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Citation for published version (APA):

Schipper, P., Castenmiller, W. A. M., Haan, de, J. W., & Buck, H. M. (1973). Formation of the 7-triphenylphosphonio-norbornen-7-ylum dication : a non-classical dication. *Journal of the Chemical Society, Chemical Communications*, (16), 574-575. <https://doi.org/10.1039/c39730000574>

DOI:

[10.1039/c39730000574](https://doi.org/10.1039/c39730000574)

Document status and date:

Published: 01/01/1973

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Formation of the 7-Triphenylphosphonio-norbornen-7-yl-ium Dication: a Non-classical Dication

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Summary While the norbornen-7-yl-ium cation dissolved in liquid SO_2 does not undergo 7-substitution with PPh_3 , the analogous reaction with the 7-methoxynorbornen-7-yl-ium cation produces the 7-methoxynorbornen-7-yl-triphenylphosphonium cation; the intermediate 7-triphenylphosphonio-norbornen-7-yl-ium 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 methyldide 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-yl-ium cation with PPh_3 in liquid 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-yl-ium 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-yl-ium 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-ylum 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 $\text{HSO}_3\text{F}-\text{SbF}_5$ 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-ylum cation.

First-order kinetics were observed for the isomerisation of compound (IV) to (III) in liquid SO_2 at -14° ($k = 2.7 \times 10^{-4} \text{ s}^{-1}$). 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, 16th 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.