Tetrahedron Letters, Vol. 35, No. 1, pp. 77-80, 1994
Printed in Great Britain

0040-4039/94 $6.00 + .00
Pergamon Press Ltd

Diels-Alder- and Ene-Reactions of 2-Azaallenium Salts

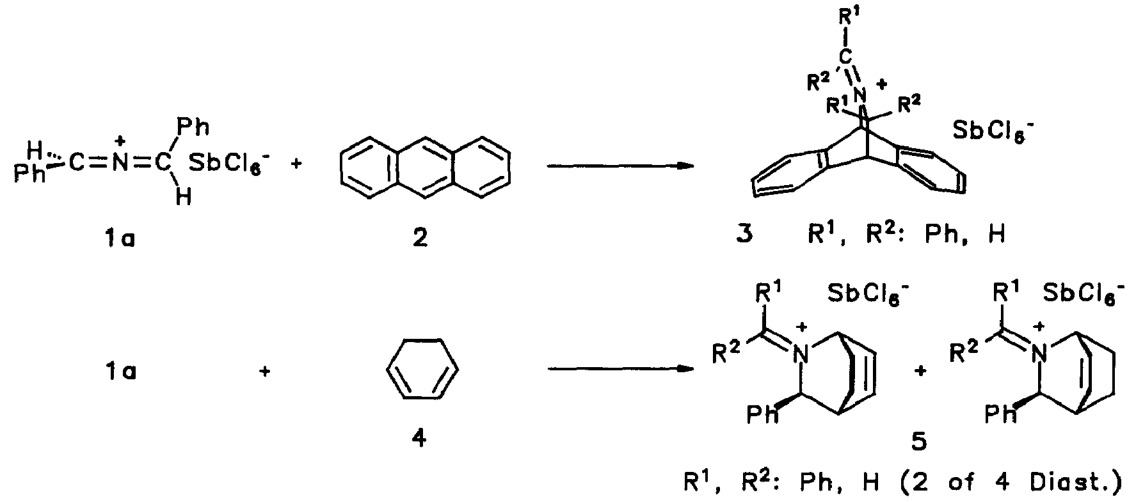
Andre Geisler and Ernst-Ulrich Würthwein*

Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität
Münster, Corrensstrasse 40, D-48149 Münster, Germany

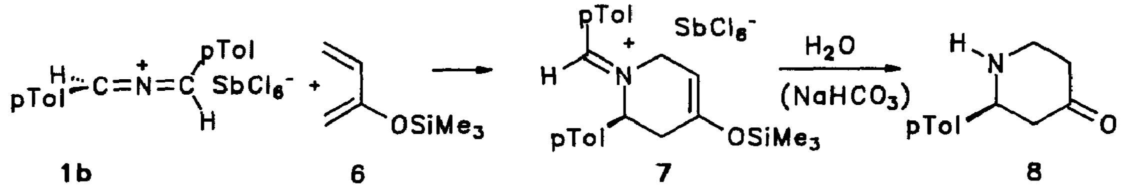
Abstract: 2-Azaallenium salts 1 react with cyclic 1,3-dienes to form six-membered heterocyclic iminium salts from a Diels-Alder type reaction. With acyclic dienes, mixtures of heterocyclic and acyclic iminium salts are formed; the acyclic products result from an ene type reaction.

2-Azaallenium salts are now easily accessible and several routes for their synthesis have been described [1)]. Similarly, their electronic and structural properties (2-azaallenium - 2-azaallyl cation valence isomerization) are well known [1c,2)]. However, in comparison with the widespread use of keteniminium salts ("1-azaallenium salts") in organic chemistry, the application of the isomeric 2-azaallenium salts has found relatively little attention [3)]. To our knowledge, reports on their reactions with olefins and dienes are completely lacking. Few examples of cycloaddition reactions of simple iminium salts [4)] encouraged us to investigate such reactions also for 2-azaallenium ions, which may be understood as "double" Mannich salts (" dimethyleneammonium salts"). Due to the biselectrophilic nature of these salts, even sequences of electrophilic reactions (domino reactions) may be expected.

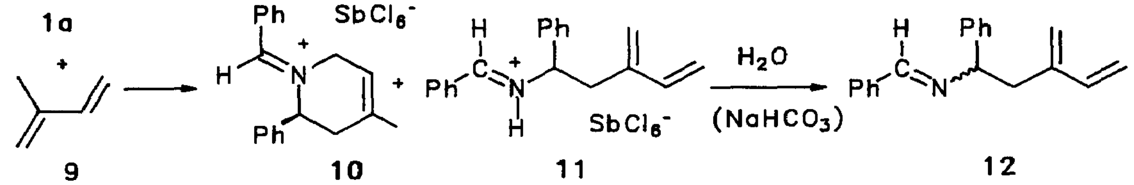
Dienes with a fixed or preferred cis conformation undergo straightforward [4+2] cyclizations forming six-membered iminium salts with exocyclic methylene groups. In a typical experiment, a solution of the 2-azaallenium salt **1** is treated at -78°C with an equimolar amount of diene; after warming up to room temperature and stirring for a short period of time, until the intense IR absorption at 1910 cm^{-1} of the 2-azaallenium salt has disappeared, the solvent is removed in vacuo, and the dark residue is purified by recrystallization. Thus, anthracene **2** furnishes the cycloadduct **3** as mixture of diastereomers (1:1.3)(crude yield: 51%; 22% yield after three recrystallizations). With 1,3-cyclohexadiene **4**, one obtains a mixture of two stereoisomers **5** (1:2.9) in 20% yield (pure; much loss occurs during the recrystallizations) [5)].

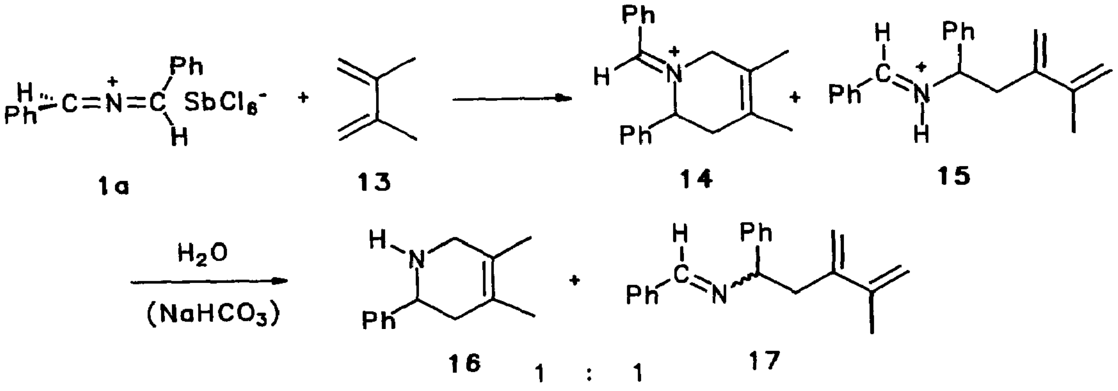


2-Trimethylsiloxy-1,3-butadiene **6** leads regioselectively (NOE experiments) to a mixture of E/Z isomers **7** (9:1); no byproduct could be detected. After hydrolysis with sat. $NaHCO_3$ solution the piperidone **8** is isolated in a total yield of 42%.



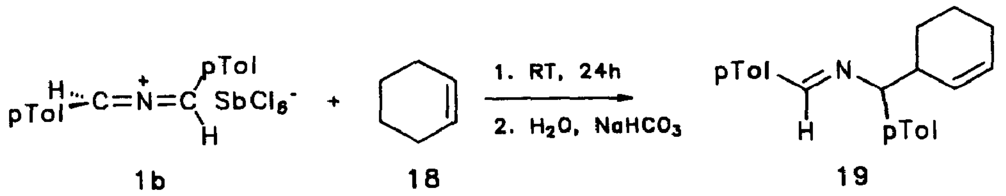
Reactions with other acyclic dienes take a more complicated course. For instance, from the reaction of **1** with isoprene **9** after evaporation of the solvent and recrystallization the expected cyclic product **10** is obtained (only one regioisomer, E/Z = 7.5 : 1; crude yield 49%, yield after recrystallization from acetonitrile/ether (1:1) 11%). In contrast, aqueous work up of the reaction mixture (sat. $NaHCO_3$) and subsequent Kugelrohr distillation yields the unsaturated imine **12** in 14% yield. Similarly, from 2,3-dimethylbutadiene **13** also two products were isolated, depending on the workup. After removal of the solvent in vacuo the salt **14** (crude yield 33%, after purification 8%) was obtained; aqueous work up gave a mixture of its hydrolysis product **16** together with the acyclic imine **17** (16% after Kugelrohr distillation; crude yield 42%).





The formation of the heterocyclic products **3**, **5**, **7**, **10**, and **14** may be rationalized by assuming a [4+2] cycloaddition ("aza-Diels-Alder reaction"). The acyclic products **11** and **15** may be the result of an ene reaction 6), in which the 2-azaallenium salt **1** attacks the dienes **9** or **13** at one of the double bonds. The positions of the double bonds in the products obtained after proton transfer to the nitrogen atom is compatible with a concerted mechanism involving a six-membered cyclic transition state. As suggested by H.M.R. Hoffmann 6a), the competition between Diels-Alder type reactions and ene reactions may be governed by the amount of s-cis conformer present in the reaction mixture.

As expected, cyclohexene **18** reacts with **1** under formation of the ene product. After aqueous work up, **19** was isolated in 30% yield.



In this paper, we have shown, that the strongly electrophilic 2-azaallenium salts **1** are potent starting materials for diene and ene synthesis, leading to new heterocyclic and acyclic structures 7) incorporating a nitrogen atom at positions, which are often not easily accessible by other synthetic routes.

Acknowledgement:

The financial support of this work by the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie is gratefully acknowledged.

References and Notes:

1. a) Alu-El-Halawa, R.; Jochims, J. C. *Synthesis* **1992**, 871-874. b) A-Talib, M.; Jochims, J. C. *Chem.Ber.* **1984**, *117*, 3222-3230. c) Hamed, A.; Jochims, J. C.; Przybylski, M. *Synthesis* **1989**, 400-402. d) Würthwein, E.-U. *Angew. Chem.* **1981**, *93*, 110-111; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 99. e) Kupfer, R.; Meier, S.; Würthwein, E.-U. *Chem. Ber.* **1992**, *125*, 2487-2492. f) Liebscher, J. *Synthesis* **1988**, 655-669.

2. a) Würthwein, E.-U. *J.Org.Chem.* **1984**, *49*, 2971-2978. b) Al-Talib, M.,; Jibril, I.; Würthwein, E.-U.; Jochims, J. C.; Huttner, G. *Chem.Ber.* **1984**, *117*, 3365-3373.

3. a) Weidner, R.; Maas, G.; Würthwein, E.-U. *Chem. Ber.* **1989**, *122*, 1711-1718. b) Schleimer, R.; Hornig, K.; Möller, M. H.; Würthwein, E.-U. *Chem. Ber.* **1993**, *126*, 133-141. c) Al-Talib, M.; Jibril, I.; Jochims, J. C.; Huttner, G. *Tetrahedron* **1985**, *41*, 527-536.

4. a) Böhme, H.; Hartke, K.; Müller, A. *Chem. Ber.* **1963**, *96*, 607-608. b) Babayan, A. T.; Martirosyan, G. T.; Grigoryan, D. V. *J. Org. Chem. USSR (Engl. Trans.)* **1968**, *4*, 955-956. c) Möhrle, H.; Dwuletski, H. *Arch. Pharm. (Weinheim, Ger.)* **1987**, *320*, 298-303. d) Marchand-Brynaert, J.; Ghosez, L. *Tetrahedron Lett.* **1974**, 377-380. e) Danishefski, S.; Kitahara, T.; Mc Kee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 6715-6717. f) Schmied, B. Dissertation, Universität Regensburg **1980**. g) Böhme, H.; Ahrens, K. H. *Tetrahedron Lett.* **1971**, 149-152. h) Larsen, S. D.; Grieco, P. A. *J. Am. Chem. Soc.* **1985**, *107*, 1768-1769. i) Waldmann, H.; Braun, M. *Liebigs Ann. Chem.* **1991**, 1045-1048.

5. Racemic salts **1** were used throughout; only one of the possible enantiomers of **1** and of the products is shown in the figures.

6. a) Hoffmann, H. M. R. *Angew. Chem.* **1969**, *81*, 597-618; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 556. b) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford. 1990; pp. 241-268. c) Böhme, H; Fresenius, W. *Arch.Pharm. (Weinheim, Ger.)* **1972**, *305*, 601-610.

7. All compounds were completely characterized by spectroscopic methods. For example:

   $\underline{5}$: colorless crystals, m.p. 206°C: ^{1}H-NMR (300 MHz, CD$_3$NO$_2$): δ = 1.35/1.55 (m, 2H, PhCH-CH-C$\underline{\mathrm{H}}_2$, Diast. I, II), 1.95/2.49 (m, 2H, N$^+$-CH-C$\underline{\mathrm{H}}_2$, Diast. I, II), 3.18 (m, 1H, PhCH-C$\underline{\mathrm{H}}$, Diast. II), 3.31 (m, 1H, PhCH-C$\underline{\mathrm{H}}$, Diast. I), 5.34 (m, 1H, N$^+$-C$\underline{\mathrm{H}}$, Diast. I, II), 5.62 (m, 1H, Ph-C$\underline{\mathrm{H}}$, Diast I), 5.92 (m, 1H, Ph-C$\underline{\mathrm{H}}$, Diast. II), 6.53 (m, 1H, $\underline{\mathrm{H}}$-C=C, 6-H, Diast. II), 6.68 (m, 1H, $\underline{\mathrm{H}}$-C=C, 6-H, Diast. I), 6.95 (m, 1H, C=C-$\underline{\mathrm{H}}$, 5-H, Diast. I), 7.01 (m, 1H, C=C-$\underline{\mathrm{H}}$, 5-H, Diast. II), 7.25-7.50 (m, 5H, C$\underline{\mathrm{H}}_{\mathrm{ar.}}$, Ph-CH, Diast. I, II), 7.58-7.87 (m, 5H, C$\underline{\mathrm{Har.}}$, Ph-C=N$^+$, Diast I, II), 8.84 (m, 1H, $\underline{\mathrm{H}}$-C=N$^+$, Diast. II), 9.12 (m, 1H, $\underline{\mathrm{H}}$-C=N$^+$, Diast. I) ppm.

   ^{13}C-NMR (75.47 MHz, CD$_3$CN): δ = 15.76/24.54 (-$\underline{\mathrm{C}}$H$_2$-$\underline{\mathrm{C}}$H$_2$-, Diast. II), 16.54/24.03 (-$\underline{\mathrm{C}}$H$_2$-$\underline{\mathrm{C}}$H$_2$-, Diast. I), 38.35 (Ph-CH-$\underline{\mathrm{C}}$H, Diast. II), 39.25 (Ph-CH-$\underline{\mathrm{C}}$H, Diast. I), 56.91 (N$^+$-$\underline{\mathrm{C}}$H, Diast II), 67.18 (N$^+$-$\underline{\mathrm{C}}$H, Diast. I), 67.71 (Ph-$\underline{\mathrm{C}}$H, Diast. I), 71.84 (Ph-$\underline{\mathrm{C}}$H, Diast. II), 127.3 ($\underline{\mathrm{C}}_{\mathrm{i\ ar.}}$, Ph-C=N$^+$, Diast. I, II.), 133.7 ($\underline{\mathrm{C}}_{\mathrm{i\ ar.}}$, Ph-CH, Diast. I, II), 127.6/ 128.7/ 129.4/129.9/130.1/130.2/130.4/130.7/132.4/135.1/136.7/137.5/139.2/140.6 (12 $\underline{\mathrm{C}}$H$_{\mathrm{ar.}}$, 4 $\underline{\mathrm{C}}$H$_{\mathrm{olef.}}$, Diast. I, II), 170.1 (H$\underline{\mathrm{C}}$=N$^+$, Diast. I, II) ppm.

   $\underline{10}$: lightyellow plates, m.p. 204°C: ^{1}H-NMR (300 MHz, CD$_3$NO$_2$): δ = 1.91 (m, 3H, -C$\underline{\mathrm{H}}_3$), 3.08 (m, 2H, PhCH-C$\underline{\mathrm{H}}_2$), 4.53 (d, br, ^{2}J=18.0 Hz, 1H, N$^+$-C$\underline{\mathrm{H}}_2$), 4.89 (d, br, ^{2}J=18.0 Hz, 1H, N$^+$-C$\underline{\mathrm{H}}_2$)5.46 (m, 1H, E-isomer, C=C-$\underline{\mathrm{H}}$), 5.53 (m, 1H, Z-isomer, C=C-$\underline{\mathrm{H}}$), 5.69 (t, ^{3}J= 5.3 Hz, 1H, E-isomer, Ph-C$\underline{\mathrm{H}}$), 6.38 (m, 1H, Z-isomer, Ph-C$\underline{\mathrm{H}}$), 7.35-7.57 (m, 5H, CH-Ph-$\underline{\mathrm{H}}$), 7.65-7.96 (m, 5H, N$^+$=C-Ph-$\underline{\mathrm{H}}$), 9.08 (s, 1H, E-isomer, $\underline{\mathrm{H}}$C=N$^+$), 9.27 (s, 1H, $\underline{\mathrm{H}}$C=N$^+$, Z-isomer) ppm.

   ^{13}C-NMR (75.47 MHz, CD$_3$CN): δ = 22.58 (-$\underline{\mathrm{C}}$H$_3$), 34.20 (Ph-CH-$\underline{\mathrm{C}}$H$_2$), 51.02 (N$^+$-$\underline{\mathrm{C}}$H$_2$), 70.55 (Ph-$\underline{\mathrm{C}}$H), 115.0 (C=$\underline{\mathrm{C}}$H), 127.8 ($\underline{\mathrm{C}}_{\mathrm{i\ ar.}}$, Ph-C=N$^+$), 129.2 ($\underline{\mathrm{C}}H_{\mathrm{ar.}}$), 130.4 ($\underline{\mathrm{C}}H_{\mathrm{ar.}}$), 130.6 ($\underline{\mathrm{C}}H_{\mathrm{ar.}}$), 130.9 ($\underline{\mathrm{C}}H_{\mathrm{ar.}}$), 133.6 ($\underline{\mathrm{C}}H_{\mathrm{ar.}}$), 134.2/134.4 ($\underline{\mathrm{C}}_{\mathrm{i\ ar.}}$, Ph-CH, $\underline{\mathrm{C}}_{\mathrm{q\ olef.}}$), 137.0 ($\underline{\mathrm{C}}H_{\mathrm{ar.}}$), 171.4 (H$\underline{\mathrm{C}}$=N$^+$) ppm.

   $\underline{12}$: colorless, unstable oil, b.p. 110°C/0.01 mbar: ^{1}H-NMR (300 MHz, CDCl$_3$): δ = 2.87 (dd, ^{3}J=5.1 Hz, ^{2}J=13.8 Hz, 1H, PhCH-C$\underline{\mathrm{H}}_2$), 2.79 (dd, ^{3}J=8.4 Hz, ^{2}J=13.8 Hz, 1H, PhCH-C$\underline{\mathrm{H}}_2$), 4.45 (dd, ^{3}J= 8.4 Hz, ^{3}J= 5.0 Hz, 1H, Ph-C$\underline{\mathrm{H}}$-CH$_2$), 4.88 (s, br, 1H, C=C$\underline{\mathrm{H}}_2$), 5.03 (s, br, 1H, C=C$\underline{\mathrm{H}}_2$), 5.12 (d, ^{3}J$_{\mathrm{cis}}$=10.8 Hz, 1H, H-C=C-$\underline{\mathrm{H}}_{\mathrm{cis}}$), 5.35 (d, ^{3}J$_{\mathrm{trans}}$=17.6 Hz, 1H, H-C=C-$\underline{\mathrm{H}}_{\mathrm{trans}}$), 6.35 (dd, ^{3}J$_{\mathrm{cis}}$=10.8 Hz, ^{3}J$_{\mathrm{trans}}$=17.6 Hz, 1H, H$_2$C=C-$\underline{\mathrm{H}}$), 7.10-7.47 (m, 8H, C$\underline{\mathrm{H}}_{\mathrm{m/p}}$, Ph-C=N, C$\underline{\mathrm{H}}_{\mathrm{ar.}}$, Ph-CH), 7.74-7.77 (m, 2H, C$\underline{\mathrm{H}}_{\mathrm{o}}$, Ph-C=N), 8.17 (s, 1H, N=C$\underline{\mathrm{H}}$) ppm.

   ^{13}C-NMR (75.47 MHz, CDCl$_3$): δ = 41.20 (PhCH-$\underline{\mathrm{C}}$H$_2$), 73.52 (Ph-$\underline{\mathrm{C}}$H), 113.6 (=$\underline{\mathrm{C}}$H$_{2\ \mathrm{olef.}}$), 119.2 (=$\underline{\mathrm{C}}$H$_{2\ \mathrm{olef.}}$), 126.9 ($\underline{\mathrm{C}}$H$_{\mathrm{ar.}}$), 128.2 ($\underline{\mathrm{C}}$H$_{\mathrm{ar.}}$), 128.3 ($\underline{\mathrm{C}}$H$_{\mathrm{ar.}}$), 128.4 ($\underline{\mathrm{C}}$H$_{\mathrm{ar.}}$), 128.5 ($\underline{\mathrm{C}}$H$_{\mathrm{ar.}}$), 130.3 ($\underline{\mathrm{C}}$H$_{\mathrm{ar.}}$), 136.4 ($\underline{\mathrm{C}}_{\mathrm{i\ ar.}}$, Ph-C=N), 138.6 (H$_2$C=$\underline{\mathrm{C}}$H-), 142.7/144.2 ($\underline{\mathrm{C}}_{\mathrm{i\ ar.}}$, Ph-CH, $\underline{\mathrm{C}}_{\mathrm{q\ olef.}}$), 159.6 ($\underline{\mathrm{C}}$H=N) ppm.

(*Received in Germany* 15 *October* 1993; *accepted* 31 *October* 1993)