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REACTIONS OF t-ACETYLENIC HALIDES WITH GRIGNARD REAGENTS

PREPARATION OF CUMULENES

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Abstract—The diacetylenic chloride, 6-chloro-6-methyl-2,4-heptadiyne (I) reacted with methylmagnesium bromide to give a complex mixture of products, including the allene, 2-methyl-2,3-heptadien-5-yne (III). The treatment of the acetylenic dichloride, 2,5-dichloro-2,5-dimethyl-3-hexyne (VI) with methylmagnesium bromide gave the cumulene, 2,5-dimethyl-2,3,4-hexatriene (VII), and a similar reaction with 2,7-dichloro-2,7-dimethyl-3,5-octadiyne yielded the extremely unstable cumulene, 2,7-dimethyl-2,3,4,5,6-octapentaene (XII). The formation of these compounds can be explained by a functional exchange-elimination mechanism involving radicals.

INTRODUCTION

IN THE course of some work aiming at the synthesis of cumulative tetraenes our attention was focused on some papers by Zakharova[1] in which are described the formation of allenes[2] from reactions of t-propargylic halides with Grignard reagents. Others have also reported[3–6] similar results, and particularly the astounding results by Pasternak[7] are interesting in this connection. He reports the isolation of allenes in almost quantitative yields from reactions of t-propargylic bromides and methylmagnesium bromide. On the other hand Campbell and Eby[8] prepared t-acetylenes in good yields by reactions of t-propargylic chlorides with alkylmagnesium bromides. No allenes were reported as products of any of these reactions, although at that time no good method for the identification of such compounds was available. The best method still for the preparation of di-t-butylacetylene is the treatment of the appropriate propargylic chloride *viz.* 2-chloro-2,5,5-trimethyl-3-hexyne with methylmagnesium bromide.[9]

If an acetylene-allene rearrangement were to take place in a reaction of a Grignard reagent with a t-diacetylenic halide one of the expected products would be a cumulene with four double bonds:

$$R_2CX{-}C{\equiv}C{-}C{\equiv}C{-}R \xrightarrow{R'MgX} R_2C{=}C{=}C{=}C{=}CRR'$$

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[1] A. I. Zakharova, *Zh. Obshch. Khim.* **17**, 1277 (1947); *Chem. Abstr.* **42**, 3722 (1948); *Ibid.* **19**, 1297 (1949); *Chem. Abstr.* **44**, 1001 (1950); A. I. Zakharova and R. A. Sapozhnikova, *Ibid.* **22**, 1804 (1952); *Chem. Abstr.* **47**, 6857 (1953).

[2] T. L. Jacobs and R. A. Meyers, *J. Amer. Chem. Soc.* **86**, 5244 (1964), failed to obtain allenes from the reaction of 4-chloro-4-methyl-2-pentyne with methyl- or phenylmagnesium bromide. However more recent work (T. L. Jacobs, private communication) has shown that this reaction is very dependent on the conditions employed; allenes are obtained under slightly different conditions.

[3] T. Y. Lai, *Bull. Soc. Chim. Fr.* [4] **53**, 1537 (1933).

[4] M. Gaudemar, *Ann. chim.* [13] **1**, 161 (1956).

[5] A. A. Petrov and K. A. Molodova, *Zh. Obshch. Khim.* **32**, 3510 (1962).

[6] G. Peiffer, *Bull. Soc. Chim. Fr.* [5] **29**, 776 (1962).

[7] Y. Pasternak, *C. R. Acad. Sci. Paris* **255**, 3429 (1962).

[8] K. N. Campbell and L. T. Eby, *J. Amer. Chem. Soc.* **62**, 1798 (1940).

[9] G. F. Hennion and T. F. Banigan, *J. Amer. Chem. Soc.* **68**, 1202 (1946).

Reactions of α-halogenodiacetylenes with Grignard reagents had not previously been reported.

At the time the present work was initiated only cumulenes with an odd number of double bonds had been described.[10] Just recently Kuhn *et al.*[11] were able to prepare the first compounds containing four cumulative double bonds. The latter compounds are of considerable interest both from a stereochemical and spectroscopic point of view.

RESULTS

In order to test the possibility of such a diacetylene–tetraene rearrangement described above we chose as starting material 6-chloro-6-methyl-2,4-heptadiyne (I). It was prepared in 90% yield from the corresponding carbinol using concentrated aqueous hydrochloric acid and calcium chloride.[12] The reaction of I with methylmagnesium bromide proceeded, after an induction period, exothermally with gas evolution. From the reaction mixture a crystalline compound and a liquid were isolated together with some polymeric material. The former was proven to be 6,6,7,7-tetramethyl-2,4,8,10-dodecatetrayne (II), m.p. 140°, on the basis of analysis and spectroscopic evidence. Gas chromatography of the liquid revealed the presence of three compounds with close retention times and with a peak area ratio of approximately 7:3:1. We were able to separate each compound by preparative gas chromatography. The main product was assigned the structure 2-methyl-2,3-heptadiene-5-yne (III) on the basis of analysis, spectroscopic data, and the identity of III with a compound prepared from I with zinc in ethanol.[13] Only a small amount of the intermediate fraction was obtained pure, m.p. 27°. It exhibited an UV spectrum characteristic of a dialkyldiacetylene, and with additional information from the IR spectrum the structure 6-methyl-2,4-heptadiyne (IV) has been assigned to this substance. The physical data of the last and minor component were identical with those of 2-methyl-1-heptene-3,5-diyne (V). This compound was only in part a product of the reaction since the starting material I invariably contained small amounts of V. No evidence for the formation of the desired cumulene was obtained.

In one experiment the reaction mixture was decomposed with deuterium oxide. The compounds were separated and both II and V were found to be unchanged. However, the IR and NMR spectra of the allene showed clearly that 4-deuterio-III was actually formed, and the IR spectrum of the diacetylene indicated that deuterium was incorporated at the tertiary carbon of the isopropyl group. The mechanistic significance of these results will be discussed later.

The halide was normally added to the Grignard reagent, and as expected variations in the concentration of the latter changed the rate of the reaction. In addition, however, the product ratio also appeared to be influenced. At higher concentrations (> 1 mol/litre) considerably more of II was formed, while the amount of liquid product was reduced. The latter still consisted of the compounds III, IV, and V

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[10] For a review on this subject see P. Cadiot, W. Chodkiewicz and J. Rauss-Godineau, *Bull. Soc. Chim. Fr.* [5] **28**, 2176 (1961), and also R. Kuhn and B. Schulz, *Chem. Ber.* **96**, 3200 (1963).

[11] R. KUHN, H. FISCHER and H. H. FISCHER, *Chem. Ber.* **97**, 1760 (1964).

[12] G. F. Hennion, J. J. Sheehan and D. E. Maloney, *J. Amer. Chem. Soc.* **72**, 3542 (1950).

[13] Treatment of propargylic halides with Zn is a general route to allenes [G. F. Hennion and J. J. Sheehan, *J. Amer. Chem. Soc.* **71**, 1964 (1949)]. Relatively pure allenes, however, are obtained only from t-halides; with secondary and primary halides one gets much more of the normal acetylenic products [T. L. Jacobs, E. G. Teach and D. Weiss, *Ibid.* **77**, 6254 (1955)].

together with a small amount of a fourth compound, the structure of which has not been investigated. A reaction took place also with ethylmagnesium bromide. The product consisted of all the compounds described above besides two higher-boiling compounds, which were not investigated because of separation difficulties.

With methylmagnesium bromide the gaseous product consisted of ethane and traces of methane, and from reactions with ethylmagnesium bromide the gas was shown to be a mixture of ethane and ethylene in approximately equal amounts. No alkyl chlorides could be detected. The following scheme summarizes the results:

$$\underset{\text{I}}{(CH_3)_2CCl-C\equiv C-C\equiv C-CH_3} \xrightarrow{RMgBr} \underset{\text{II}}{[CH_3-C\equiv C-C\equiv C-C(CH_3)_2-]_2} +$$

$$\underset{\text{III}}{(CH_3)_2C=C=CH-C\equiv C-CH_3} + \underset{\text{IV}}{(CH_3)_2CH-C\equiv C-C\equiv C-CH_3} +$$

$$\underset{\text{V}}{CH_2=C(CH_3)-C\equiv C-C\equiv C-CH_3} + R_2 \text{ or } R_{(-H)} + R_{(+H)}$$

$$(R=CH_3 \text{ or } C_2H_5)$$

Despite the fact that no cumulene was obtained from this reaction, the formation of the allene III proved indeed that a rearrangement had taken place. This prompted us to study the reaction of Grignard reagents with t-acetylenic dihalides because of the possibility of obtaining cumulenes in this way.

The first dihalide to be studied was 2,5-dichloro-2,5-dimethyl-3-hexyne (VI). The reaction of this chloride with methylmagnesium bromide proceeded smoothly at room temperature with gas evolution. From the reaction mixture a highly oxygen-sensitive crystalline compound, m.p. 40°, was obtained in about 90% yield. It was subsequently assigned the structure of a cumulene, *viz.* 2,5-dimethyl-2,3,4-hexatriene (VII), on the basis of the following evidence: the carbon–hydrogen ratio agreed with the formula C_6H_{12}. The IR spectrum showed a weak band at 1900 cm^{-1} and a medium intensity band at 1645 cm^{-1}. It is well established that the carbon–carbon stretching vibration of an allenic grouping gives rise to an intense band in the 1950 cm^{-1} region.[14] It appears that also cumulenes generally exhibit absorption in approximately the same region. Butatriene[15] shows medium intensity absorption at 2030 and an intense band at 1610 cm^{-1}, and the pentaene bis[2,2,6,6-tetramethylcyclohexylidene]butatriene (XI)[16] absorbs weakly at 1980 cm^{-1}.[17] Aryl-substituted cumulenes also show a weak band in the 2000 cm^{-1} region,[18] and the particularly interesting compound 5-methyl-2,3,4-hexatrienal absorbs intensely at 2066 cm^{-1}.[19]

The NMR spectrum showed only one single peak at 8·19τ in accordance with the structure VII. Furthermore, UV absorption maxima at 230 and 262·5 mμ are in good agreement with maxima at 230 and 271·5 mμ observed for the similar triene bis[2,2,6,6-tetramethylcyclohexylidene]ethylene (VIII).[16]

Both Krestinsky[20] and Zalkind[21] reported that the cumulene VII was the product

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

[15] W. M. Schubert, T. H. Liddicoet and W. A. Lanka, *J. Amer. Chem. Soc.* **76**, 1929 (1954). See also C. J. Cyvin, *Acta. Chem. Scand.* **17**, 2123 (1963).

[16] F. Bohlmann and K. Kieslich, *Chem. Ber.* **87**, 1363 (1954).

[17] F. Bohlmann, private communication.

[18] W. Otting, *Chem. Ber.* **87**, 611 (1954); R. Kuhn and H. Fischer, *Ibid.* **92**, 1849 (1959).

[19] E. M. Kosower and T. S. Sorensen, *J. Org. Chem.* **28**, 687 (1963).

[20] W. Krestinsky, *Ber. Dtsch. Chem. Ges.* **59**, 1930 (1926).

[21] Y. S. Zalkind, B. Rubin and A. Kruglow, *J. Russ. Phys. Chem. Soc.* **58**, 1044 (1926); *Chem. Abstr.* **22**, 1137 (1928).

from zinc reduction of 3,4-dihalo-2,5-dimethyl-2,4-hexadienes. This was later confirmed,[22] and it was furthermore shown that treatment of the chloride VI with zinc also yielded VII, with physical data identical to those presented here.

As already observed by the Russian authors[20,21] the cumuleme VII is extremely sensitive to oxygen. Both in solution and in the crystalline state mixtures of polymeric oxides $(C_6H_{12}O_2)_x$ were formed, practically insoluble in most ordinary solvents. A substance, m.p. 112–113°, was separated from the mixture by extraction with chloroform. The compound was thermally unstable and decomposed violently, when heated rapidly above its m.p. The low solubility, however, hampered the structural investigation. The IR spectrum showed strong absorption at 1142 cm^{-1} in the region of the carbon–oxygen stretching vibration. Two sharp bands at 1355 and 1320 cm^{-1} indicated the presence of *gem*-dimethyl groups. Furthermore, a weak maximum at 1625 cm^{-1} might be due to double bonds. The compound liberated iodine from a solution of potassium iodide in acetic acid, and acetone was obtained by ozonolysis. Based on this evidence the general structure IX has been proposed for the polymeric peroxides.

The reaction of VI with methylmagnesium bromide has previously been reported in the literature. Hennion and Banigan[9] obtained only an insoluble white substance which decomposed by heating. It is probably identical with the mixture of polymeric peroxides described here. These authors also mention the evolution of an inflammable gas during the reaction. Levina and Shabarov[23] obtained, besides the polymeric material, an unstable liquid. This, they suggested, was a mixture of 5-chloro-2,5-dimethyl-1-hexen-3-yne and 2,5-dimethyl-1,5-hexadien-3-yne. We were not able to detect either of these compounds in our reaction mixture, although they may have been present in small amounts. The same authors have also described the treatment of 1,4-dichloro-2-butyne[24] and 2,5-dichloro-3-hexyne[25] with alkylmagnesium halides. In the former case in addition to a small yield of the normal condensation product i.e. the respective dialkylacetylene, the main product was a polymer $(C_4H_4)_x$. In view of the present results it is most likely the polymeric substance derived from butatriene, bearing in mind the extreme instability of this cumulene.[16] In the other paper[25] only the condensation products were described.

The diacetylenic halide 2,7-dichloro-2,7-dimethyl-3,5-octadiyne (X) reacted in a similar way with methylmagnesium bromide yielding a substance too unstable to be isolated. In fact polymerization occurred to a considerable extent during the reaction. Only qualitative IR and UV spectra were obtained on solutions of this product. The former showed a weak band at 2002 cm^{-1} and a somewhat stronger band at 1625 cm^{-1}, similar to those observed for VII. The UV spectrum exhibited a high intensity maximum at 228 mμ and maxima at 215, 308, and 321 mμ with about one fifth the intensity of the former. The spectrum compares very well with that of the pentaene (XI) prepared by Bohlmann and Kieslich,[16] which showed maxima at 225, 238, 317 and 339 mμ. Furthermore, the product showed the same spectral properties as the product obtained from a reaction of the chloride X with zinc in ether.[22] On the basis of this

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[22] E. R. H. Jones, L. Skattebøl and M. C. Whiting, unpublished results.

[23] R. Ya. Levina and Yo. S. Shabarov, *Vestnik Moscovskova Universiteta*, **8**, No. 2, *Ser. Fiz.-Mat. i Estestven. Nauk*. No. 1, 77 (1953); *Chem. Abstr.* **49**, 5261 (1955).

[24] R. Ya. Levina and Yo. S. Shabarov, *Dokl. Akad. Nauk. S.S.S.R.* **84**, 509 (1952).

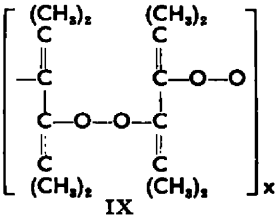
[25] R. Ya. Levina and Yo. S. Shabarov, *Dokl. Akad. Nauk. S.S.S.R.* **84**, 709 (1952).

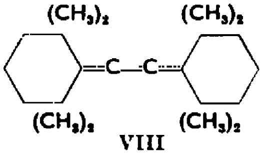
information the cumulene structure 2,7-dimethyl-2,3,4,5,6-octapentaene (XII) has been assigned to this compound, which also is in accordance with its extreme tendency to polymerize and oxidize.

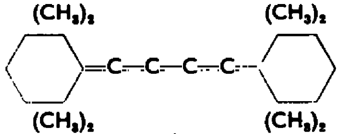
$$\underset{\text{VI}}{(CH_3)_2CCl-C\equiv C-CCl(CH_3)_2} \xrightarrow{CH_3MgBr} \underset{\text{VII}}{(CH_3)_2C=C=C=C(CH_3)_2}$$

$$\underset{\text{X}}{(CH_3)_2CCl-(C\equiv C)_2-CCl(CH_3)_2} \xrightarrow{CH_3MgBr} \underset{\text{XII}}{(CH_3)_2C=C=C=C=C=C(CH_3)_2}$$

$$\underset{\text{XIII}}{(CH_3)_2CBr-CBr(CH_3)_2} \xrightarrow{RMgBr} \underset{\text{XIV}}{(CH_3)_2C=C(CH_3)_2}$$


IX


VIII


XI

In the reaction of both VI and X dehalogenation had obviously taken place, and it was subsequently shown that the *vic.* dihalide 2,3-dibromo-2,3-dimethylbutane (XIII) reacted readily with methylmagnesium bromide yielding 2,3-dimethyl-2-butene (XIV) as the sole isolable product.

The gases obtained from the last reactions showed the same structural relationship to the Grignard reagent used as already described for the reactions of the chloride I. The fact that ethane was almost exclusively formed using methylmagnesium bromide led us into the thought that this dehalogenation reaction also could be useful as a way of dimerizing Grignard reagent radicals under rather mild conditions. The dibromide XIII was chosen for this study because it is reasonably stable, and moreover the product XIV is quite volatile.

The reaction of XIII with phenylmagnesium bromide gave biphenyl in 77% yield. More interesting, however, was the reaction with phenylacetylenylmagnesium bromide, which produced 1,4-diphenyl-1,3-butadiyne (XV). It was necessary to heat this reaction for several hours in order to obtain a reasonable yield of XV, and with 1-butynylmagnesium bromide no 3,5-octadiyne was detected even after 24 hours of heating under reflux.

DISCUSSION

Despite the fact that a great number of reactions of Grignard reagents with organic halides have been reported, it is still one of the least understood Grignard reactions.[26] One of the main reasons for this is most probably the fact that most of the work has been carried out with impure magnesium of undefined quality. It was first discovered by Kharasch and co-workers[26] that these impurities, particularly transition metals, can lead to drastic changes in the reaction path. Furthermore any detailed mechanistic

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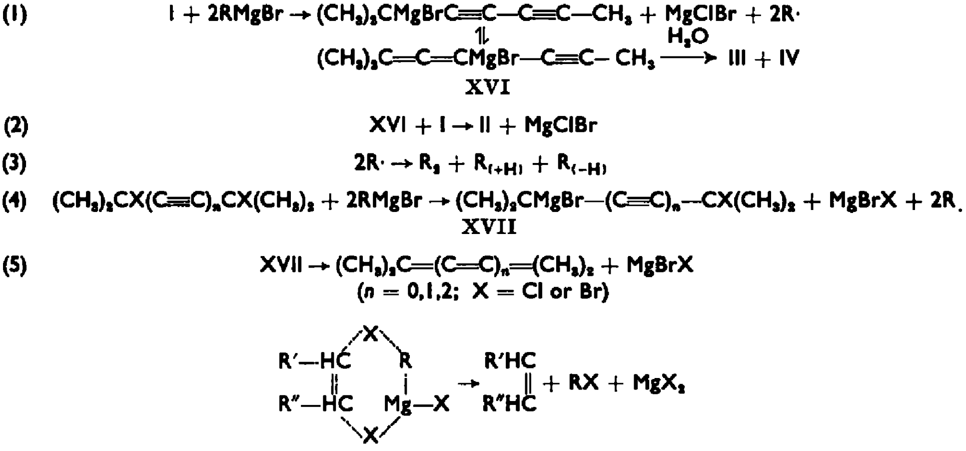
[26] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances* Chap. V and XVII Prentice-Hall, New York (1954).

study of Grignard reactions has been hampered by the uncertainty as to the structure of the reagent, which even at present is very much a matter of controversy.[27] For the present work only an attempt will be made to rationalize the results into a mechanistic scheme.

The reactions taking place between alkyl halides and Grignard reagents can be divided into three principal classes[26] *viz.* (a) condensation, (b) coupling, and (c) functional exchange. The last two reactions appear to be of a radical type. They are strongly influenced by catalytic amounts of heavy metal salts, and evidence for the presence of *free* radicals in such induced reactions has been obtained.[28] Our results can all be explained by assuming a functional exchange as the first step as depicted in Chart 1. Functional exchange is a well known reaction in organolithium chemistry,[29] but in Grignard reactions it has been regarded as rather obscure, in particular the uncatalyzed reaction.[26] Recent work,[30,31] however, suggests that it might be considerably more common than previously thought. The literature contains a number of reactions for which a functional exchange mechanism could be involved. In connection with the present work some reactions of *vic.* dihalides are of special interest. A 60% yield of cyclohexene has been obtained from *trans*-1,2-dibromocyclohexane and isopropyl magnesium bromide in the presence of cobaltous chloride,[32] and a gas consisting of propane and propylene evolved during the reaction. The reaction has

Chart 1



(1) $\mathrm{I} + 2\mathrm{RMgBr} \rightarrow (\mathrm{CH_3})_2\mathrm{CMgBrC{\equiv}C{-}C{\equiv}C{-}CH_3} + \mathrm{MgClBr} + 2\mathrm{R}\cdot$

$\rightleftharpoons$

$(\mathrm{CH_3})_2\mathrm{C{=}C{=}CMgBr{-}C{\equiv}C{-}CH_3} \xrightarrow{\mathrm{H_2O}} \mathrm{III} + \mathrm{IV}$

XVI

(2) $\mathrm{XVI} + \mathrm{I} \rightarrow \mathrm{II} + \mathrm{MgClBr}$

(3) $2\mathrm{R}\cdot \rightarrow \mathrm{R_2} + \mathrm{R_{(+H)}} + \mathrm{R_{(-H)}}$

(4) $(\mathrm{CH_3})_2\mathrm{CX}(\mathrm{C{\equiv}C})_n\mathrm{CX}(\mathrm{CH_3})_2 + 2\mathrm{RMgBr} \rightarrow (\mathrm{CH_3})_2\mathrm{CMgBr}{-}(\mathrm{C{\equiv}C})_n{-}\mathrm{CX}(\mathrm{CH_3})_2 + \mathrm{MgBrX} + 2\mathrm{R}\cdot$

XVII

(5) $\mathrm{XVII} \rightarrow (\mathrm{CH_3})_2\mathrm{C}{=}(\mathrm{C{=}C})_n{=}(\mathrm{CH_3})_2 + \mathrm{MgBrX}$

$(n = 0,1,2;\ \mathrm{X} = \mathrm{Cl\ or\ Br})$

XVIII

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[27] For a review on this subject see R. M. Salinger in *Survey of Progress in Chemistry* p. 301. Academic Press, New York (1963) and also R. E. Dessy, S. E. I. Green and R. M. Salinger, *Tetrahedron Letters* 1369 (1964).

[28] M. S. Kharasch, F. L. Lambert and W. H. Urry, *J. Org. Chem.* **10**, 298 (1945); M. S. Kharasch and W. H. Urry, *ibid.* **13**, 101 (1948).

[29] The mechanism of the reaction is still uncertain. For a review see R. G. Jones and H. Gilman, *Organic Reactions* **6**, 339 (1951).

[30] R. T. Morrison, N. P. Loire and F. L. Bach, Jr., *Abstr. of papers, ACS meeting* p. 20. Cleveland, Ohio, April 5–14 (1960).

[31] L. H. Slaugh, *J. Amer. Chem. Soc.* **83**, 2734 (1961); see however M. S. Kharasch, M. Weiner, W. Nudenberg, A. Bhattacharya, T. I. Wang and N. C. Yang, *Ibid.* **83**, 3232 (1961).

[32] M. S. Kharasch, J. S. Sallo and W. Nudenberg, *J. Org. Chem.* **21**, 129 (1956).

also been reported[33] to proceed without the presence of a metallic catalyst. The reaction of 2,3-dichloro-1,4-dioxane with methylmagnesium bromide gave mainly 1,4-dioxane along with a gas consisting essentially of ethane,[34] the amount corresponding very well with that of 1,4-dioxane. More recently diisobutenyl ether was prepared[35] in 65% yield by dehalogenation of the corresponding tetrabromide with ethylmagnesium bromide.

In Chart 1 the functional exchange reaction (reactions 1 and 4) is depicted as a radical reaction, which is strongly indicated by the products derived from the different Grignard reagents. However, the absence of any significant amounts of products expected from a reaction of the radical with the solvent[36] precludes the presence of *free* radicals in the reaction, and it is suggested that the radical is complexed in some way with the magnesium of the Grignard reagent or the magnesium halide. Kochi and Rust[37] have recently shown that metal ions can promote the dimerization of methyl radicals.

Irrespective of the actual functional exchange mechanism the isolation of 4-deuterio-III proves that in this particular reaction (Chart 1, reaction 1) such an exchange took place, and the predominant formation of III rather than IV by hydrolysis is explained by the equilibrium between the acetylenic and allenic structures in XVI. There is precedent for expecting this equilibrium to be shifted towards the allenic structure. The Grignard derivative of 2-bromo-2-methyl-3-octyne gave upon carbonation only the allenic acid *viz.* 4-carboxy-2-methyl-2,3-octadiene.[38] Moreover, it is well established that propargylmagnesium halide really has the allenic structure in ether solution.[39] The formation of the dimer II can be vizualized by condensation of the Grignard reagent XVI with the chloride I (reaction 2). A coupling reaction, however, would give the same result and there is really no experimental reason for preferring one for the other. Since no allenic dimer was obtained, it appears that in this particular reaction the acelyenic isomer of XVI is the most reactive. It has been shown that several allenyl Grignard reagents condense with carbonyl compounds to give the corresponding acetylenic carbinols. The formation of 2-methyl-1-heptene-3,5-diyne (V) can be explained by dehydrohalogenation of I,[40] but it is doubtful whether this compound really is a product of the reaction (see above).

In the case of the dihalides functional exchange would produce the Grignard derivative of the general structure XVII (reaction 4), and subsequent elimination of magnesium halide (reaction 5) would lead to products in agreement with the experimental results. It is reasonable to expect the elimination step to be very fast,[41] which would explain why these reactions gave essentially no by-products, assuming the

[33] M. Mousseron and F. Winternitz, *Bull. Soc. Chim. Fr.*, [5] **13**, 604 (1946).

[34] R. K. Summerbell and L. N. Bauer, *J. Amer. Chem. Soc.* **57**, 2364 (1935); **58**, 759 (1936).

[35] B. T. Gillis and K. F. Schimmel, *J. Org. Chem.* **25**, 2187 (1960).

[36] Methyl radicals react with diethyl ether giving methane, ethane, and ethylene; M. S. Kharasch, F. Engelmann and W. H. Urry, *J. Amer. Chem. Soc.* **66**, 365 (1944).

[37] J. K. Kochi and F. F. Rust, *J. Amer. Chem. Soc.* **83**, 2017 (1961).

[38] J. H. Wotiz and R. T. Palchak, *J. Amer. Chem. Soc.* **73**, 1971 (1951).

[39] C. Prevost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar and M. Andrac, *Bull. Soc., Chim. Fr.* [5] **26**, 679 (1959).

[40] Dehydrohalogenation by Grignard reagents is not a common reaction[28] and more drastic conditions are usually required than those employed here.

[41] The related 1-lithio-2-halo-alkanes eliminate lithium halide even at −110°, G. Köbrich and K. Flory, *Tetrahedron Letters* 1137 (1964).

functional exchange as the rate determining step. Clearly the mechanism suggested by Kharasch[28] involving a cyclic transition state (XVIII) is not compatible with the experimental data.

In order to establish whether the reactions were influenced by the small amounts of impurities present in the commercial magnesium, methylmagnesium bromide was prepared from sublimed magnesium.[42] The reaction of this with the dibromide XIII did take place, but on the other hand addition of a few crystals of anhydrous ferric chloride caused a considerable rate increase, the products remaining the same. Similar results were obtained with the other reactions and hence they may be regarded, with certainty in the case of I, as examples of noncatalysed functional exchange reactions.

EXPERIMENTAL

Grignard reagents. These were prepared in the usual way from Mg and the respective bromide with absolute ether as solvent. The reagent thus obtained was allowed to settle, and the clear supernatant solution transferred to a storage flask previously flushed with N_2. The concentration was determined by adding an aliquot to standard HCl, and then titrating to phenolphthalein endpoint with standard NaOH.

Table 1. Magnesium Analysis

Element	Impurities in ppm. Grignard grade	Sublimed
Al	50	ND
Cu	10	4
Cr	1	ND
Fe	40	10
Mn	400	ND
Ni	3	ND
Si	4	1
Zn	30	10

ND = not detected. In addition the elements Co, Ti, V, and Ag were not detected in either of the samples.

The bromides were freshly distilled before use. Grignard grade Mg turnings and sublimed Mg[42] were used, and both were analyzed spectroscopically.[43]

6-*Chloro*-6-*methyl*-2,4-*heptadiyne* (I). A mixture of 30·5 g (0·25 mole) 2-methylhepta-3,5-diyn-2-ol,[44] 28 g (0·25 mole) $CaCl_2$, 104 ml conc. HCl, and a small amount of hydroquinone was mechanically shaken for 3½ hr. The product was extracted with pet. ether (30–40°), and the extract treated with anhydrous Na_2CO_3. Distillation of the solvent and fractionation of the residue gave 31·8 g (90%) of I, b.p. 64–69° (10 mm), n_D^{20} 1·5116; λ_{max} (EtOH) 223 (ε 620) 234 (970), 247 (1245), and 261 mμ (930). An additional maximum appeared at 277 mμ. This belongs to V, and on the basis of the extinction coefficient it is present in about 1%. Analysis by gas chromatography was unsuccessful because of decomposition. Found: C, 68·68; H, 6·60. Calc. for C_8H_9Cl: C, 68·33; H, 6·45%.)

2,5-*Dichloro*-2,5-*dimethyl*-3-*hexyne* (VI). A mixture of 188 g (1·32 moles) 2,5-dimethyl-3-hexyne-2,5-diol, 294 g (2·65 moles) $CaCl_2$, 1110 ml conc. HCl and 0·2 g hydroquinone was shaken mechanically for 4 hr. The product was extracted with pet. ether (30–40°), and the extract dried (Na_2CO_3). Distillation through a column gave 145 g (61%) of VI, b.p. 64–67° (15 mm), n_D^{25} 1·4612. The compound solidified by cooling and was further purified by recrystallization from a small amount of pet. ether (30–40°), m.p. 24°, n_D^{25} 1·4582 (reported[9] m.p. 22–23°, n_D^{20} 1·4602).

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[42] We thank Societe General du Magnesien, France, for a generous gift of this grade of magnesium.

[43] Kindly carried out by Mr. F. Haftka. The results are shown in Table 1.

[44] W. Chodkiewicz, *Ann. chim.* **2**, 819 (1957).

2,7-Dichloro-2,7-dimethyl-3,5-octadiyne (X). A mixture of 26·0 g (0·157 mole) 2,7-dimethyl-3,5-octadiyne-2,7-diol,[45] 35 g (0·315 mole) $CaCl_2$, 130 ml conc. HCl and a small amount of hydroquinone, was shaken mechanically for 5 hr. The reaction mixture was filtered and the product extracted with pet. ether (30–40°); 2·5 g unreacted diol, which is practically insoluble in this solvent, was recovered. The extract was dried (Na_2CO_3), and the solvent subsequently evaporated under red. press. Recrystallization of the residue from MeOH gave 20·0 g (70%) of X as colourless needles, m.p. 68–71° (reported[46] m.p. 69°).

Reaction of 6-chloro-6-methyl-2,4-heptadiyne (I)

With methylmagnesium bromide. The chloride I (14·8 g; 0·105 mole) in 15 ml dry ether was added dropwise during 1 hr to MeMgBr (170 ml; 0·70 M) with stirring at room temp. The reaction mixture was stirred overnight and finally heated under reflux for 1 hr. The gas that evolved during the reaction passed through a trap cooled to −78° and was collected over water. The reaction mixture was hydrolysed with dil. HCl aq. The product was isolated in the usual way, and distillation gave 6·1 g liquid, b.p. 50–52° (13 mm), n_D^{26} 1·4998. From the residue 4·1 g of a crystalline compound was obtained. Purification by chromatography on alumina and recrystallization from MeOH gave II as colourless crystals, m.p. 140°; λ_{max} (EtOH) 218 (ε 1200), 230 (1450), 242 (1640), and 255 (990) mμ. (Found: C, 91·14; H, 8·54. Calc. for $C_{16}H_{18}$: C, 91·37; H, 8·63%.) The NMR spectrum[47] shows singlets at τ: 8·68 ($-CH_3$) and 8·10 ($CH_3{-}C{\equiv}C$), with peak area ratio 2:1.

Gas chromatography of the liquid revealed the presence of essentially three compounds A, B, and C in 64, 27 and 9% respectively. There was a small amount of a fourth component at almost the same retention time as compound C, which we were not able to separate. The other compounds were obtained pure by preparative gas chromatography:

Compound A was shown to be III, b.p. 50° (13 mm.), n_D^{25} 1·5023; λ_{max} (*n*-hexane) 220 mμ (ε 17300). (Found: C, 90·26; H, 9·43. Calc. for C_8H_{10}: C, 90·50; H, 9·50%.) The IR spectrum shows weak bands at 2220 ($-C{\equiv}C-$) and 1950 cm^{-1} ($>C{=}C{=}C<$). A strong band at 790 cm^{-1} is probably the out of plane bending vibration of an allenic hydrogen. The NMR spectrum shows a multiplet at τ: 4·99 ($C{=}C{=}C{-}H$) and doublets at 8·17 ($-C{\equiv}C{-}CH_3$) and 8·33 ($(CH_3)_2C{=}C$), with relative peak areas 1:3:6.

Compound B was difficult to separate from the other two components. After repeated preparative gas chromatography a liquid was obtained, n_D^{25} 1·4792, which after low temp crystallization from pentane melted at 27°; λ_{max} (*n*-hexane) 214 (ε 250), 225 (330), 238 (340) and 253 mμ (220). The IR spectrum shows weak bands at 2190 and 2150 cm^{-1} ($-C{\equiv}C{-}C{\equiv}C-$) and the absence of double bond and allenic absorption. Two bands at 1362 and 1378 cm^{-1} are indicative of an isopropyl group. Unfortunately, not enough material was available for either NMR spectrum or C, H analysis. On the basis of this evidence structure IV is assigned to this compound.

Compound C was shown to be V by the identity of the IR and UV spectra with those of an authentic sample (see below).

The gas which evolved in the reaction was analysed by gas chromatography on a 12 ft column of 30% *n*-heptane on Embacel[48] at −78°. When MeMgBr was used in the reaction the gas consisted of 99·9% ethane and traces of methane, and in the case of EtMgBr 61% ethane, 39% ethylene and traces of methane were detected. With the use of MeMgBr, prepared from sublimed Mg, the gas consisted of 99% ethane with traces of ethylene and methane.

Hydrolysis with deuterium oxide. The reaction mixture from 14·1 g (0·1 mole) I and MeMgBr (140 ml; 1·50 M) was cooled, and 15 ml 99% D_2O was added. After 3 hr at room temp some 2 M HCl was added and the product isolated as described above, yielding 4·4 g of the liquid mixture. The components were separated by preparative gas chromatography, and the IR and NMR spectra compared with those described above.

Compound A. The band at 790 cm^{-1} is absent in the IR spectrum, and a new weak band at 2225 cm^{-1} has appeared. It is at the expected region for the olefinic C—D stretching vibration. In the NMR spectrum the absorption at τ: 4·99 due to the allenic proton is absent.

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[45] N. A. Milas and O. L. Mageli, *J. Amer. Chem. Soc.* **75**, 5970 (1953).

[46] C. Cook, Thesis, University of Manchester (1951).

[47] The NMR spectra were recorded at 60 Mc. with a Varian spectrometer. CS_2 or CCl_4 were used as solvents, and tetramethylsilane as internal standard.

[48] R. S. Porter and J. F. Johnson, *Analyt. Chem.* 33, 1152 (1961).

Compound B. A medium strong band at 1320 cm^{-1}, which is present in the nondeuterated compound, is absent. This is probably the C—H bending vibration of a t-hydrogen. A new weak band is present at 760 cm^{-1}. Otherwise the spectra are identical.

2-*Methyl*-2,3-*heptadiene*-5-*yne* (III). The chloride I (14·05 g; 0·1 mole) was added dropwise during 45 min to a stirred slurry of 10·4 g (0·16 g atom) of Cu activated Zn powder in 40 ml abs. EtOH. The reaction was exothermic, and after this had subsided, heating at 60–70° was applied for 30 min. Solvent and volatile products were distilled under red. press. (0·1 mm) into a cooled flask. Brine was added, and the organic layer separated and dried ($CaCl_2$). The liquid (5·5 g) was shown by gas chromatography to consist to 80% III along with two other components. The allene (III) was obtained pure by preparative gas chromatography, n_D^{24} 1·5056. The IR and NMR spectra were identical with those of compound A.

From the distillation residue 1·1 g of a crystalline compound was obtained by ether extraction. After recrystallization from MeOH it melted at 140°, undepressed on admixture with II.

2-*Methyl*-1-*heptene*-3,5-*diyne* (V). The chloride I (5·0 g; 35 mmoles) was added to MeONa, prepared from 1·5 g (0·065 g atom) Na in 30 ml dry MeOH. After 2 hr at room temp the mixture was heated under reflux for 15 min. Water was then added, and the product extracted with pentane. The extract was washed with water until neutral and dried (Na_2SO_4). Fractionation gave 2·0 g (53%) V, b.p. 53° (13 mm.), n_D^{25} 1·5402; λ_{max} (*n*-hexane) 205 (ε 30,000), 211 (46,800), 225 (2000), 236·5 (5000), 248 (10,400), 262·5 (15,700), and 277·5 mμ (12.000). (Found: C, 92·24; H, 7·39. Calc. for C_8H_8: C, 92·26; H, 7·74%.) The IR spectrum shows bands at 2230 and 2190 cm^{-1} (—C≡C—C≡C) and bands at 3050, 1600 and 895 cm^{-1} ($>C{=}CH_2$). The compound is quite unstable and can only be kept unchanged for any time at low temp under N_2.

2,5-*Dimethyl*-2,3,4-*hexatriene* (VII). Compound VI (5·4 g; 30 mmoles) in 15 ml dry ether was added dropwise during 30 min to MeMgBr (50 ml; 1·54 M) with stirring at room temp. The gas evolved was passed through a trap cooled to −78° and collected. The reaction mixture was further stirred for 1 hr. and finally heated with reflux for 1 hr. Practically no polymeric material was formed during the reaction. Excess Grignard reagent was hydrolysed with dil. HCl aq, the ether layer separated and dried (Na_2CO_3). As far as possible all manipulations were carried out under N_2. Evaporation of the ether under red. press. yielded 3 g (92%) crude crystalline VII. Sublimation at 20° (0·1 mm) gave pure VII, m.p. 40° (sealed tube); λ_{max} (*n*-hexane) 230 (ε~7000) and 262·5 mμ (~17,000). (Found:[49] C, 88·74; H, 11·26. Calc. for C_8H_{12}: C, 88·82; H, 11·18%.) The IR spectrum shows a weak band at 1900 cm^{-1} and a medium intensity band at 1645 cm^{-1}. These are probably the stretching vibrations of a cumulative triene.[15] The NMR spectrum shows only one band at τ: 8·19 due to the 4 equivalent Me groups.

The gas evolved in the reaction consisted of 99·9% ethane and traces of methane. EtMgBr was used with practically the same result as described above, but the gas consisted of 51% ethane and 49% ethylene, with traces of methane.

The reaction proceeded with MeMgBr prepared from sublimed Mg. The cumulene VII was formed, and the gas consisted of 97% ethane, 3% methane, and traces of ethylene.

Polymeric peroxide (IX). The cumulene is extremely sensitive to oxygen both in solution and in the crystalline state. A white polymeric substance is formed, which is practically insoluble in most ordinary solvents. Extraction of this solid with hot methylene chloride or chloroform, and subsequent evaporation of the solvent gave a small amount of a crystalline compound, m.p. 112–113°. (Found: C, 67·82; H, 8·28; O, 23·00. Calc. for $C_8H_{12}O_2$: C, 68·54; H, 8·63; O, 22·83%.) The IR spectrum shows strong bands at 1260 and 1142 cm^{-1}, which is the region expected for the C—O stretching vibration of vinyl ethers. The substance liberated I_2 from a solution of KI in acetic acid. Ozonolysis of the polymeric oxide in CCl_4 and subsequent treatment with Zn and water gave acetone, characterized as the 2,4-dinitrophenylhydrazone, m.p. 127°.

2,7-*Dimethyl*-2,3,4,5,6-*octapentaene* (XII). Compound X (10·1 g; 50 mmoles), dissolved in 15 ml dry ether, was added dropwise during 1 hr. to MeMgBr (80 ml; 1·5 M) with stirring at room temp. The gas evolved was collected in the usual way. A white flocculent precipitate was formed during the reaction. After 1 hr at room temp the reaction mixture was decomposed with dil. HCl aq.

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[49] Weighing of the substance was impossible because of rapid uptake of O_2, and the values are calculated from the C:H ratio determined by the method of J. Unterzaucher, *Microchem. Acta* 448 (1957).

The ether layer was separated and dried (Na_2CO_3). Qualitative UV and IR spectra of the ether solution were obtained: λ_{max} (EtOH) 215, 228, 308, and 321 mμ, with relative intensities 1·8:5·1:1:1·1. The IR spectrum shows medium intensity bands at 2002 and 1625 cm^{-1}, which probably are the stretching vibrations of a cumulative pentaene. Any attempt to isolate the cumulene resulted in formation of polymeric material. This material is insoluble in all ordinary solvents, and in one instance when heated to 70–80° an explosion occurred. The IR spectrum shows a band at 1140 cm^{-1} (C—O). The analysis was unsatisfactory because invariably explosions occurred. (Found: C, 83·78; H, 8·17; O, 4·53%.) It shows, however, that this polymeric material contains considerably less O_2 than the peroxide IX.

Reactions of 2,3-dibromo-2,3-dimethylbutane (XIII)

A *With methylmagnesium bromide.* An ethereal solution of MeMgBr (140 ml; 1·4 M) was added dropwise during 2 hr to 19·5 g (80 mmoles) bromide XIII in 25 ml of dry ether. The reaction mixture was then heated for 1 hr, cooled, and hydrolyzed with dil. HCl aq. The ether layer was separated, washed until neutral with water, and dried (Na_2SO_4). Fractionation through a packed column gave 5·1 g (76%) of XIV, b.p. 70–72°, n_D^{20} 1·4101. The IR spectrum was identical with that of an authentic sample. Gas chromatography of the total reaction product prior to fractionation showed that XIV was the sole liquid product.

The gaseous product consisted of 99·9% ethane with traces of ethylene and methane. Using MeMgBr prepared from sublimed Mg, the gas consisted of 99% ethane along with traces of methane and ethylene, and XIV was the sole liquid product.

B *With ethylmagnesium bromide.* In this reaction XIV was also the only the only liquid product, and the gas consisted of 52% ethane, 48% ethylene, and traces of methane.

C *With phenylmagnesium bromide.* PhMgBr (30 ml, 1·16 M) was added dropwise during 1 hr to a stirred solution of 12·2 g (50 mmoles) XIII in 50 ml of dry ether. The procedure was then continued as described under A. The crystalline residue obtained after distillation of the ether was recrystallized from MeOH yielding 5·5 g. (71%) biphenyl, m.p. 69–70°, undepressed by admixture with an authentic sample. The distilled ether solution contained only XIV.

D *With phenylacetylenylmagnesium bromide.* To a solution of 5·1 g (50 mmoles) phenylacetylene in 20 ml dry ether was added the equimolar amount of MeMgBr (34 ml; 1·48 M). The bromide XIII (6·1 g, 25 mmole) was added all at once, and the reaction mixture was heated under reflux for 6 hr. The reaction mixture was worked up in the usual way, the ether being distilled into a cooled flask under red. press. The residue was recrystallized from MeOH giving 3·2 g (63%) of 1,4-diphenyl-1,3-butadiyne m.p. 87–88° (reported[50] m.p. 88°). Gas chromatography of the ether solution revealed the presence of XIV and phenylacetylene. The amount of the former was estimated on the basis of gas chromatography to be 1·3 g (62%), and 1·4 g phenylacetylene was recovered by distillation.

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[50] C. Glaser, *Liebigs Ann.* **154**, 159 (1870).