Tetrahedron Letters, Vol.22, No.20, pp 1889 - 1890, 1981
Printed in Great Britain

0040-4039/81/201889-02$02.00/0

A 1,2-PHENYL SHIFT TO THE DOUBLE BOND OF A VINYL CATION

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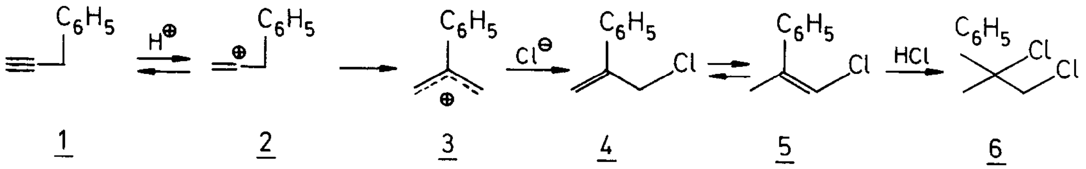
Abstract: Reaction of HCl with 3-phenylpropyne (1) afforded 1,2-dichloro-2-phenylpropane (6) among other products. The reaction proceeds by a 1,2-phenyl shift to the 3-phenyl-1-propene-2-yl cation (2).

Whereas 1,2-alkyl shifts towards the double bonds of vinyl cations have been repeatedly reported (1), there is no experimental evidence (2) for an analogous 1,2-phenyl shift (3). We shall report such evidence in the following:

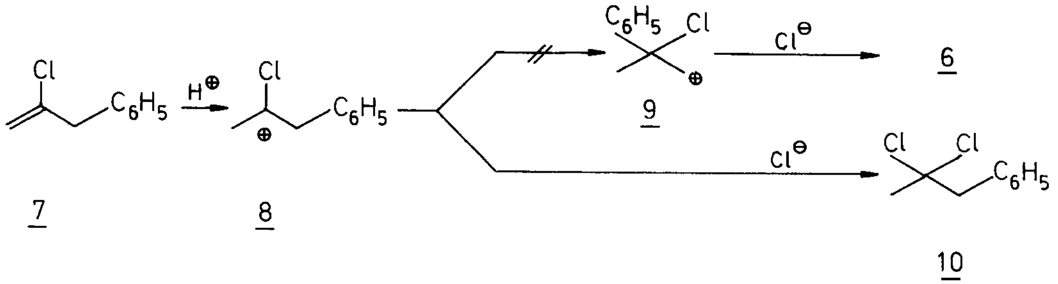
Liquid phase reactions of anhydrous hydrogen chloride with 1 in molar ratios of 10:1, 5:1 and 1:1 have been carried out in sealed glass ampoules at ambient temperatures. After 10-14 days of reaction, the unreacted hydrogen chloride was removed and the liquid crude reaction products were recovered. ^{1}H-NMR-analysis showed besides those of other components the CH_3- and the CH_2-signals of the diadduct 6. The assignment of these signals was substantiated by isolation of 6 from the crude product of the 5:1 reaction by means of adsorption chromatography (column 2.5 x 74 cm, 260 g silicagel, n-pentane) and by its subsequent ^{1}H-NMR-analysis: (CCl_4, TMS) δ = 1.98, s, 3H; δ = 3.89, s, 2H; δ = 7.1 - 7.6, m, 5H. Quantitative ^{1}H-NMR-analysis of the crude reaction products showed that 6 was obtained in approx. 6 % from the 1:1 reaction, in 11 % from the 5:1 reaction and in 17 % from the 10:1 reaction.

Attempts at isolating 6 from a distillate fraction of the 5:1 reaction product (b.p. 45-62 °C/0.12 Torr) by means of preparative g.l.c. (column 0.50 x 500 cm, 5 % nitrilesiliconoil XE 60 on chromosorb G, 140 °C) afforded the monoadducts of structures 4 and 5. The ^{1}H-NMR-data of 4 and 5 (CCl_4, TMS; 4 : δ = 4.36, d, 1.0 Hz, 2H; δ = 5.38, m, 1H; δ = 5.48, m, 1H; δ = 7.23-7.58, m, 5H; 5 : δ = 2.20, d, 1.5 Hz, 3H; δ = 6.24, m, 1H; δ = 7.25, s, 5H) were in good agreement with those reported in the literature (5) (6).

The formation of 6 during the reaction of HCl with 1 is rationalized by the reaction sequence depicted below. It involves a 1,2-phenyl shift to the double bond of the vinyl cation 2 to afford the allylic cation 3. Although the latter has primary-type cationic resonance structures, the resonance stabilization gained appears to provide sufficient driving force for the phenyl migration. The intermediacy of 4 and of 5 has not been proven in these reactions, i.e. 4 and 5 have not been definitely identified in the product mixtures. Their isolation by g.l.c. may have been preceded by dehydrohalogenation of 6 in the gas chromatograph.



A conceivable alternate mode of formation of 6, viz. phenyl migration to the cation 8 was unlikely, since it would require the formation of the non-stabilized primary cation 9. Indeed, it could be ruled out experimentally: Reaction of HCl with 7 afforded diadduct 10, but no detectable amounts of 6.



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6. All new compounds showed satisfactory elemental analyses.

(Received in Germany 9 January 1981)