CHEMISTRY OF ACETALS

COMMUNICATION 8. GRIGNARD REACTIONS WITH 1, 1, 3, 3-TETRAETHOXYPROPANE, 1, 1, 3, 5, 7, 7-HEXAETHOXYHEPTANE, AND 1, 1, 3, 5, 7, 9, 9-HEPTAETHOXYNONANE

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 10, pp. 1830-1834, October, 1961 Original article submitted February 21, 1961

As is well known [1-5], acetals of saturated, aromatic, and aliphatic-aromatic aldehydes react with various alkylmagnesium halides, including ethynylmagnesium halides, in accordance with the general scheme

$RCH(OC_2H_5)_2 + R'MgX \rightarrow RCH(OC_2H_5)R'$

However, the reactions of diacetals with Grignard reagents have not yet been studied. Here it would be of interest to carry out reactions with diacetals at one of the acetal functions, which would make it possible to pass to many difficultly accessible α , β -unsaturated aldehydes:

$$(C_{2}H_{5}O)_{2}CHCH(R)CH(OC_{2}H_{5})_{2} \xrightarrow{R MgX}$$

$$H^{+}$$

$$(C_{2}H_{5}O)_{2}CHCH(R)CH(OC_{2}H_{5})R' \xrightarrow{R'}CH = C(R)CHO$$

In view of this we studied the reaction of malonaldehyde bis [diethyl acetal] (1, 1, 3, 3-tetraethoxypropane) with ethylmagnesium bromide, with 3-methyl-3-buten-1-ynylmagnesium bromide, and with the Grignard reagent formed from dehydrolinalool at a molar ratio of reactants of 1 : 1. These reactions were carried out under the conditions described for reactions with monoacetals, i.e. careful addition of the solution of the Grignard reagent to an ethereal solution of the diacetal, removal of the ether, and heating of the residue in a water bath for several hours.

It was found that all the Grignard reagents used reacted with 1, 1, 3, 3-tetraethoxypropane, but the normal reaction products (I) were formed in yields of only about 10-15%. The main reaction was the elimination of alcohol and the formation of 3-ethoxyacrolein diethyl acetal (II) in a yield of about 55-60%. We detected also the presence of small amounts of propiolaldehyde acetal (III) in the reaction mixture. Hence, the over-all course of the reaction may be expressed as follows:

$$(C_2H_5O)_2CHCH_2CH(OC_2H_5)_2 + RMgX \rightarrow (C_2H_5O)_2CHCH = CHOC_2H_5 + (II)$$
$$+ (C_2H_5O)_2CHCH_2CH(OC_2H_5)R + HC \equiv CCH(OC_2H_5)_2$$
(I) (III)

The composition of the reaction mixture after the reaction with ethylmagnesium bromide was studied by the method of gas-liquid chromatography. Fig. 1 shows the chromatogram of the main fraction, b, p. 115-119° (25 mm) and n_D^{20} 1.4220, obtained by the fractionation of the reaction mixture. Also, Fig. 1 gives chromatograms of the main fraction after the addition of known samples of propiolaldehyde acetal (III), 3-ethoxyvaleraldehyde diethyl acetal (I; $R = C_2H_5$), and 3-ethoxyacrolein diethyl acetal (II). From these chromatograms it will be seen that the peak ((1) belongs to propiolaldehyde diethyl acetal, the peak (3) belongs to 3-ethoxyvaleraldehyde diethyl acetal, and the peak (4) belongs to 3-ethoxyacrolein diethyl acetal. We have not yet succeeded in identifying the substance giving rise to the peak (2). According to the areas under the peaks, the average composition of the reaction mixture was 87-92% of 3-ethoxyacrolein diethyl acetal, 4-8% of 3-ethoxyvaleraldehyde diethyl acetal, 1.5-3% of propiolaldehyde diethyl acetal, and 1-2% of the unidentified substance.



Fig. 1. Chromatograms: A) fraction of b.p. 115-119° (25 mm); B) ditto after the addition of propiolaldehyde diethyl acetal; C) ditto after the addition of 3-ethoxyvaleraldehyde diethyl acetal; D) ditto after the addition of 3-etho-xyacrolein diethyl acetal.

The reaction between 1, 1, 3, 3-tetraethoxypropane and 3-methyl-3-buten-1-ynylmagnesium bromide led to the formation of two products: the first of these, the main product, had similar characteristics (boiling point and refractive index) to the mixture obtained in the reaction with ethylmagnesium bromide; in this product we found 3-ethoxyacrolein diethyl acetal (98% of the mixture) and propiolaldehyde diethyl acetal (about 2% of the mixture) by means of gas-liquid chromatography (Fig. 2). According to elementary analysis, the second, higher-boiling fraction was 3ethoxy-6-methyl-6-hepten-3-ynal diethyl acetal (I; R' = C \equiv CC(CH₈) = CH₂); the yield of this did not exceed 10-15%.

Analogous results were obtained in the study of the reaction of 1, 1, 3, 3-tetraethoxypropane with the Grignard reagent from dehydrolinalool. As a result of this reaction we isolated about 7% of product, which elementary analysis indicated to be 3-ethoxy-6-hydroxy-6, 9-dimethyl-9-undecen-4-ynal diethyl acetal (I; $R = C \equiv CCOH(CH_3)CH_2CH_2$ CH = C(CH₃)₂). In this reaction the main product was again 3-ethoxyacrolein diethyl acetal with some admixture of a little propiolaldehyde diethyl acetal.

Under the above-described conditions, 1, 1, 3, 5, 7, 7-hexaethoxyheptane (IV) and 1, 1, 3, 5, 7, 9, 9-heptaethoxynonane (V) reacted with ethylmagnesium bromide and again formed, according to elementary analysis, mainly products of the elimination of one alcohol group: 1, 3, 5, 7, 7-pentaethoxy-1-pentene (VI) and 1, 3, 5, 7, 9, 9-hexaethoxy-1-nonene (VII)

$$(C_{2}H_{5}O)_{2}CH[CH_{2}CH(OC_{2}H_{5})]_{2}CH_{2}CH(OC_{2}H_{5})_{2}$$

$$(IV)$$

$$(C_{2}H_{5}O)_{2}CH[CH_{2}CH(OC_{2}H_{5})]_{2}CH = CHOC_{2}H_{5}$$

$$(VI)$$

$$(C_{2}H_{5}O)_{2}CH[CH_{2}CH(OC_{2}H_{5})]_{3}CHCH_{2}CH(OC_{2}H_{5})_{2}$$

$$(V)$$

$$(C_{2}H_{5}O)_{2}CH[CH_{2}CH(OC_{2}H_{5})]_{3}CH = CHOC_{2}H_{5}.$$

$$(VI)$$

$$(C_{2}H_{5}O)_{2}CH[CH_{2}CH(OC_{2}H_{5})]_{3}CH = CHOC_{2}H_{5}.$$

$$(VII)$$



Fig. 2. Chromatograms: A) main fraction obtained in the reaction of 1, 1, 3, 3-tetraethoxypropane with 3-methyl 1-3-butten-1ynylmagnesium bromide; B) ditto after the addition of propiolaldehyde diethyl acetal.

To confirm the structures of (VI) and (VII), their Raman spectra were determined*. The spectra of both products contained a band at 1598 cm⁻¹, characteristic for the CH = CHOC₂H₅ group. It may therefore be considered to a fair degree of probability that (VI) and (VII) are indeed products formed by the elimination of one acetal ethoxy group. We did not succeed in checking the individual elimination products by the method of gas-liquid chromatography as they were retained firmly by the column which we used.

The elimination of alcohol from 1, 1, 3, 3-tetraethoxypropane under the conditions of the Grignard reaction cannot be explained by the catalytic effect of magnesium bromide. Special experiments showed that all the diacetals studied by us underwent scarcely any change when heated with magnesium bromide under the conditions of the Grignard reaction. It is probable that the ready elimination of alcohol under the action of Grignard reagents is a specific property of diacetals of this kind, and this reaction is appreciably quicker than the corresponding reaction proceeding by the scheme of the Grignard synthesis.

The formation of propiolaldehyde diethyl acetal may be represented as the reesult of the simultaneous elimination of two molecules of alcohol from a molecule of the original 1, 1, 3, 3tetraethoxypropane via an allene system:



The formation of propiolaldehyde acetal may be represented also as occurring by the elimination of alcohol from 3-ethoxyacrolein diethyl acetal, but the amount of propiolaldehyde diethyl acetal formed is independent of reaction time, so that we considered the scheme given above to be the more probable.

EXPERIMENTAL

Reaction of 1, 1, 3, 3-Tetraethoxypropane with Ethylmagnesium Bromide. A solution of ethylmagnesium bromide (from 1.2 g of magnesium and 5.4 g of ethyl bromide) in 30 ml of dry ether was added dropwise to a solution of 11 g (0.05 mole) of 1, 1, 3, 3-tetraethoxypropane in 30 ml of ether with simultaneous removal of ether by distillation. For this purpose the temperature of the bath was gradually raised to the boil, and the mixture was heated for several hours (2-10). The reaction product was cooled, treated with ammonium chloride solution, and carefully extracted with ether. After two fractionations (after reaction had been carried on for 4-10 hours), we isolated about 5 g of fraction of b.p. 115-119° (25 mm) and $n_D^{19.5}$ 1.4220. A viscous brown residue (1.04 g) remained.

The main product was analyzed by the method of gas-liquid chromatography. A simple chromatograph with a thermal-conductivity detector [6] was used; the column was 2 m in length and 6 mm in diameter. The liquid stationary phase was a silicone oil applied to ground brick (particle diameter 0.25-0.5 mm). The mobile phase was hydrogen. The chromatography was carried out at 120°. The results of the analysis are given above.

<u>Reaction of 1, 1, 3, 3-Tetraethoxypropane with 3-Methyl-3-buten-1-ynylmagnesium Bromide.</u> The reaction was carried out in an analogous way with the same amounts of substances. After two fractionations of the reaction mixture we isolated 4.9 g of fraction of b.p. 75° (1 mm) and n_D^{21} 1.4230 and 1.6 g of a fraction of b.p. 90-93° (1 mm)

^{*} The Raman spectra were determined by G. A. Kogan.

and n_D^{22} 1.4498. The low-boiling fraction was investigation by means of gas-liquid chromatography. The higher-boiling fraction corresponded in analysis to 3-ethoxy-6-methyl-6-hepten-3-ynal. Found: C 70.00; 69.92; H 10.01; 9.96%. C₁₄H₂₄O₃. Calculated: C 69.96; H 10.07%.

Reaction of 1, 1, 3, 3-Tetraethoxypropane with the Grignard Reagent from Dehydrolinalool. The procedure was analogous to the above. From 11 g (0.05 mole) of 1, 1, 3, 3-tetraethoxypropane we obtained 9 g of a product which consisted of a mixture of 3-ethoxyacrolein diethyl acetal, propiolaldehyde diethyl acetal, and unchanged dehydro-linalool. In addition we isolated 1.2 g of a product of b.p. 135-137° (1 mm) and n_D^{21} 1.4580, which corresponded in analysis to 3-ethoxy-6-hydroxy-6, 9-dimethyl-9-undecen-4-ynal diethyl acetal. Found: C 69.94; 69.93; H 10.55; 10.50%. C₁₉H₃₄O₄. Calculated C 69.90; H 10.50%.

Reaction of 1, 1, 3, 5, 7, 7-Hexaethoxyheptane with Ethylmagnesium Bromide. The procedure was as described above. From 9.1 g (0.025 mole) of 1, 1, 3, 5, 7, 7-hexaethoxyheptane, after two fractionations of the reaction mixture, we obtained 3.9 g of the product of the elimination of 1, 3, 5, 7, 7-pentaethoxy-1-heptene. Found: C 64.28; 64.37; H 11.17; 10.96%. $C_{17}H_{34}O_5$. Calculated: C 64.12; H 10.76%.

Reaction of 1, 1, 3, 5, 7, 9, 9-Heptaethoxynonane with Ethylmagnesium Bromide. The procedure was analogous to that described above. From 22.3 g (0.05 mole) of 1, 1, 3, 5, 7, 9, 9-heptaethoxynonane, after two fractionations of the reaction mixture, we obtained 10.58 g of a product of b.p. 160-164° (1 mm) and n_D^{17} 1.4330, which corresponded in analysis to 1, 3, 5, 7, 9, 9-hexaethoxy-1-nonene. Found: C 64.48; 64.32; H 11.18; 11.04%. C₂₁H₄₂O₆. Calculated: C 64.58; H 10.84%.

In addition we obtained 8 g of a mixture of boiling range 166-195° (1 mm) and n_D^{17} 1.4350; this was not investiated more closely.

SUMMARY

1. A study was made of the reactions of 1, 1, 3, 3-tetraethoxypropane, 1, 1, 3, 5, 7, 7-hexaethoxynonane with several Grignard reagents.

2. In all cases the main reaction was the elimination of alcohol and the formation, respectively, of 3-ethoxy-acrolein, 1, 3, 5, 7, 7-pentaethoxy-1-heptene, and 1, 3, 5, 7, 9, 9-hexaethoxy-1-nonene.

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