

REACTIONS OF ORGANIC ANIONS.XXIV. CATALYTIC METHOD FOR PREPARATION  
OF DICHLOROCYCLOPROPANE DERIVATIVES IN AQUEOUS MEDIUM <sup>x/</sup>

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An elegant synthesis of dichlorocyclopropane derivatives by dichlorocarbene addition to olefins was discovered by Doering (1) and then thoroughly investigated throughout the last 15 years. In addition to the Doering's original procedure for generating dichlorocarbene ( $\text{CHCl}_3 + \text{dry } t\text{-C}_4\text{H}_9\text{OK}$ ), many other methods have been developed for example:  $\text{CBrCl}_3 + \text{BuLi}$ ;  $\text{CCl}_3\text{COOCH}_3 + \text{CH}_3\text{ONa}$ ; decarboxylation of anhydrous  $\text{CCl}_3\text{COONa}$  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.

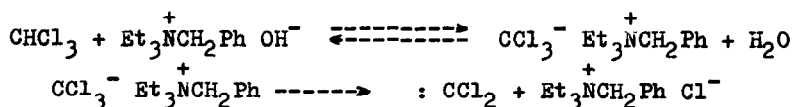
In an earlier work (3), we have observed that dichlorocarbene was formed in the reaction between chloroform and arylacetonitriles in the presence of aqueous NaOH with triethylbenzylammonium chloride (TEBA) as catalyst; when the reaction was carried out with excess of cyclohexene added, dichloronorcarane 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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<sup>x/</sup> Part XXIII. M. Małosza, M. Jawdosiuk, Bull. Acad. Polon. Sci., Ser. sci. chim.,  
16, 597 /1968/



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.

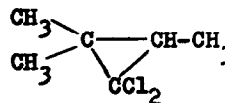
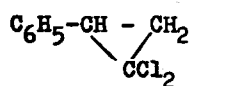
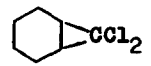
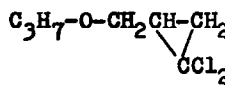
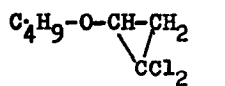


After diffusion into the organic phase, the derivative is transformed into dichlorocarbene and ammonium chloride. Dichlorocarbene reacts rapidly with the olefin present in the organic layer, whereas ammonium chloride passes to the phase boundary and reenters the transformation cycle. Thus, dichlorocarbene 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

Compound	Yield	Max.yield reported	2
	60 %	66 %	
	80 % <sup>x</sup>	76 %	
	72 %	91 %	
	64 %	b.p. 86°/20 mm Hg	<sup>n<sub>D</sub> 22</sup> 1,4533 <sup>xx</sup>
	71 %	83°/20 mm Hg	1,4508 <sup>xx</sup>

<sup>x</sup>When molar ratio styrene + chloroform was 1:2 yield exceeded 90 %

<sup>xx</sup> New compound; satisfactory analytical data were obtained.

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