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

By Pieter Schipper,* Wim A. M. Castenmiller, Jan W. de Haan, and Henk M. Buck
(*Department of Organic Chemistry, Eindhoven University of Technology, The Netherlands*)

Summary While the norbornen-7-ylium cation dissolved in liquid SO_2 does not undergo 7-substitution with PPh_3, 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).

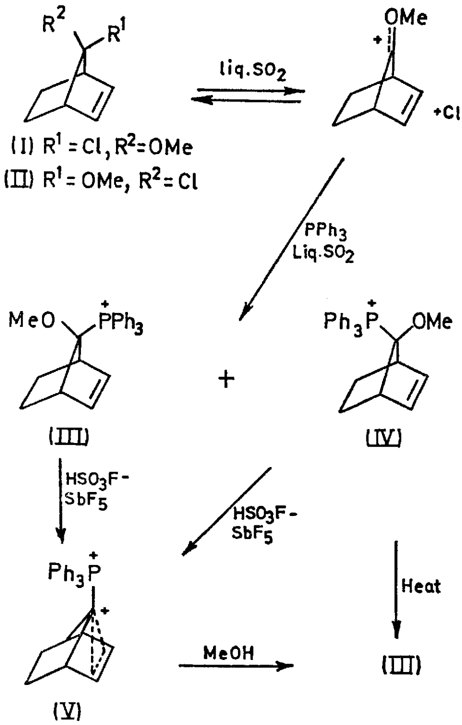
Attempts to prepare the norbornadien-7-ylphosphonium salt by treatment of norbornadien-7-yl chloride or the norbornadien-7-ylium cation with PPh_3 in liquid SO_2 failed. Only weakly nucleophilic phosphines like $P(C_6F_5)_3$ appeared to form 7-substituted salts. Probably, charge delocalisation in the norbornadien-7-ylium gives rise to 2- or 3-substituted products with stronger nucleophiles, like PPh_3, 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 PPh_3 in formic acid, where equilibrium conditions are prevailing, does yield the 7-substituted product.

Stabilisation of charge by double-bond participation in norbornen-7-ylium cations decreases with increasing electron donating ability of the 7-substituents.[3] Reaction of PPh_3 with 7-chloro-7-methoxynorbornene gives rise only to substitution of PPh_3 at the 7-position.

Reaction of 7,7-dimethoxynorbornene with PCl_5 yields a mixture of the isomers (I) (76%) and (II) (24%), which reacts readily with PPh_3 in liquid SO_2 (−60°) to yield a mixture (28:72) of the isomeric cations (III) and (IV). At −60°, the ratio of the isomers is constant, but at *ca.* −14°, 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 SO_2 with HSO_3F–SbF_5 at −60°. Quenching of this dication with methanol yields only (III). The structures of compounds (I)—(V) were confirmed by their n.m.r. (^1H and ^{13}C) spectra.

In solution in liquid SO_2, 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 PPh_3 indicate absence of double-bond participation in the intermediate 7-methoxy-norbornen-7-ylium cation.

First-order kinetics were observed for the isomerisation of compound (IV) to (III) in liquid SO_2 at −14° ($k = 2{\cdot}7 \times 10^{-4}\ s^{-1}$). In liquid SO_2–HSO_3F, compound (III) is stable, whereas compound (IV) decomposes at a rate comparable to the rate of isomerisation in liquid SO_2. During the decomposition no 7-methoxy-carbonium ion 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 SO_2–HSO_3F. In this dication, double-bond participation, which is increased by the PPh_3^+ group explains the irreversible formation of compound (III) (*vide supra*).



(*Received*, 16*th April* 1973; *Com.* 548.)

---

[1] P. Schipper and H. M. Buck, *Phosphorus*, 1971, **1**, 93.

[2] P. Schipper and H. M. Buck, *Phosphorus*, to be published.

[3] P. G. Gassman and A. F. Fentiman, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 1545; 1970, **92**, 2549; H. G. Richey, jun., J. D. Nichols, P. G. Gassman, A. F. Fentiman, jun., S. Winstein, M. Brookhart, and R. K. Lustgarten, *ibid.*, p. 3783; R. K. Lustgarten, M. Brookhart, and S. Winstein, *Tetrahedron Letters*, 1971, **2**, 141.