REACTION OF α,α-DICHLORO-ω-BROMOALKANES AND α,α-DICHLORO-ω-BROMOALKENES WITH BENZYLMAGNESIUM AND ALLYLMAGNESIUM HALIDES

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Various polychlorohydrocarbons of structure $R(CH_2)_nHal$, where $R = CCl_3$, $CHCl_2$, $CCl_2{=}CH$, or $CCl_2{=}CCl$, which are readily available by means of telomerization, are widely used in synthesis both via chemical transformations of the R grouping (hydrolysis, reduction, dehydrochlorination, dechlorination) and by replacement of the terminal chlorine by various nucleophilic groups. The use of such compounds in organometallic synthesis has hardly been studied. The alkylation [1] and arylation [2] of 1,1,3-trichloropropene, involving the allylic chlorine, by Grignard reagents has been described, and also the alkylation of polychloroethylenes at the vinylic chlorine [3]. Attempts to extend this reaction to the above indicated types of polychloroalkanes when $n > 2$ have proved to be unsuccessful.

As is known, the alkylation of n-alkyl halides with alkyl Grignard reagents, leading to the formation of a "mixed" condensation product

$$RHal + R'MgHal \rightarrow R - R' + MgHal_2 \qquad (1)$$

goes with great difficultly and very slowly in ether [4] or hydrocarbons [5]. In a number of cases good yields of the R–R' products are obtained in solvating solvents like THF, dimethoxyethane and hexamethyl triamidophosphate [6, 7]. Here it is customary to start with the n-alkylmagnesium halides and the quite reactive alkyl halides [5, 6]

$$C_5H_{11}MgBr + CH_3I \rightarrow C_5H_{11}CH_3 + MgBrI$$

Theories exist that such reactions, depending on the medium, proceed by various mechanisms [4, 6] and that in solvating solvents, which facilitate nucleophilic substitution, a heterolytic course of the reaction is the most probable [3, 6, 7]. From a number of observations is also known that, together with the main condensation reaction, it is possible to have exchange of the radicals according to the scheme:

$$RMgHal + R'Hal \rightarrow R'MgHal + RHal \qquad (2)$$

with the subsequent reaction of RMgHal and R,MgHal with RHal and R'Hal in all of the combinations according to scheme 1 [3, 6, 7]. The exchange goes rapidly in THF or dimethoxyethane (even at 0°C), and hardly goes at all in ether [6, 7]. Phenylmagnesium bromide hardly enters into the exchange reaction with alkyl halides. In RHal the ease of exchange increases in the order; $RCl < RBr < RI$ [6, 7].

For the polychloroalkanes we previously found that the α,α-dichloro-ω-bromoalkanes $CHCl_2CH_2(CH_2)_n \cdot Br$ and α,α-dichloro-ω-bromoalkenes $CCl_2{=}CH(CH_2)_nBr$, when n = 3 or 5, react with magnesium in ether to give the corresponding Grignard reagents [8]. However, the yields of the latter are low, since the reaction is complicated by a number of side processes, such as cyclization (in the case of $CHCl_2(CH_2)_4Br$) and condensation of the Wurtz type, with the formation of products having the structure $[CHCl_2CH_2(CH_2)_n-]_2$ and $[CCl_2{=}CH(CH_2)_n-]_2$.

The present paper is devoted to a study of the reaction of α,α-dichloro-ω-bromoalkanes $CHCl_2CH_2 \cdot (CH_2)_nBr$ and α,α-dichloro-ω-bromoalkenes $CCl_2{=}CH(CH_2)_nBr$, when n = 1, 3, or 5, with some Grignard reagents, and also with magnesium, in order to use this reaction in the synthesis of condensation products.

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TABLE 1. $RBr + R'MgX \rightarrow R-R' + MgBrX$, $R = CHCl_2CH_2(CH_2)_n-$, $CCl_2=CH(CH_2)_n-$, $R' = C_6H_5CH_2-$, $CH_2=CHCH_2-$ (2 h, 60-65°C)

R—R′	Yield,* %	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	MR		Found, %			Calc., %		
					found	calc.	C	H	Cl	C	H	Cl
$CHCl_2(CH_2)_3C_6H_5$ †	69,7	126 (10)	1,5318	1,1530	54,57	54,51	58,87 59,03	5,87 5,81	35,24 35,08	59,13	5,95	34,92
$CHCl_2(CH_2)_5C_6H_5$	92,0	159 (13)	1,5200	1,1012	63,75	63,82	62,51 62,61	6,97 6,90	30,29 30,36	62,42	6,98	30,82
$CHCl_2(CH_2)_7C_6H_5$	70,5	154 (2)	1,5122	1,0640	73,13	72,98	64,67 64,72	7,52 7,62	26,89 27,04	64,86	7,78	27,36
$CHCl_2(CH_2)_3CH=CH_2$	80,2	86,5 (64)	1,4590	1,0698	39,11	39,17	46,76 46,80	6,66 6,62	46,19 46,42	47,08	6,59	46,34
$CHCl_2(CH_2)_5CH=CH_2$	95	114 (40)	1,4600	1,0230	48,49	48,41	53,06 52,95	7,85 7,76	39,10 39,16	53,05	7,79	39,16
$CCl_2=CH(CH_2)_4C_6H_5$	90	141 (8)	1,5310	1,1190	63,34	63,28	63,05 62,83	6,11 6,11	30,37 30,82	62,90	6,16	30,95
$CCl_2=CH(CH_2)_6C_6H_5$	89	167,5 (8)	1,5220	1,0816	72,53	72,52	65,10 65,26	6,97 7,06	27,80 27,50	65,38	7,05	27,57
$CCl_2=CH(CH_2)_4CH=CH_2$	81	109 (48)	1,4735	1,0493	47,92	47,94	53,44 53,64	6,63 6,84	39,57 39,46	53,65	6,75	39,60

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*The yield of the products was based on the charged RBr.

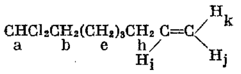
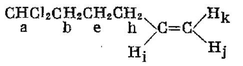
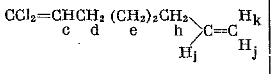
†For analysis the product was purified by preparative chromatography.

Of the Grignard reagents we selected the n-butyl-, phenyl-, benzyl-, and allylmagnesium halides, while as the solvent we used ether or THF. As was to be expected, the indicated bromides practically do not react with n-butylmagnesium bromide in either ether or THF. Analogous results were obtained with phenylmagnesium bromide. In ether the reaction is also sluggish with the benzyl- and allylmagnesium halides. In THF solution the indicated bromides react almost quantitatively with excess benzylmagnesium chloride and allylmagnesium bromide to give ω,ω-dichloroalkyl(alkenyl)benzenes $CHCl_2CH_2(CH_2)_{n+1}C_6H_3$ (I), $CCl_2=CH(CH_2)_{n+1}C_6H_5$ (II), ω,ω-dichloroalkenes $CHCl_2CH_2(CH_2)_{n+1}CH=CH_2$ (III) and α,α-dichloroalkadienes $CCl_2=CH(CH_2)_{n+1}CH=CH_2$ (IV), where n = 1, 3, or 5. The reaction products are isolated sufficiently pure by ordinary distillation in vacuo or through a column. The yields, constants and elemental analysis data for the obtained products are given in Table 1. The structure of the compounds was established by means of the IR and NMR spectra. In the IR spectra of compounds of type (I)-(IV), besides the frequencies of the $(-CH_2-)_m$ group at 2840, 2980, 1450, 1470, and 720 cm^{-1} (the latter appears in the compounds where $m > 4$), and the frequencies of the benzene ring at 1610, 1500, 3030, 3040, and 3090 cm^{-1}, for the first two types of compounds are respectively observed the vibration frequencies for the $CHCl_2CH_2$ group at 660 and 750 cm^{-1} [8, 9], and for $CCl_2=CH$ at 465, 880, and 610 cm^{-1} [8, 10]. In addition, for compounds of type (III) and (IV) are observed the vibration frequencies of the $RCH=C$ group at 3040 cm^{-1}, of a terminal $=CH_2$ group at 915 cm^{-1}, and of the $C=C$ bond at 1640 cm^{-1}.

The NMR spectra, taken for a number of pure (with a solvent) compounds, are given in Table 2 (a Perkin–Elmer instrument, P-12, 60 MHz, internal standard = hexamethyldisiloxane). In the spectra of the first two compounds is observed five types of protons. In the more complex spectra of compounds 3-5 (Table 2) is observed seven types of protons. Protons a and c of the $\underset{a}{CH}Cl_2CH_2-$ and $CCl_2=\underset{c}{CH}-CH_2-$ groups give a spin–spin splitting as a simple triplet, and their chemical shifts are found in the region of known shifts [3, 8, 11, 12]. For compounds 1 and 2, in harmony with [13], a certain shift of the protons of the alkyl portion upfield when compared with the expected is apparently associated with the effect of the benzene ring. The assignment of the shifts of protons b, d, and f is made on the basis of the data given in [8, 13]. In compounds 3-5 the protons of the vinyl group give a spectrum of the ABX system, with a superimposition of the coupling with the h protons of the CH_2 group. The assignment of the chemical shifts of protons b, d, and h of compounds 3 and 5 was made in harmony with the data given in [8, 14]. Protons b-h of compounds 4 give the spectrum of a strongly bonded six-spin system. The spin–spin coupling constants of the trans-, cis-, and gem-protons of the terminal vinyl group correspond to the literature data [13].

It should be mentioned that under the selected conditions the α,α,ω-trichloroalkanes and α,α,ω-trichloroalkenes practically do not react with the benzyl- and allylmagnesium halides. As a result, from a comparison of our data and the literature data it is possible to assume that the alkylation of the α,α-dichloro-ω-bromoalkanes and α,α-dichloro-ω-bromoalkenes with the benzyl- and allylmagnesium halides in a solvating solvent (THF) apparently proceeds via a heterolytic route. The reaction of the α,α-dichloro-ω-bromoalkanes and α,α-dichloro-ω-bromoalkenes with the benzyl- and allylmagnesium halides in THF can be used as a method for the synthesis of difficultly available ω,ω-dichloroalkyl(alkenyl)benzenes, ω,ω-dichloroalkenes and α,α-dichloroalkadienes, with a retention of the polychlorinated grouping.

TABLE 2. Data of NMR Spectra of Polychlorohydrocarbons

No.	Compound	δ, ppm					
		CH	CH_2	$(CH_2)_n$	H_i	H	H_k
1	$\underset{a}{CHCl_2}\underset{b}{CH_2}\underset{e}{(CH_2)_3}\underset{f}{CH_2}\underset{g}{C_6H_5}$	a 5,40	b 1,91 f 2,45	1,30			
2	$CCl_2{=}\underset{c}{CH}\underset{d}{CH_2}\underset{e}{(CH_2)_2}\underset{f}{CH_2}\underset{g}{C_6H_5}$	c 5,60	d 1,95 f 2,45	1,26			
3		a 5,66	b 2,11 h 1,99	1,34	5,68	4,86	4,89
4		a 5,66			5,66	4,91	4,91
5		c 5,75	d 2,08 h 1,97	1,33	5,67	4,86	4,88

*The $\delta_{C_6H_5}$ for compounds 1 and 2 is respectively 7.05 and 7.07 ppm. For compound 3, J_{ab} 6.1, J_{ih} 6.3 j_{ij}9.3 J_{ik} 17.3 J_{jk} 2.5 $J_{kh, ih}$ 1.3 Hz. For compound 4, J_{ab} 5.8, J_{ih} 6.0, J_{ij} 9.2, J_{ik} 17.3 H_2. For compound 5 J_{cd} 7.2, J_{ih} 6.2, J_{ij} 9.6, J_{ik} 17.5, J_{jk} 2.5, $J_{kh, ih}$ 1.3 Hz. The integral intensities and the multipleticity of the protons of the groups correspond to the indicated structures. The centers of the undeciphered multiplets are given as the chemical shifts of the protons of the CH_2 groups.

As an expansion of a previous paper [8] we also studied the reaction of the α,α-dichloro-ω-bromoalkanes $CHCl_2CH_2(CH_2)_nBr$ and the α,α-dichloro-ω-bromoalkenes $CCl_2 = CH(CH_2)_nBr$ with magnesium in ether, in the presence of symmetrizing agents like I_2, $BrCH_2CH_2Br$ and AgBr in order to increase the yield of the condensation products of type $[CHCl_2CH_2(CH_2)_n-]_2$ and $[CCl_2 = CH(CH_2)_n-]_2$. However, the products were obtained in better yields only in individual cases. Thus, the reaction of $CHCl_2(CH_2)_6Br$ with magnesium and 10 mole % of dibromoethane gives 1,1,14,14-tetrachlorotetradecane in 56% of the theoretical yield; from $CCl_2 = CH(CH_2)_3Br$ and magnesium in the presence of silver bromide is formed 1,1,10,10-tetrachloro-1,9-decadiene in 60% of the theoretical yield.

EXPERIMENTAL

The α,α,ω-dichloroalkyl and α,α,ω-dichloroalkenyl bromides were obtained as described in [8]. All of the experiments with magnesium and the Grignard reagents, as well as the purification of the reaction products, which contained olefinic groups, were run in an argon atmosphere. The course of the reaction, and the purity of both the starting and the obtained products, were followed by GLC (flame-ionization detection, glass colums with lengths of 2 and 2 m, and diameters of 4 and 3 mm, stationary phase = either 6% Silicone E-301 or 10% poly(ethylene glycol adipate) deposited on Chromosorb W, temperature 100-150°C). The compounds were identified by the retention time on two phases of different polarity.

1,1-Dichloro-6-phenyl-1-hexene. With stirring, to 10 g of 1,1-dichloro-5-bromo-1-pentene was added a solution of $C_6H_5CH_2MgCl$, which was obtained from 2.5 g of Mg and 8.5 g of $C_6H_5CH_2Cl$ in 90 ml of THF at 40-50°. The temperature of the reaction mixture rose up to 45°. The mixture was heated at 60-65° for 2 h, and then worked up in the usual manner. The following fractions were collected on distillation: I) 0.7 g with bp 124-156° (15 mm); II) 10.4 g with bp 156-160.5° (15 mm), and residue 1.0 g. Fraction II, based on the GLC data, is 1,1-dichloro-6-phenyl-1-hexene, contaminated with a small amount of dibenzyl; the yield was 90% of theory. Redistillation of fraction II through a column gave a product with the constants given in Table 1.

1,1-Dichloro-8-phenyl-1-octene and compounds of the type $CHCl_2CH_2(CH_2)_{n+1}C_6H_5$, where n = 1, 3, or 5, were obtained in a similar manner (Table 1).

6,6-Dichloro-1-hexene. With stirring, to 28.8 g of 1,1-dichloro-3-bromopropane was rapidly added a chilled (3-5°) solution of $CH_2 = CHCH_2MgBr$, which was obtained from 18 g of Mg and 36.6 g of $CH_2 = CH \cdot CH_2Br$ in 330 ml of absolute THF as described in [5]. The temperature of the reaction mixture rose up to 60°. After heating the mixture at 60-65° for 2 h, followed by the usual workup and distillation of the reaction product through a column in an argon stream, we obtained 18.8 g (80% of theory) of 6,6-dichloro-1-hexene with bp 156-158°. The constants of the redistilled product are given in Table 1.

1,1,10,10-Tetrachloro-1,9-decadiene. To a stirred mixture of 0.9 g of Mg, activated with iodine, 6.0 g of freshly prepared silver bromide and 5 ml of absolute ether, was added in drops a solution of 6.6 g of 1,1-dichloro-5-bromo-1-pentene in 30 ml of absolute ether. The reaction began after adding 2-3 ml of the bromide solution. After heating the mixture for 2 h the solution was decanted from the precipitate into chilled dilute HCl solution. After the usual workup and vacuum-distillation we collected a fraction with bp 117-120° (1 mm), which, based on the GLC data, was mainly 1,1,10,10-tetrachloro-1,9-decadiene. The yield was 2.4 g (60% of theory). Redistillation gave a product with bp 134° (4 mm); n_D^{20} 1.5030; d_4^{20} 1.2149; found MR 67.17, calculated MR 66.91, which corresponds to the data given in [8].

1,1,14,14-Tetrachlorotetradecane. With stirring, to 1.0 g of Mg, activated with iodine, was added a mixture of 9.9 g of 1,1-dichloro-7-bromopentane and 0.9 g of 1,2-dibromoethane in 80 ml of absolute ether. The reaction started immediately. After heating the mixture for 3 h, followed by the usual workup and vacuum-distillation, we obtained 0.9 g of 1,1-dichloroheptane, 2.9 g of the starting bromide, and 2.7 g of 1,1,14,14-tetrachlorotetradecane with bp 171-174° (<1 mm). The latter after redistillation had bp 156-158° (0.5 mm); n_D^{20} 1.4808, d_D^{20} 1.1060, calculated MR 86.32, which corresponds to the data given in [8].

CONCLUSIONS

The α,α-dichloro-ω-bromoalkanes and α,α-dichloro-ω-bromoalkenes react with the benzyl- and allylmagnesium halides in tetrahydrofuran solution to give ω,ω-dichloroalkyl(alkenyl)benzenes, ω,ω-dichloroalkadienes in high yields. For all practical purposes the reactions do not go in ether.

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