Tetrahedron Letters No.59, pp. 5147-5150, 1969. Pergamon Press. Printed in Great Britain.

CHEMISTRY OF THE VINYL CATION - THE ADDITION OF DCl TO ALLENE

Barbara S. Charleston, Cecile K. Dalton, Stephen S. Washburne and D. R. Dalton (1)

Department of Chemistry, Temple University
Philadelphia, Pennsylvania 19122

and

Stephen R. Schraeder

Wyeth Laboratories, Inc.
Radnor, Pennsylvania 19087

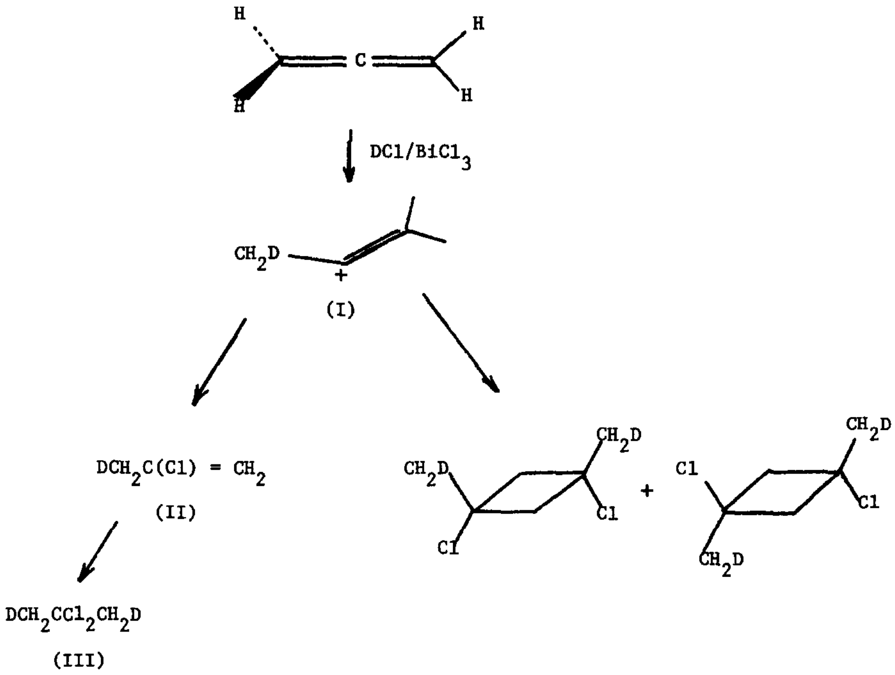
(Received in USA 14 November 1969; received in UK for publication 20 November 1969)

Pivotal to the concept of the vinyl cation generated *via* the protonation route (2,3) are the results of the addition of HCl to allene (4 - 7). Thus, this addition, at -70° generates a mixture of 2-chloropropene, 2,2-dichloropropane, and the dimers, *cis*- and *trans*-1,3-dichloro-1,3-dimethylcyclobutane. The reports (4 - 7) indicate that significant quantities (4%) of these compounds are formed at this temperature only in the presence of air and bismuth trichloride catalyst.

The formation of the observed products has been ascribed to initial generation of a vinyl cation (I, D = H) which reacted with chloride before or after dimerization (SCHEME). However, since the same products could be obtained, under the conditions of the reaction from methyl acetylene, albeit more slowly, concrete evidence that (I, D = H) did not undergo proton loss, followed by reprotonation and reaction with chloride, was lacking.

We report here (i) the results of the addition of DCl to allene, under the previously reported conditions, which uniquely serves to distinguish the above possible routes and (ii) preliminary results on the possible advantageous use of other catalysts.

DCl (8) and allene (1.1:1 molar ratio) were stirred at -78° in the presence of air and $BiCl_3$ (9) for 14 days. Under these conditions, a 0.83% yield (10) of chlorinated products,



SCHEME

consisting of 2-chloro-3-deuteriopropene-1 (63%) (II), 2,2-dichloro-1,3-dideuteriopropane (35%) (III), and a small amount (2%) (deuterium content unknown) of 1,3-dichloro-1,3-dimethylcyclobutane, were obtained.

Compounds (II) and (III) and the dimers were separated by preparative glpc (10) along with unreacted allene. Examination of the pmr spectra (11) and the mass spectra (12a) of (II), (III) and recovered allene, demonstrated that, within experimental error, (i) all deuterium in (II) resided only in the methyl group (m/e, $^{35}ClC^{+}{=}CH_2$ [61] : $^{37}ClC^{+}{=}CH_2$ [63] of 1:3 in both the deuterated and nondeuterated 2-chloropropene and an m/e ratio of masses 61:62:63 of 1:4.5:3 for both were in accord with this result, as well as a fragment for CH_2D^{+}, m/e 16 (12b)); (ii) in (III) each methyl group bore one, and only one, deuterium atom (m/e $^{35}Cl^{35}ClCCH_2D^{+}$ [98], $^{35}Cl^{37}ClCCH_2D^{+}$ [100] and $^{37}Cl^{37}ClCCH_2D^{+}$ [102]) by comparison to nondeuterated material; and (iii) recovered allene contained no deuterium.

That a deuterium isotope effect is present is indicated by the reduced yield in the reaction with DCl. A quantitative estimate is, however, in our opinion, inappropriate because of the low yields and the uncertain nature of the role of the catalyst. Indeed, although it has been pointed out that metal ion catalysis in necessary for the reaction to proceed even to the extent noted (7) the role of $BiCl_3$ as a catalyst is not understood and, while it may in fact (13) act to promote the polarization of the HCl or DCl bond, concrete evidence is lacking.

Thus, although the results of this work tend to substantiate the intermediacy of the vinyl cation in this reaction, it appears likely that until definite information concerning the role of the catalyst is obtained, such a conclusion may be unwarranted.

Finally, in this regard, we have found that the same reaction, in the presence of titanium tetrachloride ($TiCl_4$) generates, under conditions identical to those given, an 80% (14) yield of chlorinated products (74% 2,2-dichloropropane; 24% 2-chloropropene; 2% dimers) and a 58% yield (67% 2,2-dichloropropane; 31% 2-chloropropene; 2% dimers) in the presence of ferric bromide ($FeBr_3$) and that, within the limits of detectability <u>no</u> organic bromine containing compounds are present in the latter case.

Kinetic investigations of this reaction in the presence of $TiCl_4$ and $FeBr_3$ catalysts are in progress.

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(8) DCl was obtained from the Matheson Company and had a typical analysis of 98.4% DCl, 1.5% HCl, 0.14% deuterium and "an undetectable amount of chlorine".

(9) The $BiCl_3$, ultra pure grade, was obtained from Alfa Inorganics.

(10) Preparative glpc was carried out on an Aerograph A90 - P3 using a 20 ft. 3/8 in. column of 20% didecyl phthalate on Chromsorb W with helium as a carrier gas.

(11) PMR spectra were recorded with a Varian A - 60A spectrometer in CCl_4 solvent using TMS as an internal standard. Integrals were in accord with the mass spectral data for all deuterated compounds. Authentic samples of nondeuterated materials for pmr and mass spectral comparison were obtained from Chemical Samples Co., Columbus, Ohio and repurified by glpc.

(12) (a) Mass spectra were obtained for nondeuterated and deuterated compounds on an AEI MS-9 mass spectrometer using an unheated inlet and at various voltages up to and including 70 volts. (b) Because of the presence of HCl in the DCl (8) an m/e fragment 15 (CH_3^+) was present in the 2-chloro-3-deuteriopropene-1 and the 2,2-dichloro-1,3-dideuteriopropane. Thus, in 2-chloropropene derived from addition of HCl to allene, the peak height ratio m/e (CH_2D^+)/(CH_3^+) [16/15] was 0.11, while in the deuterated product, the same ratio was 4.0. For this compound, the m/e fragments assigned to $CH_2{=}CHCl^+$, as pointed out, vide supra, remain unchanged regardless of their source (i.e. deuterated or nondeuterated product).

(13) P. B. de la Mare and R. Bolton, "Electrophilic Addition to Unsaturated Systems," Elsevier Co., New York, N. Y., 1966, p. 213

(14) This corresponds to a 100% yield of chlorinated products on the basis of HCl as the limiting reagent.