

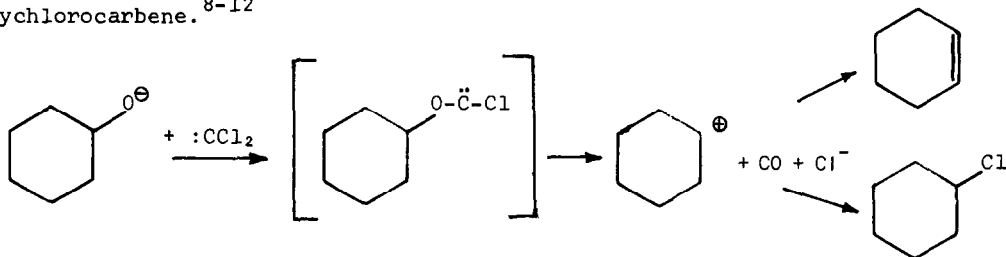
REACTION OF 1,2-GLYCOLS WITH DICHLOROCARBENE PRODUCED BY PHASE TRANSFER CATALYSIS

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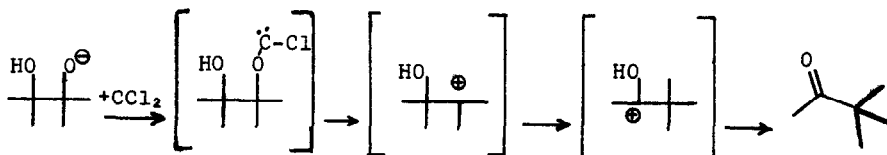
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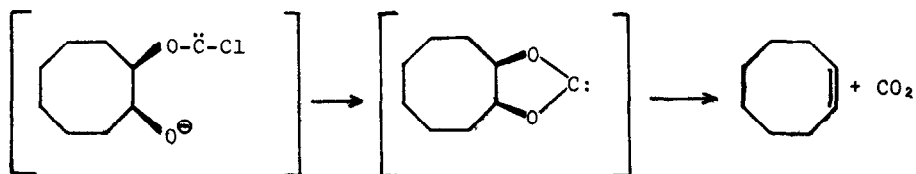
The reaction of aliphatic alcohols with dichlorocarbene generated by the reaction of CHCl_3 with base has been reported to yield alkenes, cyclopropanes, or alkyl chlorides depending on reaction conditions.¹⁻⁷ These results have been interpreted in terms of the following reaction sequence: displacement of chloride from dichlorocarbene by an alkoxide anion leads to an alkoxychlorocarbene which decomposes to yield a carbonium ion, carbon monoxide, and a chloride ion.² While considerable evidence for the intermediacy of a carbonium ion in this reaction has been presented, relatively little is known about the precursor alkoxychlorocarbene.⁸⁻¹²



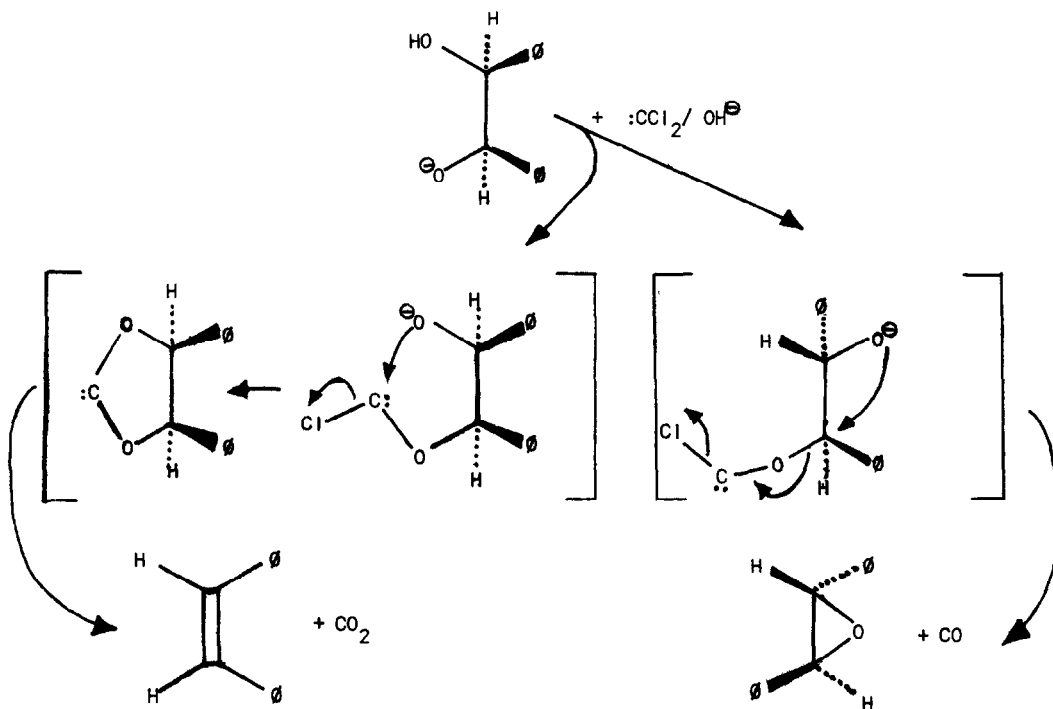
In analogy to the reaction of aliphatic alcohols with dichlorocarbene under basic conditions, one would predict that formation of a carbonium ion as the product determining intermediate in the reaction of 1,2-glycols with dichlorocarbene would lead to ketones and or aldehydes as primary reaction products. Despite this, we find products from the reaction of 1,2-glycols with dichlorocarbene under basic phase transfer catalysis conditions (PTC)¹³⁻¹⁵ which can best be accounted for if the proposed alkoxychlorocarbene intermediate has a sufficient lifetime to be trapped by an internal alkoxide nucleophile prior to its ionization to a carbonium ion.



Specifically the reaction of cis-1,2-cyclooctanediol¹⁶ with dichlorocarbene under PTC conditions yields in addition to cyclooctanone, (and products presumed to be formed by aldol condensation of cyclooctanone) cyclooctene, and the dichlorocarbene adduct of cyclooctene.¹⁷ The relative amounts of cyclooctene and its dichlorocarbene adduct depend on the amount of CHCl_3 used. The dichlorocarbene adduct of cyclooctene was isolated in 25% yield when CHCl_3 and base were present in large excess. Apparently under PTC conditions the adjacent alkoxy group reacts with the alkoxychlorocarbene center displacing the second chloride ion affording a cyclic dialkoxycarbene. This decomposes to yield carbon dioxide and the corresponding alkene. Subsequent addition of dichlorocarbene to the olefin yields the observed adduct. An identical cyclic dialkoxycarbene intermediate has been proposed by Corey^{18,19} to explain the stereospecific formation of alkenes from the reaction of trimethylphosphite with thiocarbonates of 1,2-glycols.



Two additional cases have been examined. A 15% yield of the dichlorocarbene adduct of 2,3-dimethyl-2-butene²⁰ was isolated from the reaction of CHCl_3 with pinacol under PTC conditions. Treatment of meso-dihydrobenzoin under basic PTC conditions with CHCl_3 results in cis-stilbene²¹ (15% yield), the product expected from decomposition of a cyclic dialkoxycarbene intermediate and trans-stilbene oxide (35% yield), a product whose formation may be rationalized by the following reaction scheme.²²



Experimental Procedure: In a 500 ml round bottom flask equipped with a magnetic stirring bar and reflux condenser were placed 3 g of cis-1,2-cyclooctanediol,¹⁶ 100 ml of CH_2Cl_2 , 100 ml of a 50% aqueous NaOH solution, 2 g of benzyltriethylammonium chloride (the PTC catalyst), and 5 cc of $CHCl_3$. The reaction was carried out in an efficient hood since small amounts of carbon monoxide are generated by hydrolysis of dichlorocarbene under these conditions. The exothermic reaction was stirred for two hours at which time another 5 cc of $CHCl_3$ was added to maximize the yield of the dichlorocarbene adduct. Stirring was continued over night and then the reaction was worked up. The crude reaction mixture was chromatographed over alumina. The dichlorocarbene adduct of cyclooctene (25% yield) was eluted with hexane. Small amounts of benzyl chloride, apparently formed by decomposition of the PTC catalyst, were also found.

The reaction of dichlorocarbene with pinacol was carried out in a similar

manner. Whereas, the reaction of meso-dihydrobenzoin was run in three times the volume of CH_2Cl_2 and was worked up after three hours.

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