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It is known that cyclopropene compounds undergo various transformations in the presence of acids. The most probable mechanism of these transformations consists in the addition of a proton to the double bond with the formation of the cyclopropyl cation, which opens up in a disrotator manner to give the allyl cation, the subsequent fate of which depends on the structure of the starting cyclopropene and the reaction conditions [1]. Since the allyl cation easily undergoes intramolecular rearrangements with involvement of the substituents, it is difficult to judge its original structure on the basis of the reaction products [2-5].

The purpose of the present paper was to fix the original structure of the allkyl cation, which would make it possible to confirm the mechanism of the rearrangements of cyclopropene compounds in the presence of acids and examine the practically unknown stereochemistry of the cleavage of the cyclopropyl cation. We selected 1, 2, 3-triphenylcyclopropene (I) as the study object, which in acid medium is converted to 1, 2-diphenylindene [2]. The advantages of (I) in studying the stereochemistry of opening the ring are associated with the fact that, first, attack of the double bond of the ring by a proton is apparently possible only from the less shielded side of the ring; second, the unsymmetrical nature of the molecule with respect to the plane of the ring makes it possible to judge the direction of bond rotation during ring opening. The reaction was run with a 2-3-fold excess of CF_3COOH at ~ 20°C in methylene chloride in the presence of an equimolar amount of triethylsilane. The triphenylallyl cation was fixed by the transfer of hydride (or deuteride) ion to it from triethylsilane (or deuterotriethylsilane) [6]. Mild reaction conditions made it possible to avoid undesirable secondary transformations, and cis-1, 2, 3-triphenyl-1-propene (cis-IV) or cis-1,2,3-triphenyl-1-propene-d₃ (IVa) was obtained in $\sim 100\%$ yield. The structure of these compounds was confirmed by the fact that their constants and spectral characteristics coincided with the literature data [7, 8]. The absence of the trans-isomer in the reaction product was judged by the NMR spectrum of the reaction mixture, which did not have a signal at 4.00 ppm, which is characteristic for the benzyl protons of this isomer [7]; for the cis-isomer this signal is found at 3.7 ppm.

The obtained results can be interpreted in the following manner. Attack of the double bond of (I) by a proton actually occurs from the less hindered side of the ring (Scheme, path A), since in the opposite case (path B) the formation of the cyclopropyl cation (VIII) and its disrotator opening to the allyl ion in the presence of a hydride donor would lead to the formation of a mixture of two isomeric propenes (cis-IV) and (trans-IV) (conrotator opening is forbidden by the orbital symmetry) [9]. This circumstance simplifies the stereochemical picture of the reaction, since the addition of a proton to (I) should lead only to the cyclopropyl cation (II). The quantitative formation of the cis-isomer and the absence of the trans-isomer leave the sole possibility of the opening of cation (II), and specifically in a disrotator manner, with a rotation of the substituents on the outside, since a rotation of the substituents on the inside, and also the forbidden conrotator opening, should lead to the respective formation of the trans-isomer or a mixture of the cisand trans-isomers. To form 1, 2-diphenylindene (VII) the triphenylallyl cation should be found in the (VI) configuration. The direct formation of (VI) from (II) is forbidden by the orbital symmetry. Consequently, (VI) is formed as the result of the secondary transformation of (III) to (VI) via allyl ion (V) [10].

The above said makes it possible to assume that by the transfer of a hydride ion we were able to fix the allyl cation that is formed directly during ring opening in the reaction of 1, 2, 3-triphenylcyclopropene with CF₃COOH, and testifies to the fact that this opening proceeds stereospecifically and in harmony with the Woodward—Hoffman rule.

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EXPERIMENTAL METHOD

The GLC analysis was run on a Pye-104 instrument, using a 0.5×120 cm glass column, packed with 3% SE-30 deposited on Gas-Chrom Z (80-100 mesh), at 225°. The IR spectra were taken on a UR-20 instrument, the UV spectra were taken on a Specord UV-VIS instrument, the NMR spectra were taken on a Varian DA-60-IL instrument, and the mass spectra were taken on a Varian MAT CH-6 instrument. The commercial CF₃CQOH was refluxed for 2 h with conc. H₂SO₄ and then was distilled in a dry nitrogen stream, bp 72.5°, mp -15.2°. Triethylsilane was obtained by reacting ethylmagnesium bromide with HSiCl₃ [11], bp 108-109°. 1, 2, 3-Triphenylcyclopropene (I) was obtained as described in [12], mp 112-114° (from alcohol).

cis-1, 2, 3-Triphenyl-1-propene (cis-IV). To a suspension of 0.27 g of (I) in 2 ml of CH₂Cl₂ were added in sequence 0.14 g of Et₃SiH and 0.3 g of CF₃COOH. After 30 h (20°) the mixture was decomposed with water, neutralized, extracted with CHCl₃, and dried over MgSO₄. The solvent was removed, while the residue was recrystallized from alcohol. We obtained 0.21 g of (cis-IV), mp 64-65° (slender needles). Found: C 92.35; H 6.78%. C₂₁H₁₈. Calculated: C 93.29; H 6.71%. Infrared spectrum (KBr, ν , cm⁻¹): 3040, 1600, 1500, 1030, 920, 880, 750, 735, 690. Ultraviolet spectrum [alcohol, $\lambda_{max}(\epsilon)$]: 210, 227 (16600), 260 (11600), 269 (11400). NMR spectrum (CCl₄, HMDS, δ , ppm): 3.7 (2H, CH₂C₆H₅); 6.3 (1H, = CHCC₆H₅), 6.85-7.1 (15H, C₆H₅). Based on the GLC data, the reaction mixture consists of 93% of (cis-IV), 2.5% of (I), and 4.5% of an unidentified substance. Mass spectrum of (cis-IV) (m/e, %): M⁺ 270 (72.0), 178 (82.50), 192 (100).

<u>cis-1, 2, 3-Triphenyl-1-propene-d_3</u>. Compound (IVa) was obtained in the same manner as (cis-IV) by the treatment of (I) with Et₃SiD, containing 91 atom % of deuterium, and CF₃COOH. NMR spectrum of (IVa) (CCl₄, HMDS, δ , ppm): 3.7 (1H, CHDC₆H₅); 6.3 (1H, = CHC₆H₅); 6.85-7.1 (15 H, C₆H₅). Mass spectrum of (IVa) (m/e, %): M⁺ 271 (100), 179 (81.0), 193 (76.6). The amount of deuterium at C₃ was 87 atom %.

CONCLUSIONS

1. The triphenylallyl cation, obtained directly in the acid cleavage of 1, 2, 3-triphenylcyclopropene, was fixed by its quantitative conversion to cis-1, 2, 3-triphenyl-1-propene in the presence of a hydride-ion donor, which experimentally confirms the adopted mechanism of the rearrangements in the cyclopropene series under the influence of acids.

2. The opening of the three-membered ring in the studied reaction proceeds stereospecifically, with a disrotator rotation of the substituents on the outside in harmony with the Woodward-Hoffman rule.

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