

## Formation of the 7-triphenylphosphonio-norbornen-7-ylum dication : a non-classical dication

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

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*Summary* While the norbornen-7-ylum cation dissolved in liquid  $\text{SO}_2$  does not undergo 7-substitution with  $\text{PPh}_3$ , the analogous reaction with the 7-methoxynorbornen-7-ylum cation produces the 7-methoxynorbornen-7-yl-triphenylphosphonium cation; the intermediate 7-triphenylphosphonio-norbornen-7-ylum 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 methylyde when the related radical and

dipositive ion were formed.<sup>1</sup> 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-ylum cation with  $\text{PPh}_3$  in liquid  $\text{SO}_2$  failed. Only weakly nucleophilic phosphines like  $\text{P}(\text{C}_6\text{F}_5)_3$  appeared to form 7-substituted salts. Probably, charge delocalisation in the norbornadien-7-ylum gives rise to 2- or 3-substituted products with stronger nucleophiles, like  $\text{PPh}_3$ , and the latter products apparently decompose under the reaction conditions.<sup>2</sup> These nucleophiles underwent similar reactions with the norbornen-7-ylum cation, but reaction of 7-*anti*-chloronorbornene with  $\text{PPh}_3$  in formic acid, where

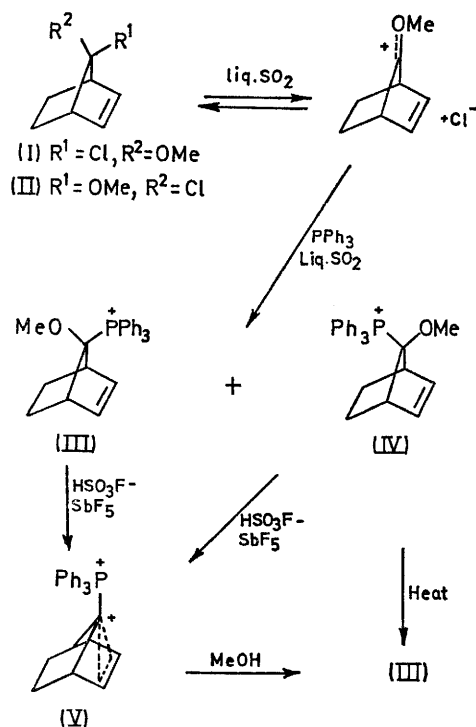
equilibrium conditions are prevailing, does yield the 7-substituted product.

Stabilisation of charge by double-bond participation in norbornen-7-ylum cations decreases with increasing electron donating ability of the 7-substituents.<sup>3</sup> Reaction of  $\text{PPh}_3$  with 7-chloro-7-methoxynorbornene gives rise only to substitution of  $\text{PPh}_3$  at the 7-position.

Reaction of 7,7-dimethoxynorbornene with  $\text{PCl}_5$  yields a mixture of the isomers (I) (76%) and (II) (24%), which reacts readily with  $\text{PPh}_3$  in liquid  $\text{SO}_2$  ( $-60^\circ$ ) to yield a mixture (28:72) of the isomeric cations (III) and (IV). At  $-60^\circ$ , the ratio of the isomers is constant, but at *ca.*  $-14^\circ$ , 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  $\text{SO}_2$  with  $\text{HSO}_3\text{F}-\text{SbF}_5$  at  $-60^\circ$ . Quenching of this dication with methanol yields only (III). The structures of compounds (I)–(V) were confirmed by their n.m.r. ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra.

In solution in liquid  $\text{SO}_2$ , 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  $\text{PPh}_3$  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  $\text{SO}_2$  at  $-14^\circ$  ( $k = 2.7 \times 10^{-4} \text{ s}^{-1}$ ). In liquid  $\text{SO}_2$ - $\text{HSO}_3\text{F}$ , compound (III) is stable, whereas compound (IV) decomposes at a rate comparable to the rate of isomerisation in liquid  $\text{SO}_2$ . 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  $\text{SO}_2$ - $\text{HSO}_3\text{F}$ . In this dication, double-



bond participation, which is increased by the  $\text{PPh}_3^+$  group explains the irreversible formation of compound (III) (*vide supra*).

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<sup>1</sup> P. Schipper and H. M. Buck, *Phosphorus*, 1971, 1, 93.

<sup>2</sup> P. Schipper and H. M. Buck, *Phosphorus*, to be published.

<sup>3</sup> 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.