Formation of the 7-Triphenylphosphonio-norbornen-7-ylium Dication: a Non-classical Dication

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Summary While the norbornen-7-ylium cation dissolved in liquid SO₂ does not undergo 7-substitution with PPh₃, the analogous reaction with the 7-methoxynorbornen-7-ylium cation produces the 7-methoxynorbornen-7-yl-triphenylphosphonium cation; the intermediate 7-triphenylphosphonio-norbornen-7-ylium dication could be detected.

In order to investigate the 7-cations and 7-radicals of unsaturated norbornyl systems, we tried to prepare the 7-triphenylphosphonium salts, which could serve as precursors of these intermediates. A similar method was successful in the oxidation of diphenylmethyltriphenylphosphonium methylide when the related radical and dipositive ion were formed.¹ We discuss here the preparation of compounds (III) and (IV) and the dipositive ion (V) (see Scheme).

Attempts to prepare the norbornadien-7-ylphosphonium salt by treatment of norbornadien-7-yl chloride or the norbornadien-7-ylium cation with PPh₃ in liquid SO₂ failed. Only weakly nucleophilic phosphines like P(C₆F₅)₃ appeared to form 7-substituted salts. Probably, charge delocalisation in the norbornadien-7-ylium gives rise to 2- or 3-substituted products with stronger nucleophiles, like PPh₃, and the latter products apparently decompose under the reaction conditions.² These nucleophiles underwent similar reactions with the norbornen-7-ylium cation, but reaction of 7-anti-chloronorbornene with PPh₃ in formic acid, where
equilibrium conditions are prevailing, does yield the 7-substituted product.

Stabilisation of charge by double-bond participation in norbornen-7-ylum cations decreases with increasing electron donating ability of the 7-substituents. Reaction of PPh₃ with 7-chloro-7-methoxynorbornene gives rise only to substitution of PPh₃ at the 7-position.

Reaction of 7,7-dimethoxynorbornene with PCl₅ yields a mixture of the isomers (I) (76%) and (II) (24%), which reacts readily with PPh₃ in liquid SO₂ (-60°C) to yield a mixture (28:72) of the isomeric cations (III) and (IV). At -60°C, the ratio of the isomers is constant, but at ca. -14°C, compound (IV) isomerises to (III), which is obtained in crystalline form at room temperature. Both isomers (III) and (IV) produce the dication (V) in liquid SO₂ with HSO₃F-SbF₅ at -60°C. Quenching of this dication with methanol yields only (III). The structures of compounds (I)-(V) were confirmed by their n.m.r. (¹H and ¹³C) spectra.

In solution in liquid SO₂, isomers (I) and (II) undergo an exchange reaction at higher temperatures. This interconversion and the formation of a mixture of products in the reaction with PPh₃ indicate absence of double-bond participation in the intermediate 7-methoxy-norbornen-7-ylum cation.

First-order kinetics were observed for the isomerisation of compound (IV) to (III) in liquid SO₂ at -14°C (k = 2.7 × 10⁻⁴ s⁻¹). In liquid SO₂-HSO₃F, compound (III) is stable, whereas compound (IV) decomposes at a rate comparable to the rate of isomerisation in liquid SO₂. During the decomposition no 7-methoxy-carbocation was observed, although this cation was shown to be stable under these conditions by adding (I) and (II). Thus, isomerisation of (IV) to (III) proceeds via the dication (V), which is not stable in liquid SO₂-HSO₃F. In this dication, double-bond participation, which is increased by the PPh₃⁺ group explains the irreversible formation of compound (III) (vide supra).

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