## REACTIONS OF ORGANIC ANIONS.XXIV. CATALYTIC METHOD FOR PREPARATION OF DICHLOROCYCLOPROPANE DERIVATIVES IN AQUEOUS MEDIUM X/

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(Received in UK 17th Sectember 1969; accepted for publication 14th October 1969) An elegant synthesis of dichlorocyclopropane derivatives by dichlorocarbene addition to olefins was discovered by Doering (1) and them thoroughly investigated throughout the last 15 years. In addition to the Doering's original procedure for generating dichlorocarbene (CHCl<sub>3</sub> + dry  $t-C_{4}H_{9}OK$ ), many other methods have been developed for example: CBrCl<sub>3</sub> + BuLi; CCl<sub>3</sub>COOCH<sub>3</sub> + CH<sub>3</sub>ONa; decarboxylation of anhydrous CCl<sub>3</sub>COONa etc. These procedures, as well as their application for the synthesis of dichlorocyclopropane derivatives, are reported in detail in a number of excellent review articles (2). All authors stress the necessity of operating under strictly anhydrous conditions, because of the ready and rapid hydrolysis of dichlorocarbene.

In an earlier work (3), we have observed that dichlorocarbene was formed in the reaction between chloroform and arylacetonitriles in the presence of aqueous NaOH with triethylbenzylammonium chloride (TEBA) as catalyst; when the reaction was carried out with excess of cyclohexene added, dichloronorcarane was obtained in a yield of about 40 %. The present detailed investigation of this reaction permitted us to develop a new method for the preparation of dichlorocyclopropane derivatives by the addition of dichlorocarbene to olefins; the method involves the reaction of olefin with chloroform in the presence of a concentrated

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aqueous solution of sodium hydroxide and catalytic amounts of TEBA chloride (4).

The reaction proceds exothermically when the reagents are mixed at room temperature, and the isolation of the resulting products presents no difficulties. The yields of dichlorocyclopropane derivatives obtained by this method are high, usually about 70 %, with no excess of the olefin required. The ratio of olefin to chloroform varied from 2:1 to 1:2, depending on the availability of the olefin. Although the reaction is carried out in aqueous medium, only a small fraction of the generated dichlorocarbene is hydrolysed.

The synthesis of 1-phenyl-2,2-dichlorocyclopropane is a good illustration of the method:

10.4 g (0,1 mole) of styrene, 12 g (0,1 mole) of chloroform (alcohol-free), 20 ml of 50 % aqueous NaOH solution and 0,4 g TEBA chloride are stirred at  $40^{\circ}$ C for 4 hours. Upon dilution with water, separation of the layers and distillation, 15 g (yield 80%) of 1-phenyl-2,2-dichlorocyclo-propane are obtained. The aqueous layer contains 0,1 gram-equivalent of Cl<sup>-</sup> ions, including the 0,002 g-e. originating from the catalyst. According to the reaction equation

 $CHCl_{3} \xrightarrow{\text{CCl}_{3}} CCl_{2} + Cl_{2} + Cl_{2}$ :CCl<sub>2</sub> + PhCH=CH<sub>2</sub> -----> Ph-CH-CH<sub>2</sub>; :CCl<sub>2</sub> + 2OH<sup>-</sup> ----> CO + 2Cl<sup>-</sup> + H<sub>2</sub>O

one chlorine anion is formed per one molecule of dichlorocyclopropane, and three chlorine anions per one molecule of hydrolysed dichlorocarbene. When the yield of the phenyldichlorocyclopropane derivative is considered, simple calculation shows that only 7% of the dichlorocarbene produced undergo hydrolysis, whereas 93% react with the olefin. It is striking that the degree of dichlorocarbene utilization is so high, in spite of the reaction being carried out in aqueous medium and with only equimolar amount of olefin (without the catalyst, from cyclohexene and chloroform in the presence of 50% aqueous KOH Doering obtained dichloronorcarane in only 0,5% yield); this fact may be explained by the quaternary ammonium compound's catalytic mode of action as postulated for the catalytic alkylation of phenylacetonitrile in aqueous medium (5). In concentrated NaOH solution, TEBA chloride is transformed into the hydroxide which is insoluble in the reaction medium. Thus, quaternary ammonium hydroxide migrates to the boundary between the aqueous and organic phase, where it reacts with chloroform to yield the quaternary ammonium derivative of the trichloromethyl anion.

$$CHCl_3 + Et_3NCH_2Ph OH = CCl_3 Et_3NCH_2Ph + H_2O$$

$$CCl_3 Et_3NCH_2Ph ----- : CCl_2 + Et_3NCH_2Ph Cl^-$$

After diffusion into the organic phase, the derivative is transformed into dichlorocarbene and ammonium chloride. Dichlorocarbene reacts rapidly with the olefin present in the organic layer, whereas ammonium chloride passes to the phase boundary and reenters the transformation cycle. Thus, dichlorocarbene is formed in an anhydrous medium and, consequently, it is hydrolyzed to only a slight extent. On the other hand, the high degree of dichlorocarbene utilization, as observed despite the use of stoichiometric amounts of olefin and chloroform, is due to the fact that the quantity of dichlorocarbene which can be formed at a time is small and does not exceed the amount of the catalyst.i.e. 1%. Consequently, dichlorocarbene is always confronted with a large excess of olefin.

Similar results are obtained, when reacting chloroform with other olefins. The yields and properties of some dichlorocyclopropane derivatives are presented in Table 1.

The presented catalytic method for the synthesis of dichlorocyclopropane derivatives in aqueous medium seems to be the simplest of the procedures used so far, analogous with to the earlier developed method for catalytic alkylation of arylacetonitriles (6) and cyclopentadiene hydrocarbons (7).

| Table | 1 |
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When molar ratio styrene + chloroform was 1:2 yield exceded 90 % XX New compound; satisfactory analytical data were obtained.

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