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CHEMICAL TRANSFORMATIONS OF 1,1-DICHLORO-2,2-DIARYLETHANES

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1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane (DDT) and its analogs are commonly used substances. A simple method for the synthesis of 1,1-dichloro-2,2-diarylethanes (I) from a series of DDT has been reported in our previous work [1].

In the present work, we found a convenient method for going from (I) to 1,2-diarylacetylenes (DAA), which are valuable as monomers in the production of thermally stable polymers. Zakharkin et al. [2] have described the preparation of 4,4'-dichlorotolan (II) from (Ia) (Ar-p-ClC₆H₄) (DDD) by the action of NaNH₂ in liquid NH₃. Other dehydrochlorination methods do not give DAA [3, 4]. Thermolysis of (Ia) gives a mixture of products containing (II) [5], but this process has not been studied in detail. We have investigated the possibility of going from (I) to DAA under thermolysis conditions at 320-350°C or KOH in dioxane at 100°C, and by catalytic dehydrochlorination in the presence of $M_0(CO)_6$.

The thermolysis of (Ia) gives a complex mixture of products, which yielded (II), 1chloro-2,2-bis(p-chlorophenyl)ethylene (IIIa), and I-chloro-1,2-bis(p-chlorophenyl)ethylene (IV). Apparently, (II) is formed from initially obtained (IIIa) and (IV):

 $(p-\text{ClC}_{6}\text{H}_{4})_{2}\text{CHCHCl}_{2} \xrightarrow{320-350^{\circ}} (p-\text{ClC}_{6}\text{H}_{4})_{2}\text{C} = \text{CHCl} + (\text{Ia}) \qquad (\text{IIIa})$ $p-\text{ClC}_{6}\text{H}_{4}\text{CH} = \text{CClC}_{6}\text{H}_{4}\text{Cl} - p \qquad (\text{IV})$ $(\text{IIIa}) \xrightarrow{(\text{IIIa})} \rightarrow p-\text{ClC}_{6}\text{H}_{4}\text{C} \equiv \text{CC}_{6}\text{H}_{4}\text{Cl} - p + \text{HCl}$

The reaction of (I) with KOH in DEG at 150-155°C unexpectedly led not to the dehydrochlorination products but rather to diarylmethanes:

$$\begin{array}{rcl} \operatorname{Ar_2CHCHCl_2} & \xrightarrow{\operatorname{KOH/DEG}} & \operatorname{Ar_2CH_2} \\ & & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & \\ & & & & & \\ \operatorname{Ar_2CH_2} & & & & \\ \operatorname{Ar_$$

Such a difference had not been reported for DDD compounds, but analogous transformations were observed for DDT and 1,1-dichloro -2,2-bis(p-chlorophenyl)ethylene upon their heating at reflux with HOCH₂CH₂ONa in ethyleneglycol [6, 7].

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TABLE 1. ¹³ C NMR	Spectral	Parameters
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	Che	mical	$J^{1}_{\alpha}n_{\mu}$, Hz				
Compound	C1	C ² C ⁶	C ³ C ⁵	C4	C7	C ⁸	C-H
$\left(4\left\langle \underbrace{3 & 2 \\ 5 & 6 \\ 5 & 6 \\ \end{array}\right)_{2}^{7} CH_{2} (Vb)$	140,0	128,3	128,8	125,9	41,8	_	129 (C ⁷)
$(p-\text{ClC}_6\text{H}_4)_2\text{CH}_2$ (Va)	138,5	129,8	128,4	132,0	40,3	-	127 (C ⁷)
$\mathbf{Ph}_{2}\mathbf{C} = \mathbf{CHOCH}_{2}\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{OCH}_{2}\mathbf{CH}_{2}\mathbf{OH} *$	140,3 137,5	129,7 128,0	127,6 128,0	126,1	120,3	145,1	181,5(C ⁸)
$(p-\text{ClC}_6\text{H}_4)_2\text{C}=\text{CHCl}$ (IIIa)	138,0 141,7	128,8 131,7	128,5 128,7	134,3 134,4	141,6	116,7	195 (C ⁸)
p-ClC ₆ H ₄ CCl=CHC ₆ H ₄ Cl- $p(IV)$	135,1 137,2	128,3 128,3	$127,6 \\ 130,4$	131,3 133,0	133,9	124,8	154(C ⁸)
$p-\mathrm{ClC}_{6}\mathrm{H}_{4}\mathrm{C} = \mathrm{CC}_{6}\mathrm{H}_{4}\mathrm{Cl} - p (\mathrm{II})$	134,5	132,8	128,7	121,5	89,2	89,2	_
Ph ₂ CHCHCl ₂ (16)	138,7	128,3	128,6	127,4	62,6	74,6	137 (C ⁷), 177 (C ⁸) †
Ph₂CHCCl₃	138,1	130,0	128,2	127,8	71,0	101,6	131 (C7)

* δC^{9-12} : 67.8; 71.9; 72.4; 61.5 ppm. + $J^2 = 8$ Hz.

The nature of the substituent in the benzene ring has a marked effect on the transformation of (I) to (V). Thus, (Ia) is converted to (Va) in 83% yield, while (Ib) gives $Ph_2C =$ CHOCH₂CH₂OCH₂CH₂OH, apparently due to esterification of the intermediate dehydrochlorination product in addition to 27% (Vb). The action of KOH in dioxane at 100°C for 3 h on (Ia) gives (IIIa) in 86% yield. Product (II) is obtained in only 12% yield upon extending the reaction time to 7 h. The dehydrochlorination of (IIIa) does not occur under these conditions. On the other hand, isomeric (IV) readily undergoes dehydrochlorination upon heating at reflux in dioxane to give (II) in high yield. Thus, the direct transition from DDD to DAA by the action of alkaline agents cannot be carried out since, rearrangement with migration of an aryl group leading to a symmetrical diarylethylene (IV) proceeds only to a slight extent under these conditions.

We previously showed that $Mo(CO)_6$ is an effective catalyst for the dehydrochlorination of the CCl_3CH_2 group in polychloroalkanes [8]. This catalyst permits the dehydrochlorination of the $CHCl_2CH$ group in (Ia) with 1,2-aryl migration and formation of (IV) in 70% yield:

$$(p-\mathrm{Cl}_{6}\mathrm{C}_{6}\mathrm{H}_{4})_{2}\mathrm{CHCHCl}_{2} \xrightarrow{\mathrm{Mo}(\mathrm{CO})_{6}} p-\mathrm{ClC}_{6}\mathrm{H}_{4}\mathrm{CHClCHClC}_{6}\mathrm{H}_{4}\mathrm{Cl}-p \rightarrow p-\mathrm{ClC}_{6}\mathrm{H}_{4}\mathrm{CH}=\mathrm{CClC}_{6}\mathrm{H}_{4}\mathrm{Cl}-p \xrightarrow{(\mathrm{IA})} (\mathrm{IV})$$

These results may be used to propose a two-step method for the synthesis of (II) from (Ia) (DDD): 1) catalytic dehydrochlorination of DDD in the presence of $Mo(CO)_6$ leading to (IV) and 2) dehydrochlorination of (IV) by the action of KOH in dioxane to give (II).

The structures of the compounds synthesized were supported by the ¹³C NMR spectral data given in Table 1. The aromatic ring carbon atoms were assigned by analogy with the data for the ¹³C NMR spectra of p-disubstituted benzenes given in our previous work [9]. The assignment of the signals for the CH_2 group in (Va) was carried out by analogy to the work of Gronowitz et al. [10]. The structure of (Va) was also supported by mass spectral data (molecular ion with m/z 236).

EXPERIMENTAL

The ¹³C NMR spectra without and with C-H coupling suppression were taken on a Bruker WP-200 spectrometer at 200 MHz with CCl_4 or $CHCl_3$ as the standards. The mass spectrum was taken on a Varian MAT CH-8 mass spectrometer at 70 eV.

1,1-Diaryl-2,2-dichloroethanes were obtained by the reduction of the corresponding 1,1diaryl-2,2,2-trichloroethanes by 2-propanol in the presence of $Fe(CO)_5$ according to our previous procedure [1]: (Ia), mp 106-108°C, was obtained in 90% yield, while 1,1-diphenyl-2,2-dichloroethane, mp 72-74°C, was obtained in 65% yield. <u>Diarylmethanes.</u> A mixture of 20 mmoles (I) and 400 mmoles KOH in 50 ml DEG was heated with stirring for 5 h at 150-155°C. The reaction mixture was cooled and poured with stirring in 1 liter water. The precipitate was separated and recrystallized. (Ia) gave bis(4-chlorophenyl)methane (Va) in 83% yield, mp 50-52°C (from methanol) [7]. (Ib) gave diphenylmethane (Vb) (the ¹H and ¹³C NMR spectra were identical to those of an authentic sample) in 27% yield and 1,1-diphenyl-2,2-(hydroxyethoxy)ethylethylene in 50% yield. The latter product is a nondistilling oil, which decomposes upon standing and column chromatography. Found: C 75.19; H 7.00%. Calculated $C_{18}H_{20}O_3$: C 76.03; H 7.09%.

<u>Dehydrochlorination of DDD.</u> a) KOH in ethanol. A mixture of 20 mmoles (Ia) and 400 mmoles KOH in 50 ml abs. ethanol was heated at reflux for 5 h. After cooling, the reaction mixture was poured into water, and the precipitate was recrystallized to give (IIIa) in 63% yield, mp 64-66°C (from pentane).

b) KOH in dioxane. A mixture of 20 mmoles (Ia) and 160 mmoles KOH in 20 ml dioxane was heated for 3 h at 100°C and analogous work-up gave (IIIa) in 86% yield.

c) $Mo(CO)_6$ in tetrachloroethane. A solution of 10 mmoles (Ia) and 0.5 mmole $Mo(CO)_6$ in 30 ml 1,1,2,2-tetracloroethane was heated for 2.5 h at 140-145°C. The reaction mixture was subjected to chromatography on silica gel (100-160 mm) with CCl_4 as eluent to remove tar. The eluate gave (IV) in 70% yield, mp 96-98°C (from methanol) [4].

Dehydrochlorination of 1,1-Bis(4-chlorophenyl)-2-chloroethylene (IIIa). A mixture of 8 mmoles (IIIa) and 40 mmoles KOH in 5 ml dioxane was heated for 3 h at 100°C. Starting (IIIa) was recovered quantitatively.

Dehydrochlorination of 1-Chloro-1,2-bis(p-chlorophenyl)ethylene (IV). A mixture of 2 mmoles (IV) and 10 mmoles KOH in 10 ml dioxane was heated at reflux for 3 h. The reaction mixture was cooled and poured into water. The precipitate was extracted with benzene. Recrystallization gave 4,4-dichlorodiphenylacetylene (II) in 90% yield, mp 174-175°C [4].

<u>Thermolysis of DDD.</u> A sample of 20 mmoles DDD was heated for 5 h at 320-350°C in a nitrogen stream. Thin-layer chromatography indicated multiple components in the reaction mixture. Column chromatography with elution by hexane and CCl_4 provided for the separation of (II), (IIIa), and (IV).

CONCLUSIONS

1. Upon alkaline dehydrochlorination in diethyleneglycol, 1,1-dichloro-2,2-bis(p-chloro-phenyl)ethane (DDD) and its analogs are converted to diarylmethanes.

2. $Mo(CO)_6$ catalyzes the intramolecular rearrangement of DDD and the dehydrochlorination of the product, 1,2-bis(4-chlorophenyl)-1,2-dichloroethane to 1-chloro-1,2-bis(4-chlorophenyl)ethylene.

3. A two-step procedure was proposed for the synthesis of 1,2-diarylacetylenes involving dehydrochlorination of DDD compounds by the action of $Mo(CO)_6$ to give 1-chloro-1,2diarylethylenes and their subsequent alkaline dehydrochlorination.

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