ACTION OF SODIUM ON COMPOUNDS CONTAINING A CCl₂ = CH GROUP

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Pinner [1, 2] was the first to investigate the action of sodium on the 2,2-dichlorovinyl group, the compound selected for study being 1,1-dichloropropene. He showed that, when the product of reaction between 1,1-dichloropropene and sodium was decomposed with water, propyne was formed in low yield [2]: treatment of the reaction product with carbon dioxide gave propionic acid [3]. Pinner supposed that, in the reaction of 1,1-dichloropropene with sodium, the product had the composition C₆H₄Cl₂Na₂, the course of the reaction being as follows, with separation of sodium chloride only during the stage of decomposition with water:

\[
\text{CH₃CH = CCl₂ + 2Na} \rightarrow \text{C₆H₄Cl₂Na₂} \xrightarrow{\text{H₂O}} \text{CH₃C = CH} \rightarrow 2\text{NaCl.}
\]

This reaction has not been studied further.

Various 2,2-dichlorovinyl derivatives now being readily available [4, 5], we considered it of interest to investigate this reaction from the preparative point of view, and also to elucidate the mechanism of the conversion of the CCl₂ = CH group into the HC = C group, since we did not consider the mechanism postulated by Pinner to be very likely. We found, in agreement with previous work, that treatment of the product of reaction between 1,1-dichloro-1-pentene and sodium with carbon dioxide yielded 2-hexynoic acid, and that treatment of the product of reaction between 5,5-dichloro-N,N-diethyl-4-pentenylamine and sodium with benzaldehyde yielded 6-diethylamino-1-phenyl-2-hexyn-1-ol C₆H₅CH(OH)C≡C(CH₂)₂N(C₂H₅)₂. These results show that the product of reaction between a 2,2-dichlorovinyl derivative and sodium contains RC = CNa and that this is formed by the removal of two chlorine atoms and one hydrogen atom from the CCl₂ = CH group. It is to be expected that the chlorine will separate in the form of sodium chloride. It was found that only a very small amount of hydrogen was evolved in the reaction (2.5% of the theoretical amount), and only when the reaction product was decomposed with water was the expected amount of hydrogen liberated (0.5 mole per mole of 2,2-dichlorovinyl derivative). It was found also that in this reaction it was necessary to take 4 g atoms of sodium for each mole of the 2,2-dichlorovinyl derivative, and not 2 g-atoms, as indicated by Pinner. These results can be explained on the assumption that hydrogen from the CCl₂ = CH group becomes bound as sodium hydride, and the reaction of 2,2-dichlorovinyl derivative with sodium can be represented as follows:

\[
\text{RC = CCl₂ + 4Na} \rightarrow \text{RC = CNa + NaH + 2NaCl.}
\]

The formation of RC = CNa may proceed as follows:

\[
\text{RCH = CCl₂ + 2Na} \rightarrow \text{RC = CNa + NaH.}
\]

Confirmation of this reaction mechanism can be found in the formation of some monosubstituted acetylene and sodium or lithium hydride, which was observed in a number of cases when monohalo olefins of the type RCH = CHX were treated with sodium or lithium [6, 7]. The replacement of chlorine by sodium in RC = C–Cl occurs very readily [8]. Our study of the action of sodium on 2,2-dichlorovinyl derivatives showed that the reaction proceeds fairly smoothly: in most of the cases investigated it gave the monosubstituted acetylene in a yield of 60–80%.

The properties and yields of the monosubstituted acetylenes obtained are given in Table 1. In the case of 1,1-dichlorostyrene we did not succeed in obtaining a good yield of ethynylbenzene owing to the impossibility of carrying out the reaction to completion. In the case of (3,3-dichlorallyl)benzene the product, obtained in satisfactory yield, was a mixture of substances —mainly phenylpropadiene. Taking 4,5,5-trichloro-N,N-diethyl-4-pentenylamine as our example, we showed that the CCl₂ = CCl group is converted by sodium into the HC = C group:

\[
(C₆H₅)₂N(CH₂)₂CCl = CCl₂ + 4Na \rightarrow (C₆H₅)₂N(CH₂)₂C = CNa + 3NaCl.
\]
A good yield of N,N-diethyl-4-pentenylamine was obtained. Conversion of 5-ethoxy-1-pentyne into its organomagnesium bromide and treatment of the product with benzaldehyde gave a good yield of 6-ethoxy-1-phenyl-2-hexyn-1-ol.

**EXPERIMENTAL**

**1,1-Dichloro-1-nonene.** A mixture of 60 g of 1,1,1-trichlorononane and 3 g of anhydrous ferric chloride was heated at 60-75°C until hydrogen chloride ceased to be evolved. The mixture was cooled, ferric chloride was filtered off, and the filtrate was diluted with chloroform and washed with hydrochloric acid. Fractionation through a column yielded 39.4 g (77.5%) of 1,1-dichloro-1-nonene, b.p. 85-86°C (7 mm); n\(D\)_20 1.4597; d\(4\)_20 1.0106; found MR 52.84; calculated MR 53.03.

**1,1-Dichloro-5-ethoxy-1-pentene.** A solution of 1-1-5-trichloro-1-pentene (40 g) and sodium ethoxide (from 6.5 g of sodium) in 85 ml of absolute alcohol was heated for four hours, cooled, and poured into water. The oil that separated was extracted with chloroform. Vacuum distillation yielded 29.3 g (69%) of 1,1-dichloro-5-ethoxy-1-pentene, b.p. 79-81°C (11 mm); n\(D\)_20 1.4642; d\(4\)_20 1.1101; found MR 45.50; calculated MR 45.44.

**1,1-Dichloro-7-ethoxy-1-heptene.** A solution of 1,1,7-trichloro-1-heptene (40 g) and sodium ethoxide (from 6 g of sodium) in 80 ml of absolute alcohol was heated for six hours. The product was 32.4 g (77%) of 1,1-dichloro-7-ethoxy-1-heptene, b.p. 114-116°C (15 mm); n\(D\)_20 1.4622; d\(4\)_20 1.0603; found MR 54.71; calculated MR 54.68.

**5,5-Dichloro-N,N-diethyl-4-pentenylamine.** A solution of 50 g of 1,1,5-trichloro-1-pentene and 50 g of diethylamine in 120 ml of methanol was heated in an autoclave at 100-115°C for 5-6 hours. Excess of diethylamine and methanol was driven off from a water bath, and the residue was treated with hydrochloric acid. The undissolved oil was extracted with ether. The hydrochloric acid solution was rendered alkaline with cooling, and the oil that separated was extracted with ether. The product was 51.2 g (83.5%) of 5,5-dichloro-N,N-diethyl-4-pentenylamine, b.p. 63-64°C (2 mm); n\(D\)_20 1.4719; d\(4\)_20 1.0349; found MR 56.81; calculated MR 56.93.

**7,7-Dichloro-N,N-diethyl-6-heptenylamine.** This was prepared similarly to 5,5-dichloro-N,N-diethyl-4-pentenylamine in 88% yield. It had b.p. 89-90°C (1.5 mm); n\(D\)_20 1.4730; d\(4\)_20 1.0097; found MR 66.14; calculated MR 66.21.

**1,1-Dichloro-9-ethylthio-1-nonene.** This was prepared by heating 1,1,9-trichloro-1-nonene with a small excess of C\(_2\)H\(_2\)SNa in alcoholic solution; the yield was 92.8%. It had b.p. 120-121°C (1 mm); n\(D\)_20 14991; d\(4\)_20 1.0672; found MR 70.17; calculated MR 70.26.

**1,1-Dichloro-5-phenoxy-1-pentene.** A solution of 1,1,5-trichloro-1-pentene (40 g), sodium iodide (1.5 g), and sodium phenoxide (from 28 g of phenol) in 100 ml of alcohol was heated for 8 hours 30 minutes. The product was 37.6 g (70.5%) of 1,1-dichloro-5-phenoxy-1-pentene, b.p. 112-113°C (2 mm); n\(D\)_20 1.5375; d\(4\)_20 1.1914.