product before and after distillation were identical. $\delta P 30.36 \text{ ppm} (CH_2Cl_2)$. PMR spectrum (CDCl₃, $\delta \text{ ppm}$): 1.33 t (CH₃ in C₂H₅), 2.17, 2.30 s (CH₃), 4.26 (CH₂), 5.30 d (H_A, ²J_{PH} = 48.5 Hz), 9.35 br. s (NH). Found: C 42.05; H 5.43; N 22.08; P 12.23%. C₉H₁₃N₄O₃P. Calculated: C 42.19; H 5.11; N 21.86; P 12.09%.

When the product with mp 125-126° was dissolved in CH_2Cl_2 , $CHCl_3$, CH_3CN , alcohols, or pyridine and the solution was let stand the 1:1 adduct with mp 244-245° (from t-BuOH) deposited quantitatively. Infrared spectrum (ν , cm⁻¹): 775, 800, 870, 1020 m, 1140 s, 1180, 1260, 1280 m, 1310, 1340, 1380, 1405, 1465 s, 1615 m. sh., 1660, 1707 v.s., 3130 w, 3280 w.m. PMR spectrum (C_5H_5N , δ ppm): 1.13 t (CH_3 from C_2H_5), 2.33, 2.50 s (CH_3), 4.20 q (CH_2), 10.90, 14.27 (NH), δP 102.3, 104.2 ppm (DMSO). Found: C 42.56; H 5.22, N 21.67; P 12.19%. $C_9H_{13}N_4O_3P$. Calculated: C 42.19; H 5.11; N 21.86; P 12.09%.

CONCLUSIONS

Independent of the nature of the solvent, the reaction of 2-acetyl-5-methyl-1,2,3-diazaphosphole with diazoacetic ester proceeds without the evolution of nitrogen to give Δ^2 -phosphapyrazoline derivatives. The latter in CH₂Cl₂, CH₃CN, or alcohols are isomerized to compounds with two NH groups.

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FORMATION OF 1-ALKYNES BY ACTION OF MAGNESIUM ON THE 1,1-DICHLORO- AND 1,1-DIBROMO-1-ALKENES IN TETRAHYDROFURAN SOLUTION

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Convenient methods have been developed at the present time for the preparation of the 1,1-dichloro- and 1,1-dibromo-1-alkenes [1-3], which have found interesting use in organic synthesis. Thus, 1-alkynes were synthesized from the 1,1-dichloro-1-alkenes (DCA) by treatment with sodium [4] and with n-butyllithium [5], and from the 1,1-dibromo-1-alkenes (DBA) by treatment with n-butyllithium [6] and with lithium amalgam [6]. Based on the data in [6], magnesium is inactive in the analogous reaction with DBA.

We established that Mg powder, activated by dibromoethane, reacts vigorously with the DCA (1, 1, di-chloro-1-heptene, 1, 1-dichloro-5-alkoxy-1-pentenes, 1, 1-dichloro-5-diethylamino-1-pentene, 1, 1-dichloro-5-ethoxy-1-heptene, 1, 1-dichloro-7-diethylamino-1-heptene) and with DBA <math>(1, 1-dibromo-1-pentene and 1, 1-dibromo-1-octene) in THF solution. However, to complete the reaction it is necessary to reflux the mixture. After decomposing the reaction mixture with either acid or NH₄Cl solution the corresponding 1-alkynes are obtained in 87-95% yield.

As a result, magnesium, similar to sodium or lithium amalgam, causes the conversion of the DCA and DBA to 1-alkynes.

$$RCH_2CH=CX_2 + Mg \xrightarrow{THF, H_2O^+} RCH_2C \equiv CH,$$

X = Cl, Br

Here, together with the 1-alkynes, are formed the corresponding 1-alkenes in small amount (0.2-2%) (Table 1). For comparison, in Table 1 is given the purity of two 1-alkynes that were obtained by treating the DCA with sodium metal in diethyl ether.

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Starting compound	1-Alkyne	Purity* of 1-alkyne,%
$\begin{array}{c} CH_{3}(CH_{2})_{4}CH=CCl_{2}\\ C_{2}H_{5}O(CH_{2})_{3}CH=CCl_{2}\\ n-C_{3}H_{7}O(CH_{2})_{3}CH=CCl_{2}\\ (C_{2}H_{5})_{2}N(CH_{2})_{3}CH=CCl_{2} \\ C_{2}H_{5}O(CH_{2})_{5}CH=CCl_{2} \\ C_{2}H_{5}O(CH_{2})_{5}CH=CCl_{2} \\ CH_{5}O(CH_{2})_{5}CH=CCl_{2} \\ CH_{6}(CH_{2})_{5}CH=CBr_{2}\\ CH_{3}(CH_{2})_{6}CH=CBr_{2} \end{array}$	$\begin{array}{c} {\rm CH}_{3}({\rm CH}_{2})_{4}{\rm C}\!=\!{\rm CH}\\ {\rm C}_{2}{\rm H}_{3}{\rm O}({\rm CH}_{2})_{3}{\rm C}\!=\!{\rm CH}\\ n{\rm -}{\rm C}_{3}{\rm H}_{7}{\rm O}({\rm CH}_{2})_{3}{\rm C}\!=\!{\rm CH}\\ ({\rm C}_{2}{\rm H}_{5})_{2}{\rm N}({\rm CH}_{2})_{3}{\rm C}\!=\!{\rm CH}\\ {\rm C}_{2}{\rm H}_{0}({\rm CH}_{2})_{3}{\rm C}\!=\!{\rm CH}\\ {\rm C}_{2}{\rm H}_{5}_{0}({\rm CH}_{2})_{5}{\rm C}\!=\!{\rm CH}\\ ({\rm C}_{2}{\rm H}_{5})_{2}{\rm N}({\rm CH}_{2})_{5}{\rm C}\!=\!{\rm CH}\\ {\rm CH}_{3}({\rm CH}_{2})_{5}{\rm C}\!=\!{\rm CH}\\ {\rm CH}_{3}({\rm CH}_{2})_{5}{\rm C}\!=\!{\rm CH}\\ {\rm CH}\\ {\rm CH}_{3}({\rm CH}_{2})_{6}{\rm C}\!=\!{\rm CH}\end{array}$	99,0 99,1 99,8 98,7 99,3 99,3 99,5 99,5 99,3 99,1

TABLE 1. 1-Alkynes, Obtained by Reacting 1,1-Dichloro-1-alkenes and 1,1-Dibromo-1-alkenes with Magnesium in THF

* The corresponding 1-alkene is the impurity.

 \dagger The 1-alkyne, obtained by treatment with Na, is at least 99.2% pure.

 \ddagger The 1-alkyne, obtained by treatment with Na, is at least 99.7% pure.

The formation of 1-alkynes from DCA and DBA by treatment with magnesium apparently resembles the similar reaction of sodium with DCA [4] and begins with the conversion of the dihaloalkenes to the intermediate (I). As the result of the β -elimination of HMgHal, the latter is converted to the 1-halo-1-alkyne (II), which, reacting with Mg, forms the alkynylmagnesium halide (III), which gives the 1-alkyne on hydrolysis.

$\text{RCH}_2\text{CH}=\text{CX}_2 + \text{Mg} \xrightarrow{\text{THF}}$	RCH ₂ CH=C	-HMgX
	_ (I) `MgX_	
$\rightarrow \operatorname{RCH}_2 C \equiv CX \xrightarrow{\operatorname{Mg}} \operatorname{RCH}_{HF}$	$\underset{(III)}{\overset{H_{3}O^{+}}{\longrightarrow}} RCH$	I₂C≡CH

The formation of the alkynylmagnesium halide (III) was proved by its conversion to acetylenecarboxylic acid by treatment with CO_2 .

$$C_{2}H_{5}O(CH_{2})_{3}CH = CCl_{2} \xrightarrow{Mg} C_{2}H_{5}O(CH_{2})_{3}C \equiv CMgCl \xrightarrow{1. CO_{2}} C_{1}H_{5}O(CH_{2})_{3}C \equiv CCOOH_{2}CCC$$

The conversion of intermediate (I) to haloalkyne (II) is confirmed by the known data on the preparation of alkynylmagnesium halides by the action of Mg on alkenyl halides RCH=CHX [7]. The formation of alkynylmagnesium halides from 1-halo-1-alkynes and Mg is a well known reaction [8]. Another path, leading to 1alkynes via the cleavage of MgX₂ from (I) and subsequent rearrangement of the formed alkylidenecarbene to the 1-alkyne is fairly improbable, since in [9] it was shown that alkylidenecarbenes, which have a β -hydrogen, do not rearrange to acetylenes. The conversion of DCA and DBA to 1-alkynes by treatment with Mg in THF can serve as a method for their preparation in a number of cases.

EXPERIMENTAL

1,1-Dichloro-1-heptene, 1,1-dichloro-5-ethoxy-1-pentene, 1,1-dichloro-5-diethylamino-1-pentene, 1,1-dichloro-7-ethoxy-1-heptene, and 1,1-dichloro-7-diethylamino-1-heptene were obtained as described in [4]. 1,1-Dibromo-1-octene and 1,1-dibromo-1-nonene were obtained as described in [6, 10]. The GLC analysis of the obtained compounds was run on an LKhM-8MD chromatograph, using a $2 \text{ m} \times 0.4 \text{ cm}$ column packed with 15% SKTP-50X deposited on Chromatone N and helium as the carrier gas at a flow rate of 30 ml/ min. The structure of the obtained 1-alkynes was confirmed by comparing with known samples via GLC.

<u>1,1-Dichloro-5-n-propoxy-1-pentene</u>. A solution of 20 g of 1,1,5-trichloropentene and Na propoxide (from 3.5 g of Na) in 60 ml of dry n-PrOH was refluxed for 4 h, cooled, and poured into water. The organic layer was extracted with ether and dried over MgSO₄. Vacuum-distillation gave 15.5 g (69%) of 1,1-dichloro-5-n-propoxy-1-pentene, bp 79-81° (8 mm). Found: C 49.16; H 6.81%. $C_8H_{14}Cl_2O$. Calculated: C 48.78; H 7.08%.

Preparation of 1-Alkynes by Reaction of 1,1-Dichloro- and 1,1-Dibromo-1-alkenes with Magnesium in THF (general method). With stirring, to 0.3 g-atom of Mg (powder), previously dried in vacuo at 150°C, and

100 ml of abs. THF was added several drops of dibromoethane in order to activate the Mg. When the vigorous reaction of the dibromoethane with Mg had ceased a solution of 0.1 mole of either the 1,1-dichloro- or 1,1-dibromo-1-alkene in THF was added gradually at such a rate that either the mixture boiled gently or the temperature did not drop below 50°. When all of the dihaloalkene had been added the stirred mixture was refluxed moderately for 2-4 h, checking the disappearance of the starting dihaloalkene by GLC. Long heating of the mixture leads to an increase in the amount of by-product. The mixture was cooled and NH₄Cl solution and ether were added cautiously. The organic solution was decanted from the excess Mg, washed in succession with dilute HCl solution and water, and dried over MgSO₄. The residue from removal of the solvent was dis-tilled either at atmospheric pressure or in vacuo. The yield of the 1-alkynes was 90-95%. In the case of the amino derivatives the reaction mass was diluted with a large amount of water, ether was added, the mixture was decanted from the Mg, and the organic layer was decanted from the aqueous Mg(OH)₂ suspension, which was again extracted twice with ether. The purity of the obtained 1-alkynes was determined by GLC. The previously unknown 5-n-propoxy-1-pentyne had bp 50-51° (15 mm). Found: C 76.34; H 11.15%. C₈H₁₄O. Calculated: C 76.19; H 11.11%.

<u>6-Ethoxy-2-hexynoic Acid.</u> The reaction mixture, obtained by reacting 15 g of 1,1-dichloro-5-ethoxy-1-pentene with Mg in THF solution, was poured into a mixture of solid CO_2 and dry ether and then stirred until the temperature reached 20°. Then it was gradually poured into dilute HCl solution. The ether solution was separated and washed in succession with water and NaOH solution. The alkaline solution was acidified and extracted with ether. The ether extract was dried over MgSO₄. The residue from removal of the ether was vacuum-distilled to give 3.7 g (35%) of 6-ethoxy-2-hexynoic acid, bp 132-133° (2 mm). Found: C 61.32; H 7.57%. $C_8H_{12}O_3$. Calculated: C 61.53; H 7.69%. From the ether solution after extraction with alkali we obtained 5.4 g of 5-ethoxy-1-pentyne.

<u>Preparation of 1-Alkynes from 1,1-Dichloro-1-alkenes and Sodium in Ether (general method)</u>. With stirring, to 0.5 g-atom of Na, cut into small pieces, in 100 ml of ether was gradually added 0.1 mole of the 1,1-dichloro-1-alkene in ether at such a rate that the ether boiled moderately due to reaction heat. A precipitate deposited during reaction. After adding the dichloroalkene the mixture was refluxed for 0.5-1 h. The end of reaction was checked by GLC. Long refluxing of the mixture leads to an increase in the amount of byproduct. Then the pieces of excess Na were removed from the cooled mixture, or with shaking the mixture was poured through a glass filter with coarse openings, which retained only the Na pieces, into a dry flask under argon. The reaction mass, free of Na, was carefully decomposed with chilled water, and the ether solution was separated and dried over $MgSO_4$. The residue from removal of the ether was distilled to give the 1alkyne in 87-95% yield.

CONCLUSIONS

The 1,1-dichloro- and 1,1-dibromo-1-alkenes react with Mg in THF solution to give 1-alkynes slightly contaminated with 1-alkenes.

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