

# Onio-assistierte S<sub>N</sub>2-Reaktionen: Allgemeiner Zugang zu symmetrischen und unsymmetrischen geminal bisoniosubstituierten Methanderivaten

Onio-Assisted S<sub>N</sub>2-Reactions: General Access to Symmetrical and Unsymmetrical Geminally Bisonio Substituted Methane Derivatives

Robert Weiss\*, Matthias Handke, Silvia Reichel, Frank Hampel

Institut für Organische Chemie I der Friedrich-Alexander-Universität Erlangen-Nürnberg, Henkestraße 42, D-91054 Erlangen

Z. Naturforsch. **53b**, 599–619 (1998); eingegangen am 19. Januar 1998

Geminal Bisonium Salts, S<sub>N</sub>-Reactions, Electrostatic Effects, Synthesis, X-Ray Data

The arsonium salt [Ph<sub>3</sub>As–CH<sub>2</sub>–OTf]<sup>+</sup> OTf<sup>–</sup> **11a** contains a 1,1-biselectrophilic C<sub>sp<sup>3</sup></sub> center which permits to synthesize a wide range of symmetrical and unsymmetrical geminally bisonio-substituted methane derivatives. With neutral nucleophiles |Nu under mild conditions a series of 1,1-bisonium salts [Ph<sub>3</sub>As–CH<sub>2</sub>–Nu]<sup>2+</sup> 2OTf<sup>–</sup> **12–23** is obtained in good yields. Under more stringent conditions the triphenylarsonio function in these salts can also be mobilized as a nucleofuge in a subsequent S<sub>N</sub>-reaction with a second nucleophile |Nu', yielding a series of novel unsymmetrical 1,1-bisonium salts [Nu–CH<sub>2</sub>–Nu']<sup>2+</sup> 2OTf<sup>–</sup> **24–27**. Structures **18**, **23** and **26b** were confirmed by X-ray analysis. For certain nucleophiles a discrete stepwise substitution of both nucleofuges in **11a** cannot be realized and the corresponding symmetrical 1,1-bisonium salts (*e.g.* **28** and **30–32**) are obtained directly. The experimental material can be rationalized on the basis of a simple MO model. The conclusion is that stabilization of a hypervalent S<sub>N</sub>2 transition state by an equatorial oniosubstituent parallels the stability of the underlying ylids. This is corroborated by model calculations. The geminal bisonium salts reported are potential precursors to mono- and 1,1-bisylids and, in special cases, to functional nucleophilic carbenes.

Sonderdruckanforderungen an Prof. Dr. R. Weiss. E-mail: rweiss@organik.uni-erlangen.de