l	Ph	30	56 [a]	40

[a] Based on standard peak of pure allene. [b] Data from ref. 9. [c] Monoallene product, deca-1,2-dien-9-yne. [d] Diallene product, undeca-1,2,9,10-tetraene.

The yields and reaction times for the seven alkynes studied in this work (including an aromatic example and a diyne), in addition to the data on five other alkynes previously reported, are summarized in the Table. It may be noted that α-hydroxy substitution significantly increases the reactivity of the alkynes, while phenyl substitution and δ-hydroxyalkyl substitution seem to decrease it.

A two-step mechanism was previously proposed for this homologation, the first step being a cuprous bromide-catalyzed Mannich reaction and the second, a 1,5-sigmatropic rearrangement of hydrogen (Scheme 1).[10] The first step is a

$$RC{\equiv}CH + CH_2O + NHPr_2 \longrightarrow RC{\equiv}C{-}CH_2NPr^i{}_2$$
(1) (4)

$$RC{\equiv}C{-}CH_2{-}N{-}CHMe_2 \rightarrow RCH{=}C{=}CH_2 + Me_2CH{-}N{=}CMe_2$$
(2)

Scheme 1.

well known reaction,[13] and the presence of the Mannich base in the reaction mixture throughout most of the reaction can be demonstrated by g.c. monitoring. The second step has a precedent in the facile uncatalyzed thermolysis of 1-ethoxyalk-

1-ynes, which is considered to involve a 1,5-sigmatropic hydrogen shift.[14]

Additional evidence for this mechanism was the demonstration that pre-formed Mannich bases are converted into allenes by heating with a catalytic amount of cuprous bromide in *dioxane*.[9,10] This is, however, not absolute evidence for the intermediacy of Mannich bases in this reaction, because of the reversibility of the cuprous-catalyzed Mannich reaction. This does not appear to have been shown before, although the Mannich reaction of ketones has been demonstrated to be reversible.[15,16] When acetonitrile solutions of cuprous bromide and the Mannich base, 1-di-isopropylamino-3-phenylprop-2-yne (4l) (see Table) were mixed and heated, cleavage occurred to give phenylacetylene, isolated as a cuprous acetylide,* and presumably the di-isopropyliminium salt (5), since di-isopropylamine hydrobromide was isolated after exposure to moist air.

$$PhC{\equiv}C{-}CH_2NPr^i_2 + 2CuBr$$

(4l)

$$PhC{\equiv}C{-}Cu{\cdot}CuBr + CH_2{=}\overset{+}{N}Pr^i_2Br^-$$

(5)

$$\xrightarrow{H_2O,\ HBr}$$

$$Pr^i_2NH_2^+Br^-$$

Conclusive evidence in favour of the intermediacy of Mannich bases, however, was obtained by the use of [$^2H_2$]-formaldehyde in the reaction of three alkynes (1a, b, c), giving in each case the expected allene with complete dideuterio substitution (6) in the newly introduced methylene unit:

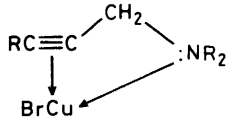
$$RC{\equiv}CH + D_2CO + Pr^i_2NH \longrightarrow \overset{1}{R}CH{=}\overset{2}{C}{=}\overset{3}{C}D_2$$

(1) (6)

Other deuterium labelling experiments have shown that the hydrogen atom introduced at C-3 in the allene product is derived from the α-hydrogen atom of the di-isopropylamine. Fillion *et al.*[10] reported that use of α-monodeuteriodi-isopropylamine gave an allene with the deuterium label at C-3 in the allene, as shown by n.m.r. spectroscopy. We have carried out experiments with [$^2H_8$]dioxane as solvent, with alk-1-ynes labelled with deuterium at C-1, and with deuterium oxide being used instead of water for quenching the reaction; in no case was deuterium labelling obtained.

While it seems certain that Mannich base formation is the rapid, reversible first step and that the new vinyl hydrogen introduced is derived from the amine, it does not necessarily follow that a direct 1,5-shift is involved. The necessity for the cuprous salt catalysis in this reaction, and the well known propensity for complexation of cuprous salts to complex with the acetylenic triple bond,[18] suggest that the copper atom may be involved in this stage.

We have some indication that the Mannich bases form π-complexes with cuprous bromide. First, there is a loss of the pale colour of cuprous bromide solution in dilute acetonitrile solution when Mannich base (4c) (see the Table) is added. Second, a precipitation of a white solid when concentrated solutions are used is compatible with cuprous halide–acetylene π-complexes, which are characteristically white.[17–20] Third, one observed a change in the u.v. absorption spectrum, in acetonitrile, with the 350 nm band of cuprous bromide disappearing or merging with the intense absorption at 220—290 nm. No u.v. studies have been reported on acetylene-copper(I) π-complexes before, but a shift of 122 cm^{-1} in the triple-bond stretching frequency in the i.r. spectrum of phenylacetylene has been attributed to π-complexing with cuprous chloride.[20] A shift of similar direction and magnitude was observed in the i.r. spectrum of compound (1c) (see the Table) on addition of cuprous bromide, confirming the tendency of copper(I) to complex at the triple bond. It is also possible that cuprous bromide complexes to the amino nitrogen atom,[21] but a chelated 1 : 1 complex, such as the organometallic complex (7), seems less likely, because the approximately 20—30° valence angle distortion of substituents on an acetylene group when the latter is π-complexed to copper(I), away from the metal atom,[22] would make it an unfavourably strained structure.



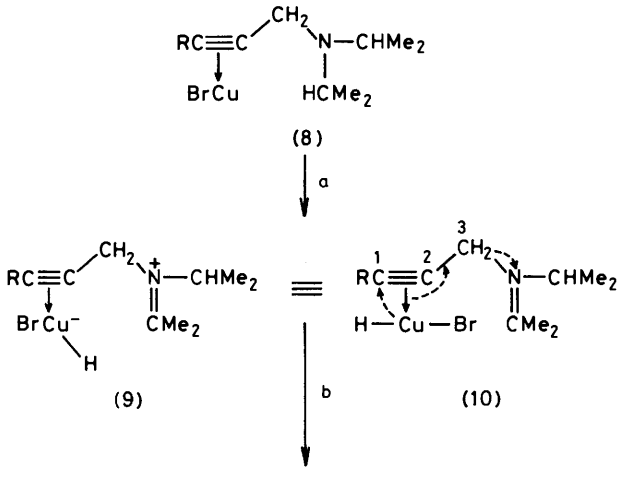
(7)

The 1 : 1 π-complex (8) seems to be ideally suited for loss of hydrogen from the α-position of an isopropyl group. In fact, an examination of the molecular model indicates that complex (8) may have a coplanar configuration with a CuH distance of less than 2 Å. Transfer of hydride ion to the copper atom would give a hydridocopper(I) complex (9) similar to the cuprate complex postulated by Pasto and co-workers [23] for the reaction of a lithium cuprate with prop-2-ynylic halides. It is also similar to known hydridoplatinum(II) chloride complexes and hydridonickel complexes [24] and to a hydridocopper acetate–quinoline complex proposed as an important intermediate in a catalytic hydrogenation method.[25] After rotation of the copper atom, the hydrogen atom would be in a favourable position for transfer to C-3, with concurrent development of the allene π-system and elimination of the amine product and cuprous bromide. These steps are outlined in Scheme 2.

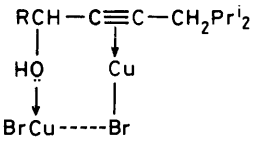
The observation that allene formation occurs much more slowly if diethylamine or di-n-butylamine is used instead of di-isopropylamine, would seem to indicate development of electron deficiency at the α-carbon atom of the amine in (or prior to) the rate-determining step. This would favour the sequence outlined in Scheme 2 and suggest that step (a) is rate-determining. Fillion and her co-workers' estimate [10] of a deuterium isotope effect, $k_H/k_D = 4$, for the α-deuterium substitution also indicates that abstraction of this hydrogen atom is the rate-determining step.

This interpretation seems to explain the enhanced reactivity associated with α-hydroxy substitution in the starting alkyne, as shown in the Table. This structure gives a possibility of bromide-bridged dicopper chelates (11). Such a structure can permit changes in electron density on copper to be shared by two copper atoms. The advantage of binuclear copper complexes for reducing the energy requirement for the electron density changes on copper, with resulting increase in reaction rates, has been observed previously for the cuprous chloride-

* The same PhC≡CCu·CuBr compound which precipitated in the alkyne homologation reactions was obtained.



Scheme 2.



catalyzed oxidation and cleavage of pyrocatechol and *o*-benzoquinone by molecular oxygen.[26,*]

A preliminary kinetic study was carried out to test the mechanism. The slow precipitation of cuprous bromide (in the coloured precipitate described previously) during the reaction does not allow determination of accurate rate constants, but initial reaction rate constants were reproducible. It was observed that the initial rate of reaction of Mannich base (4c) to form allene (2c) in dilute dioxane solution at 98 °C was not affected by the addition of four molecular equivalents of di-isopropylamine. This would indicate that *hydrogen transfer occurs intramolecularly from the amine moiety in the Mannich base*, rather than from a di-isopropylamine–copper–acetylene complex, conceivably formed from the free di-isopropylamine present due to the reversibility of the Mannich reaction.

In conclusion, it appears that this homologation of alk-1-ynes to allenes involves an intramolecular transfer of an α-hydrogen atom in an *N*-alkyl group of the intermediate Mannich base, to C-3 of the allene (10). This transfer, however, takes place in two steps, with the π-complexed Cu^{I} atom first accepting the hydrogen atom and then transferring it to the acetylenic carbon atom. Thus, a hydridocopper(III) species seems to be involved. The ability of copper to serve as both a supply and a sink for electrons, is the key to this process, as with most other cuprous-catalyzed reactions.[28]

Experimental

M.p.s were determined on a Fisher-Johns apparatus and are uncorrected. ^{1}H N.m.r. spectra were determined for $CDCl_3$ solutions (internal $SiMe_4$) with a Varian EM-360L 60 MHz spectrometer (*J* in Hz), and i.r. spectra were determined for neat samples with a Perkin-Elmer 237B spectrometer. Mass spectra were determined with a duPont 21-490 spectrometer and a C.E.C. 21-110 mass spectrometer. T.l.c. was carried out on pre-coated silica gel sheets type 60F-254 (Merck). Preparative t.l.c. was done on Silica Gel 60 GF-254 plates. Column chromatography was done on Silica Gel 60, 230–240 mesh (Merck), eluted with ethyl acetate–hexane (by gradient). Gas chromatography was carried out on a Tracor 222 instrument equipped with F.I.D., using a glass column 2 m × 2 mm, filled with 3% QF-1 on 100—120 mesh Chromosorb Q. G.c.–m.s. was done on a gas chromatographic system using a 2 m × 2 mm glass column filled with SE 30, 2.5% on Chromosorb W, coupled to a C.E.C. 21-110 double-focusing mass spectrometer.

General Procedure for Synthesis of Allenes.—A mixture of the acetylene, paraformaldehyde, di-isopropylamine, and anhydrous cuprous bromide, in the molecular ratio 1.0 : 2.5 : 2.0 : 0.5, was heated in dioxane (1.5 ml per mmol of acetylene) under reflux for the period of time given in the Table. The mixture was then cooled to room temperature and filtered. After the reaction flask and precipitate had been washed with ether, the solution was concentrated under reduced pressure, forming a gum-like residue, which was treated with dilute hydrochloric acid (pH 2 to 3) and extracted with diethyl ether several times. The combined ether extracts were washed with water to neutrality and with aqueous saturated sodium chloride. After being dried over magnesium sulphate, the ether solution was evaporated and the crude product remaining was subjected to g.c. analysis, with the identity of the allene peak confirmed by g.c.–m.s.[29] When the scale of preparation was 0.05 mol or larger (based on starting acetylene), it was fractionally distilled through a 10 cm Vigreux column. The yields and properties of the products are given in the Table and below.

4-*Hydroxynona*-1,2-*diene* (2a) from 3-hydroxyoct-1-yne (12.6 g), b.p. 41 °C at 0.15 mmHg; $\nu_{max.}$ 3 360—3 250 cm^{-1} (OH), 1 960 (C=C=C), and 850 (=CH); δ 5.22 (m, 1 H, 3-H), 4.8 (m, 2 H, 1-H), and 4.15br (s, 1 H, OH); *m/z* 140 (M^+, 0.4%), 122 (2.4%), and 69 (100%) (Found: $M^{+\cdot}$, 140.120 97. $C_9H_{16}O$ requires *M*, 140.120 11).

3-(1-*Hydroxycyclopentyl*)*propa*-1,2-*diene* (2b) from 1-ethynylcyclopentanol (5.5 g), b.p. 44—46 °C at 0.17 mmHg; $\nu_{max.}$ 3 360—3 200 (OH), 1 960 (C=C=C), and 840 (=CH) cm^{-1}; δ 5.40 (dd, 1 H, *J* 6.0 and 7.2, 3-H), 4.83 (d, 1 H, *J* 6.0), 4.82 (d, 1 H, *J* 7.2), 1.73br (8 H, cyclo CH_2); *m/z* 124 (M^+, 26%), 106 (82%), and 67 (100%) (Found: $M^{+\cdot}$, 124.089 38. $C_8H_{12}O$ requires *M*, 124.088 81).

4-*Hydroxy*-4-*methylpenta*-1,2-*diene* (2c) from 3-hydroxy-3-methylbut-1-yne (8.4 g), b.p. 117—120 °C; $\nu_{max.}$ 3 600—3 200 (OH), 1 947 (C=C=C), and 849 (=C–H) cm^{-1}; δ 5.32 (dd, 1 H, *J* 6.0 and 6.5), 4.84 (d, 2 H, *J* 6.5), 3.66 (s, 1 H, OH), and 1.33 (s, 6 H, CH_3); *m/z* 98 (M^+, 0.5%), 83 (10%), and 59 (100%) (Found: C, 73.05; H, 10.4. $C_6H_{10}O$ requires C, 73.43; H, 10.27). Because of the relatively low b.p. of this product, the reduced pressure concentration of the reaction mixture was omitted.

Undeca-1,2-*diene* (2e) from dec-1-yne (900 mg), $\nu_{max.}$ 1 960 (C=C=C), and 860 (=CH); δ 5.10 (m, 1 H, 3-H) and 4.65 (m, 2 H, 1-H); *m/z* 152 M^+ (0.1%) and 54 (100%) (Found: $M^{+\cdot}$, 152.156 51. $C_{11}H_{20}$ requires *M*, 152.156 49).

3-*Cyclohexylpropa*-1,2-*diene* (2g) from ethynylcyclohexane (500 mg), $\nu_{max.}$ 1 961 cm^{-1} (C=C=C), and 863 (=CH); *m/z* 122 M^+ (47%), 107 (82%), 93 (91%), 81 (82%), 80 (98%), 79 (90%), 67 (98%), and 55 (100%) (Found: $M^{+\cdot}$, 122.110 91. C_9H_{14} requires *M*, 122.109 54).

3-*Phenylpropa*-1,2-*diene* (2l) from phenylacetylene (5.1 g),

* A somewhat analogous argument for the electrochemical reduction of molecular oxygen by bridged dicobalt porphyrin complexes has been proposed by Collman *et al.*[27]

b.p. 80—95 °C at 20 mmHg; $\nu_{max.}$ 1 952 cm^{-1} (C=C=C) and 860 (C=CH) cm^{-1}; δ 6.18 (t, 1 H, *J* 7 Hz, 3-H) and 5.12 (d, 2 H, *J* 7 Hz, 1-H); *m/z* 116 (M^+, 67%) and 115 (100%) (Found: $M^{+\cdot}$, 116.062 75. C_9H_9 requires *M*, 116.062 59).

[$^2H_1$]*Dec-1-yne and Phenyl*[$^2H_1$]*acetylene.*—These were prepared by reaction of dec-1-yne and phenylacetylene, respectively, with an excess of butyl-lithium in hexane, followed by addition of D_2O, as described by previous workers.[30] The identity of the product was confirmed by i.r. and n.m.r. spectroscopy.

[N-^{2}H]*Di-isopropylamine.*—Di-isopropylamine (2 ml, 14 mmol) was stirred under argon with D_2O (10 ml, 0.5 mol) for 30 min. The solution was then dried with molecular sieve type 4A, and the amine collected by rinsing with anhydrous diethyl ether. Evaporation of the ether afforded the desired *N*-deuteriated amine with a labelling purity higher than 80% by n.m.r.

Retrograde Mannich Reaction.—To a stirred solution of 0.5 g of 1-di-isopropylamino-3-phenylprop-2-yne (4l) (prepared by the method of Mannich and Chang [31]) in acetonitrile (5 ml) at room temp., cuprous bromide (1.5 g) in acetonitrile (10 ml) was added. The reaction mixture was heated to 65 °C and stirred for an additional 30 min. The yellow precipitate formed was isolated by filtration, washed with dilute hydrochloric acid and then water, and dried (0.22 g). It was identical with the solid product obtained from the conversion of phenylacetylene into the corresponding allene, m.p. (decomp.) 270 °C; $\nu_{max.}$ 1 930 (C≡C) cm^{-1} (Found: C, 31.3; H, 1.6; Cu, 39.95; Br, 25.5. $C_8H_5Cu_2Br$ requires C, 30.86; H, 1.64; Cu, 41.24; Br, 25.93).

From the mother-liquor, white needles of di-isopropylammonium bromide separated; it was identified by identity of its i.r. spectrum (KBr disc) with that of authentic material.

Oxidation of Cuprous Phenylacetylide–Cuprous Bromide.—An excess of 30% hydrogen peroxide was added dropwise to a suspension of the above yellow precipitate (13.75 mg) in water (5 ml). After the resulting mixture had been stirred at room temperature for 20 h, it was filtered and extracted with ethyl acetate. The extracts were washed with water and dried over magnesium sulphate. The solvent was distilled under reduced pressure to leave a pale yellow solid (3.2 mg, 24.6%); recrystallization of this from hexane gave colourless needles, m.p. 83—85 °C (lit.,[32] 87 °C); $\nu_{max.}$ 2 150 cm^{-1} (C≡C); δ 7.2—7.7 (m); *m/z* 202 (M^+, 100%).

5-*Di-isopropylamino-2-methylpent-3-yn-2-ol* (4c).—A mixture of 2-methylbut-3-yn-2-ol (50 g, 0.6 mol), di-isopropylamine (44 g, 0.44 mol), paraformaldehyde (21.6 g, 0.72 mol), cuprous bromide (1.5 g) and dioxane (91 ml) was heated at 80 °C for 30 min. The mixture was cooled, diluted with water, acidified with hydrochloric acid to pH 2, and the neutral solution extracted with ether. The aqueous solution was made basic by addition of 10% potassium hydroxide with cooling. Extraction with ether, drying, and distillation gave a colourless oil (50 g, 59%), b.p. 80—82 °C at 1 mmHg; $\nu_{max.}$ 3 600—3 200 cm^{-1} (OH); δ 3.44 (s, 2 H, 5-H), 3.16 (hept., 2 H, *J* 6, C*H*Me_2), 2.29 (s, 1 H, OH), 1.6 (s, 6 H, CH_3), and 1.18 (d, 12 H, *J* 6, Pr^i-Me); *m/z* 197 (M^+, 7%), 182 (100%), 107 (14%), and 43 (96%) (Found: C, 72.95; H, 11.8. $C_{12}H_{23}NO$ requires C, 73.05; H, 11.75).

Kinetic Experiments.—Solutions of (4c) and cuprous bromide in dioxane, with or without di-isopropylamine, were stirred at 98 °C, with a reflux condenser provided to prevent vapour loss. Small aliquot samples were removed at 1 min intervals and analyzed by g.c. with a Carbowax on Chromosorb W column. The concentrations used of (4c), CuBr, and di-isopropylamine were, respectively: series 1: 1.32 M, 0.40 M, and either 0.0 or 1.21 M; series 2: 0.437 M, 0.133 M, and either 0.0, 0.4, or 0.8 M. The rate of reaction in each series of experiments was independent of the amine concentration. In addition, initial first order constants were calculated from the first order law and extrapolated to zero time; these also were independent of the amine concentration. (The first rate constants diminish regularly with time, due to the formation of a copper bromide precipitate as the reaction progresses.)

G.C.–M.S. Studies on the Crude Products.—In addition to the allenes previously described, the Mannich base was observed in each case. These all showed intense $M - 15$ peaks, usually as the base peak. This was proved by a metastable peak and by high-resolution mass measurement on the Mannich base derived from dec-1-yne. Oxidative coupling products [12] were found in the reactions of 1-ethylcyclopentanol and phenylacetylene; high resolution mass spectrometry on the former showed loss of H and H_2O.

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References

1 (*a*) D. F. Covey and C. H. Robinson, *J. Am. Chem. Soc.*, 1976, **98**, 5038; (*b*) H. L. Carrell, J. P. Glusker, D. F. Covey, F. H. Batzold, and C. H. Robinson, *ibid.*, 1978, **100**, 4282; (*c*) J. S. Cowie, J. D. Landor, and S. R. Landor, *J. Chem. Soc., Chem. Commun.*, 1969, 541; *J. Chem. Soc., Perkin Trans. 1*, 1973, 720.

2 M. Biollaz, R. Landeros, L. Cuellar, P. Crabbé, W. Rooks, J. A. Edwards, and J. H. Fried, *J. Med. Chem.*, 1971, **14**, 1190.

3 (*a*) P. Rona and P. Crabbé, *J. Am. Chem. Soc.*, 1969, **91**, 3289; (*b*) J. L. Luche, E. Barreiro, J. M. Dollat, and P. Crabbé, *Tetrahedron Lett.*, 1975, 4615; (*c*) J. M. Dollat, J. L. Luche, and P. Crabbé, *J. Chem. Soc., Chem. Commun.*, 1977, 761.

4 P. P. Vermeer, J. Meijer, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1975, **94**, 112; P. Vermeer, H. Westmijze, and H. Klein, *ibid.*, 1978, **97**, 56.

5 E. Galantay, I. Basco, and R. V. Coombs, *Synthesis*, 1974, 344.

6 T. Flood and P. E. Peterson, *J. Org. Chem.*, 1980, **45**, 5006.

7 F. Delbecq, R. Baudouy, and J. Goré, *J. Chem. Res.*, 1980, (*S*) 88; (*M*) 917, and references cited.

8 P. Crabbé, D. André, and H. Fillion, *Tetrahedron Lett.*, 1979, 893.

9 P. Crabbé, H. Fillion, D. André, and J. L. Luche, *J. Chem. Soc., Chem. Commun.*, 1979, 860; P. Crabbé, B. Nassim, and M. T. Robert-Lopes, *Org. Synth.*, in the press.

10 H. Fillion, D. André, and J. L. Luche, *Tetrahedron Lett.*, 1980, 929.

11 (*a*) P. Baret, E. Barreiro, A. E. Greene, J. L. Luche, M. A. Teixeira, and P. Crabbé, *Tetrahedron*, 1979, **35**, 2931; (*b*) P. Crabbé and H. Carpio, *J. Chem. Soc., Chem. Commun.*, 1972, 904; (*c*) P. Crabbé, M. Carpio, and A. Guzman, *Intra-Sci. Chem. Rep.*, 1972, **6** (1), 55; (*c*) D. M. Witherspoon, D. R. Lamond, F. N. Thompson, and W. Stevenson, *Theriogenology*, 1975, **3**, 21, 77.

12 C. Glaser, *Liebigs Ann. Chem.*, 1870, **154**, 137; reviewed by G. Eglinton and W. McCrae, *Adv. Org. Chem.*, 1963, **4**, 225—328.

13 M. F. Fegly, N. M. Bortnick, and C. H. McKeever, *J. Am. Chem. Soc.*, 1957, **79**, 4140; W. Reppe, E. Keyssner, and O. Hecht, U.S. Pat. 2 273 141 (Feb. 17, 1942) (*Chem. Abstr.*, 1942, **36**, 3806).
14 J. Nieuwenhuis and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, 1958, **77**, 761.
15 H. L. Brown, G. L. Buchanan, A. C. W. Curran, and G. W. McLay, *Tetrahedron*, 1968, **24**, 4565.
16 T. Hassel and D. Seeback, *Helv. Chim. Acta*, 1978, **61**, 2237.
17 W. Manchot, *Liebigs Ann. Chem.*, 1912, **387**, 257.
18 R. Vestin and C. Lofman, *Acta Chem. Scand.*, 1953, **7**, 398.
19 A. Borg, T. Lindblom, and R. Vestin, *Acta Chem. Scand., Ser. A*, 1975, **29**, 475.
20 I. A. Garbuzova, V. T. Aleksanyan, I. R. Gol'ding, and A. M. Sladkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, 2018.
21 J. T. Yoke III, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, 1963, **2**, 1210.
22 M. S. Pasquali, P. Leoni, C. Floriani, and A. Gaetani-Manfredotti, *Inorg. Chem.*, 1982, **21**, 4324.
23 D. J. Pasto, S.-K. Chou, E. Fritzen, R. H. Shults, A. Waterhouse, and G. F. Hennion, *J. Org. Chem.*, 1978, **43**, 1389.
24 'Transition Metal Hydrides,' R. Bau, ed., ACS Advances in Chemistry Series, No. 167, 1978.
25 B. R. James, 'Homogeneous Hydrogenation,' Wiley, New York, 1973, ch. 2; M. Calvin, *J. Am. Chem. Soc.*, 1939, **61**, 2230.
26 M. M. Rogić and R. R. Demmin, *J. Am. Chem. Soc.*, 1978, **100**, 5472.
27 J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval, and F. C. Anson, *J. Am. Chem. Soc.*, 1980, **202**, 6027.
28 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1970, p. 920.
29 S. Arseniyadis, J. Goré, and M. L. Roumestant, *Tetrahedron*, 1979, **35**, 353; J. R. Wiersig, A. N. H. Yeo, and C. Djerassi, *J. Am. Chem. Soc.*, 1977, **99**, 532.
30 J. C. Lavelly and J. Saussey in 'The Chemistry of the Carbon–Carbon Triple Bond,' S. Patai, ed., Wiley, New York, 1978, ch. 20.
31 C. Mannich and F. T. Chang, *Ber.*, 1933, **66**, 418.
32 J. P. Danehy and J. A. Nieuwland, *J. Am. Chem. Soc.*, 1936, **58**, 1609.

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