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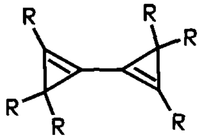
SYNTHESIS OF NEW BI-2H-AZIRIN-3-YL COMPOUNDS FROM DIAZIDES1)

Klaus Banert
Fachbereich 8 der Universität, Organische Chemie II,
Postfach 10 12 40, D-5900 Siegen, Germany

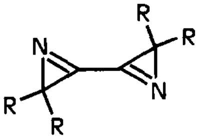
Abstract: *Starting with 2,3-diazido-1,3-butadienes 4 or 10 successive loss of molecular nitrogen by thermolysis or photolysis leads to new bi-2H-azirin-3-yl compounds 2 or 3.*

Neither the bicyclic hydrocarbon 1a nor derivatives (1b) have been synthesized, though 1 has been studied by ab initio methods.2) This paper describes simple ways to the aza analogous compounds 2 and 3.



1a R = H

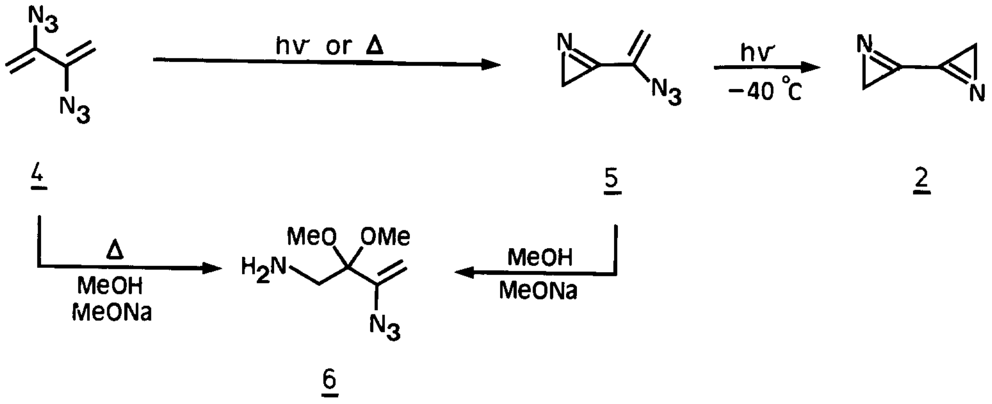
1b R ≠ H



2 R = H

3 R = CH_3

Thermolysis or photolysis of diazide 43) in chloroform or toluene yields the azirine 5 (Table 1).4) This produces on further irradiation bi-2H-azirin-3-yl (2, Table 1). Even in solution at room temperature 2 decomposes rapidly to an insoluble, non volatile, brown solid.5) On this ground it is clear that in the thermolysis of 4 beside 5 is no trace of 2, but its decay products are found. The azirine 5 is quite stable in solution at room temperature, however, the neat compound6) decomposes in some minutes. In methanol/sodium methoxide 5 is cleaved to 6 (Table 1) which is also formed by direct thermolysis of 4 in the same solvent.



Treatment of 7[7] or 8[8] with sodium azide (for example in H_2O/dioxane) yields at the most traces of diazides 9 and 10. This result can be explained by the small reactivity of 7 or 8 and by the low stability of 9 and 10. However, the desired compound 10 is prepared by a new method of nucleophilic substitution appropriate to substrates which are usually not prone to smooth S_N1 or S_N2 reactions: Treatment of 8 - 7 is less suitable - with a supercooled melt of hexadecyltributylphosphonium azide[9] affords 10 with 65% yield.[10] If the reaction time is shortened to about 5 min, the diazide 9[11] (up to 28% of the substitution products) is obtained beside 10. Structures are confirmed, not only by the spectroscopic data (Table 1), but also by the hydrogenation to 11 and meso-12[12].

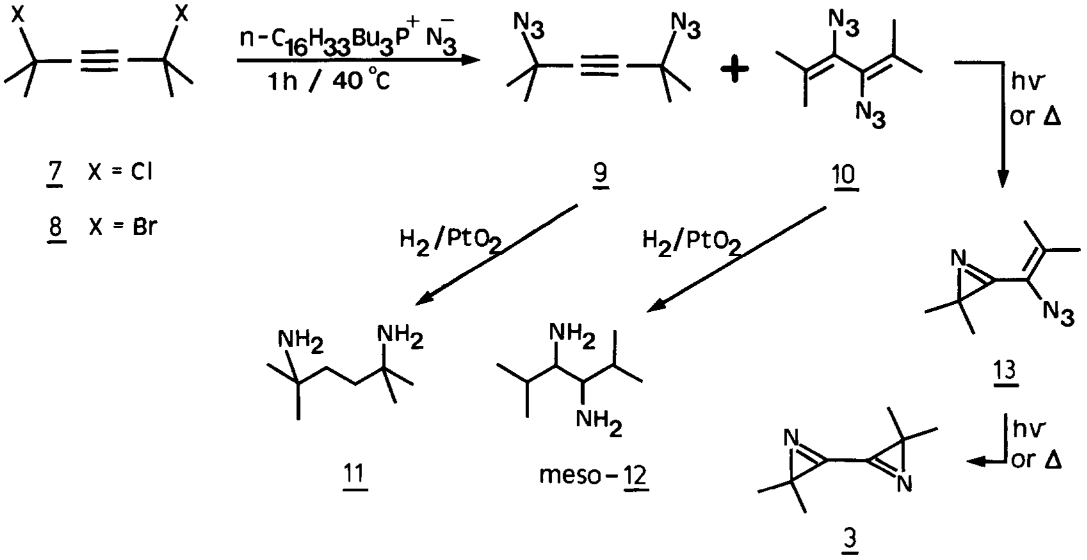


Table 1. Some physical data of the new compounds 2, 3, 5, 6, 9, 10, and 13.

2: ^{1}H NMR ($CDCl_3$): δ = 2.05 (s); ^{13}C NMR ($CDCl_3$, -40 °C): δ = 22.37 (t, J = 185 Hz), 159.45 (s)

3: IR (CCl_4): ν = 2980, 2960, 2920, 2870, 1640 (C=N), 1455, 1375, 1320, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.43 (s); ^{13}C NMR ($CDCl_3$): δ = 24.68 (q, J = 127 Hz), 36.99 (s), 171.61 (s); GC-MS (70 eV): m/z = 136 (M^+, 1%), 135 (4), 121 (25), 94 (6), 81 (10), 80 (6), 69 (39), 68 (34), 54 (13), 53 (8), 52 (6), 42 (73), 41 (100)

5: colorless liquid; IR (CCl_4): ν = 2990, 2180, 2120, 1600, 1345, 1255, 1000, 990 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.74 (s, 2 H), 5.56 (d, J = 1.55 Hz, 1 H), 5.71 (d, J = 1.55 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ = 20.2 (t, J = 182 Hz), 114.3 (dd, 162 Hz, 167 Hz), 134.2 (s), 163.9 (s); GC-MS (70 eV): m/z = 108 (M^+, 3%), 80 (3), 79 (24), 54 (13), 53 (27), 52 (42), 51 (11), 41 (13), 40 (100)

6: ^{1}H NMR ($CDCl_3$): δ = 1.27 (br, position concentration-dependent, 2 H), 2.83 (s, 2 H), 3.23 (s, 6 H), 5.10 (d, J = 1.54 Hz, 1 H), 5.40 (d, J = 1.54 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ = 42.6 (t, J = 138 Hz), 49.0 (q, 143 Hz), 101.8 (s), 103.6 (dd, 156 Hz, 167 Hz), 143.0 (s)

9: ^{1}H NMR ($CDCl_3$): δ = 1.52 (s); ^{13}C NMR ($CDCl_3$): δ = 29.13 (q, J = 129 Hz), 56.16 (s), 84.72 (s)

10: slight yellow liquid; IR (CCl_4): ν = 2990, 2920, 2860, 2110, 1440, 1370, 1290, 1265, 1245, 1085, 990 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.70 (q, J = 0.45 Hz, 6 H), 1.80 (q, J = 0.45 Hz, 6 H); ^{13}C NMR ($CDCl_3$): δ = 17.97 (qq, J = 127.4 Hz, 4.3 Hz), 20.36 (qq, 126.9 Hz, 4.2 Hz), 123.74 (sept, 6 Hz), 126.09 (sept, 7 Hz)

13: colorless liquid; IR (CCl_4): ν = 2990, 2940, 2920, 2860, 2110, 1695, 1620, 1445, 1370, 1285 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 6 H), 1.96 (q, J = 0.65 Hz, 3 H), 2.02 (q, 0.65 Hz, 3 H); ^{13}C NMR ($CDCl_3$): δ = 19.76 (q, J = 129 Hz), 20.27 (q, 128 Hz), 25.10 (q, 127 Hz), 33.23 (sept, 5 Hz), 120.34 (s), 138.68 (sept, 7 Hz), 172.92 (s)

Thermolysis or photolysis of 10 in chloroform gives the bi-2H-azirin-3-yl 3 (Table 1) with 93-97% yield. The isolation of the intermediate 13 is easily carried out$^{6)}$, because half-life periods of 10 and 13 (3.8 h for 10 and 63 h for 13 / 60 °C) differ considerably. These results emphasize the stabilizing effect of the methyl groups in 3 as compared to unsubstituted 2.

Bi-2H-azirin-3-yls which are isomers of diazabenzenes may be the starting point for new interesting reactions.

References and Notes:

1) Reactions of Unsaturated Azides, Part 2. For Part 1 see K. Banert, Angew. Chem. 97, 231 (1985); Angew. Chem. Int. Ed. Engl. 24, 216 (1985).

2) R. M. Sosa, O. N. Ventura, and A. Liberles, Theor. Chim. Acta 56, 157 (1980); A. Greenberg and J. F. Liebman, J. Am. Chem. Soc. 103, 44 (1981).

3) H. Priebe, Angew. Chem. 96, 728 (1984); Angew. Chem. Int. Ed. Engl. 23, 736 (1984). Diazide 4 can also be prepared conveniently from commercial 1,4-dichloro-2-butyne.

4) Diluted in chloroform half of 4, respectively half of 5 has been converted after 1 day at 60 °C.

5) See stability of 2H-azirine for comparison J.-C. Guillermin, J.-M. Denis, M.-C. Lasne, and J.-L. Ripoll, J. Chem. Soc., Chem. Commun. 1983, 238; R. G. Ford, J. Am. Chem. Soc. 99, 2389 (1977).

6) Compounds 3-5 and 10-13 may be purified by gas chromatography.

7) L. Skattebøl, Tetrahedron 21, 1357 (1965).

8) W. Krestinsky, Ber. Dtsch. Chem. Ges. 59B, 1930 (1926).

9) D. Landini, A. Maia, and F. Montanari, J. Am. Chem. Soc. 100, 2796 (1978); Nouv. J. Chim. 3, 575 (1979); K. Banert and W. Kirmse, J. Am. Chem. Soc. 104, 3766 (1982); K. Banert, Chem. Ber. 118, 1564 (1985).

10) Within 5 min 8 (0.84 g, 3.1 mmol) is added to a rapidly stirred supercooled melt of hexadecyltributylphosphonium azide (4.86 g, 10.3 mmol), which is kept at 40 °C. After 1 h the mixture is cooled to -196 °C and carefully re-condensed at 0.001 Torr yielding 10 (0.39 g, 2.0 mmol).6)

11) Surprisingly 9 does not rearrange to 10, but decomposes quickly ($\tau_{1/2}$ = 65 min, 32 °C in benzene) to a non volatile compound.

12) K. Pfordte and G. Leuschner, Liebigs Ann. Chem. 646, 25 (1961). meso-12 may be synthesized conveniently by hydrogenation of 2,5-dimethyl-3,4-hexandione dioxime13).

13) J. S. Preston, J. Inorg. Nucl. Chem. 42, 441 (1980).

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