

no satisfactory explanation for the complete order of the ozonide anions at room temperature, which is in contrast with the comparable $\text{RbNO}_2^{[5]}$. Intermolecular interactions between the ozonide ions (dimerization) can be ruled out on the grounds of the large intermolecular distances^[3]. Also still inexplicable are the marked differences in the stability of the compounds with 19-electron systems (NF_2 , SO_2^- , O_3^- , S_3^- , ClO_2^-) towards dimerization. Whichever of the conceivable criteria is analyzed for an explanation (repulsion of non-bonding electron pairs, differences in electronegativity^[6], charge of the monomer, state of aggregation) there are inconsistencies.

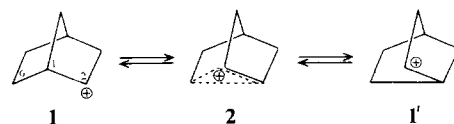
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- [1] a) L. V. Azaroff, I. Corvin, *Proc. Nat. Acad. Sci. USA* 49 (1963) 1; V. A. Sarin, V. Y. Dudarev, M. S. Dobrolyubova, *Kristallografiya* 19 (1974) 74; b) P. Smith, *J. Phys. Chem.* 60 (1956) 1471; L. Pauling: *The Nature of the Chemical Bond*, Cornell Univ. Press, New York 1980, p. 354; S. Schlick, *J. Chem. Phys.* 56 (1972) 654; c) A. D. McLachlan, M. C. R. Symons, M. G. Townsend, *J. Chem. Soc.* 1959, 952; I. I. Vol'nov, E. I. Sokevnin, V. V. Matveev, *Izv. Akad. Nauk SSSR* 6 (1962) 1127; I. I. Vol'nov, M. S. Dobrolyubova, A. B. Tsentsiper, *Izv. Akad. Nauk SSSR Ser. Khim.* 9 (1966) 1611.
- [2] Prepared analogously to the method described by A. Helms, W. Klemm, *Z. Anorg. Allg. Chem.* 242 (1939) 33; K. Wahl, Dissertation, Universität Münster 1954.
- [3] KO_3 : 14/mcm, $a = 864.80(12)$, $c = 716.40(14)$ pm (-25°C), $V = 535.78 \times 10^6$ pm³, $Z = 8$. Siemens AED2 diffractometer, $\text{MoK}\alpha$ radiation, graphite monochromator, scan width 2.0° , ω -scan, 2084 measured reflections with $6.7^\circ < 2\theta < 65^\circ$, 147 symmetry independent reflections with $F > 3\sigma(F)$, anisotropic refinement, $R = 0.063$ for 15 free parameters, $R_w = 0.046$, $w = 4.15/(\sigma^2(F))$ selected bond lengths [pm] and angles $[\circ]$ (standard deviations in brackets): O1–O2 135.7(5) ($2\times$), O2–O2' 226.9(11), O1–O2' 300.5(11) intermolecular, K–O2 285.3(6) ($8\times$); O2–O1–O2' 113.4(8).— RbO_3 : $P2_1/c$, $a = 644.10(22)$, $b = 603.00(35)$, $c = 874.60(36)$ pm (-25°C), $\beta = 122.25(2)^\circ$, $V = 287.28 \times 10^6$ pm³, $Z = 4$. Siemens AED2 diffractometer, $\text{MoK}\alpha$ radiation, graphite monochromator, scan width 2.8° , ω -scan, 1953 measured reflections with $7.5^\circ < 2\theta < 50^\circ$, 373 symmetry independent reflections with $F > 3\sigma(F)$, anisotropic refinement, $R = 0.059$ for 37 free parameters, $R_w = 0.047$, $w = 3.48/(\sigma^2(F))$. Selected bond lengths [pm] and angles $[\circ]$ (standard deviation in brackets): O1–O2 134.7(15), O1–O3 133.4(17), O2–O2' 225.6(16), O1–O3' 299.2(11) intermolecular, O2–O1–O3 114.6(13), Rb–O2 292.2(10), Rb–O3 296.7(11), Rb–O3' 300.3(12), Rb–O3'' 300.9(12); Rb–O1 305.8(11), Rb–O2' 306.4(17), Rb–O3''' 307.0(11), Rb–O2'' 308.5(12). Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depositary number CSD 51112, the names of the authors, and the journal citation.
- [4] R. W. Hughes, *J. Chem. Phys.* 24 (1956) 131.
- [5] P. W. Richter, C. W. F. T. Pistorius, *J. Solid State Chem.* 5 (1972) 276.
- [6] M. Green, *J. Chem. Soc.* 1962, 2819.

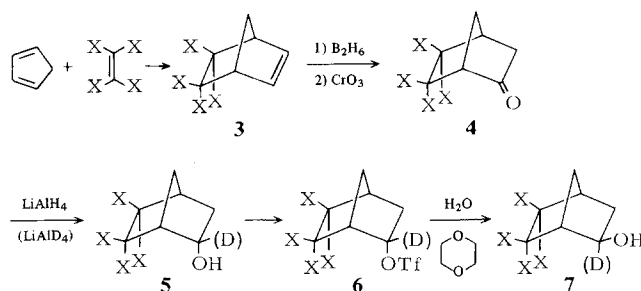
Destabilized 2-Norbornyl Cations

By Wolfgang Kirmse*, Uwe Mrotzeck, and Rainer Siegfried

A conspicuous property of the 2-norbornyl cation **1** ($\equiv \mathbf{1}'$) is the equivalence of C-1 and C-2 in its spectra and reactions^[1], as expressed by the σ -delocalized ("nonclassical") structure **2**. If an acceptor substituent is present at C-6, Wagner-Meerwein rearrangement and attack by the solvent appear to compete with each other; norbornyl cations of this type are considered to be unsymmetrically

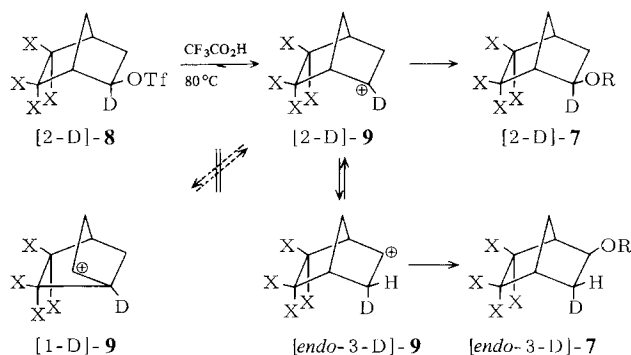


bridged^[2]. The presence of four fluorine atoms or four trifluoromethyl groups^[3] at C-5 and C-6 should intensify the electron deficiency and at the same time maintain the symmetry of the parent system. We have found that the Wagner-Meerwein rearrangement is completely forestalled by such a substitution pattern—largely with retention of the *exo*-selectivity.



Scheme 1. a, X = F; b, X = CF₃. Tf = trifluoromethylsulfonate.

The reactions of the substituted norbornenes **3**^[4] sketched in Scheme 1 proceeded in good yields. Solvolysis of the *endo*-trifluoromethylsulfonate(triflate) **6** in dioxane-water afforded predominantly the *exo*-alcohols **7** (Table 1) without scrambling of a 2D-label. The *exo*-triflate **8a**



Scheme 2. a, X = F; b, X = CF₃.

Table 1. Distribution of products upon solvolysis of the triflates **6** and **8**.

Educt	Conditions	3	7	5	<i>exo:endo</i>
<i>endo</i> -Series					
6a	Dioxane-H ₂ O (1:1), 80°C	8.6	91.2	0.2	—
6a	CF ₃ CO ₂ H, CF ₃ CO ₂ Na, 110°C	1.9	96.1	2.0	—
6b	Dioxane-H ₂ O (1:1), 100°C	1.3	98.7	—	—
6b	HCO ₂ H, HCO ₂ Na	trace	> 99	—	—
<i>exo</i> -Series					
8a	Dioxane-H ₂ O (7:3), 80°C	69.0	5.3	25.7	0.21
8a	Dioxane-H ₂ O (1:1), 80°C	71.8	6.4	21.7	0.29
8a	Dioxane-H ₂ O (3:7), 80°C	60.0	14.4	25.6	0.56
8a	CF ₃ CO ₂ H, CF ₃ CO ₂ Na, 80°C	58.1	36.6	5.3	6.85
8b	Dioxane-H ₂ O (1:1), 100°C	> 99	trace	—	—
8b	HCO ₂ H, HCO ₂ Na, 100°C	36.3	62.4	1.3	48
8b	CF ₃ CO ₂ H, CF ₃ CO ₂ Na, 65°C	59.2	40.7	trace	> 100

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(Scheme 2) reacts only three- to four-times more rapidly than the *endo*-triflate **6a** and 20-times slower than 7-norbornyl triflate (ca. 10^{11} -times slower than *exo*-2-norbornyl triflate). The strongly solvent-dependent product ratio 7 : 5 (Table 1) suggests a competition between an S_N2 and an S_N1 reaction; the S_N1 reaction dominates only in trifluoroacetic acid. In contrast, in dioxane-water the *exo*-triflate **8b** underwent practically only elimination to give the alkene **3b**; in formic acid and trifluoroacetic acid **8b** reacted with high *exo*-selectivity (S_N1) (Table 1). In trifluoroacetic acid or formic acid the labeled triflates [2-D]-**6** and [2-D]-**8** led to a scrambling of D in **7** (Table 2). As indicated by the

Table 2. Deuterium scrambling in **7** upon solvolysis of [2-D]-**6** and [2-D]-**8**.

Educt	Conditions	<i>endo</i> -2-D	<i>endo</i> -3-D
<i>endo</i> -Series			
[2-D]- 6a	CF ₃ CO ₂ H, CF ₃ CO ₂ Na, 80 °C	95	5
[2-D]- 6b	HCO ₂ H, HCO ₂ Na, 100 °C	85	15
<i>exo</i> -Series			
[2-D]- 8a	CF ₃ CO ₂ H, CF ₃ CO ₂ Na, 80 °C	61	39
[2-D]- 8b	CF ₃ CO ₂ H, CF ₃ CO ₂ Na, 80 °C	84	16
[2-D]- 8b	HCO ₂ H, HCO ₂ Na, 100 °C	78	22

chemical shift in the ²H-NMR spectrum and the coupling in the ¹H-NMR spectrum^[5], the rearrangement product bore deuterium at the *endo* 3-position, but not at the bridgehead (C-1). A Wagner-Meerwein rearrangement had therefore not occurred, but rather an *exo,exo*-3,2-H shift. Scrambling of D in the solvolysis of [2-D]-**6a** is less than in [2-D]-**8a**, which indicates a higher S_N2 contribution in the reaction of **6a**; the difference is less pronounced for **6b**/**8b**. 3,2-H shifts are also known in 2-norbornyl cations; however, here they have the highest activation energy of all rearrangements and are insignificant under solvolysis conditions^[6]. As indicated by the behavior of the cations **9**, the bridged structure **2** is more destabilized by F or CF₃ substituents than the open form **1**. The absence of Wagner-Meerwein rearrangement unequivocally characterizes **9a**, **b** as open ("classical") cations. The *exo*-selectivity of the 3,2-H shift cannot be accounted for here by σ -delocalization, but must have its origins elsewhere. The steric effects of the *endo*-substituents^[1,6], torsional effects along the C1–C2 bonds^[7], and deformation of the p-orbital at C-2 ("nonequivalent orbital extension")^[8] have all been discussed in this connection.

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3a, 2822-56-2; **3b**, 94137-40-3; **5a**, 94137-41-4; **6a**, 94137-42-5; **6b**, 94137-43-6; **7a**, 94137-44-7; **7b**, 94137-45-8; **8a**, 94137-46-9; **8b**, 94137-47-0.

[1] Recent reviews: G. A. Olah, G. K. S. Prakash, M. Saunders, *Acc. Chem. Res.* 16 (1983) 440; H. C. Brown, *ibid.* 16 (1983) 432; H. C. Brown: *The Nonclassical Ion Problem* (with comments by P. von R. Schleyer), Plenum, New York 1977.

[2] C. A. Grob, *Angew. Chem.* 94 (1982) 87; *Angew. Chem. Int. Ed. Engl.* 21 (1982) 87; *Acc. Chem. Res.* 16 (1983) 426.

[3] For destabilization of carbocations by halomethyl groups cf. P. G. Gassman, T. T. Tidwell, *Acc. Chem. Res.* 16 (1983) 279; T. T. Tidwell, *Angew. Chem.* 96 (1984) 16; *Angew. Chem. Int. Ed. Engl.* 23 (1984) 20.

[4] **3a**: J. J. Drysdale, W. W. Gilbert, H. K. Sinclair, W. H. Sharkey, *J. Am. Chem. Soc.* 80 (1958) 3762. We thank Dr. B. E. Smart (Du Pont, Wilmington) for a sample of **3a**, **3b**: Perfluoro-2,3-dimethyl-2-butene [A. N. Bell, R. Fields, R. N. Haszeldine, *J. Chem. Soc. Perkin Trans. 1* 1980, 487] was allowed to react with cyclopentadiene in ether or hexafluorobenzene at 170 °C, yield 40–60%.

[5] **7a**: 1-H (δ = 2.63 br. s), 2-H (δ = 4.34, d, J = 6.5 Hz), *endo*-3-H (δ = 2.28, dd, J = 14 and 6.5 Hz), *exo*-3-H (δ = 1.49, dq, J = 14 and ca. 2 Hz). The assignment was confirmed by comparison with [*exo*-3-D]-**7a** (from **3a** and B₂D₆). **7b**: 1-H (δ = 2.82 br. s), 2-H (δ = 4.56, d, J = 6.6 Hz), *endo*-3-H (δ = 2.65, ddd, J = 15.3, 6.6 and 3.5 Hz), *exo*-3-H (δ = 1.55, br. d, J = 15.3 Hz). The mixtures of [2-D]-**7** and [*endo*-3-D]-**7** exhibited singlets for 2-H and doublets (geminal coupling) for *endo*-3-H.

[6] Review: G. D. Sargent in G. A. Olah, P. von R. Schleyer: *Carbonium Ions*, Wiley, New York 1972, p. 1110–1121.

[7] P. von R. Schleyer, *J. Am. Chem. Soc.* 89 (1967) 699, 701; N. G. Rondan, M. N. Paddon-Row, P. Caramella, J. Mareda, P. H. Mueller, K. N. Houk, *ibid.* 104 (1982) 4974.

[8] S. Inagaki, H. Fujimoto, K. Fukui, *J. Am. Chem. Soc.* 98 (1976) 4054.

Nitrile Imines: Thermal Generation, Direct Observation, and Subsequent Trapping**

By Curt Wentrup*, Stephan Fischer, André Maquestiau, and Robert Flammang

Nitrile imines are important intermediates for 1,3-dipolar cycloadditions in solution^[1]. Diphenyl- and *N*-phenyl-nitrile imine have been observed by IR and UV spectroscopy following low-temperature irradiation of matrix-isolated precursors^[2]. Also trapping with protic solvents and use of an intramolecular cycloaddition reaction have been described^[2c]. However, no direct observation of a thermally generated nitrile imine has been reported, there is no evidence for the existence of discrete nitrile imines in the gas phase, and the crucial link between the gas-phase or matrix-isolated species and the solution-phase intermediates, trappable in intermolecular 1,3-dipolar cycloaddition reactions and presumed to be nitrile imines, has not been established. We now wish to report evidence for each of these points.

In order to observe a nitrile imine in thermal reactions, gas-phase generation with short contact times and subsequent low-temperature isolation are appropriate. However, nitrile imines with *N*-aryl groups undergo rapid cyclization to indazoles in the gas phase, thereby precluding direct observation^[3]. Furthermore, *N*-methyl and related nitrile imines isomerize in the gas phase to azines and carbodiimides^[4]. A nonisomerizing *N*-substituent is therefore required, and *N*-silyl substituents proved to be the best in this respect.

Flash vacuum pyrolysis of *C*-phenyl-2-trimethylsilyltetrazole **1**^[5] at 710 K/ 10^{-3} torr gave gaseous *C*-phenyl-*N*-trimethylsilylnitrile imine **2**, which was led directly into the ion source of a mass spectrometer situated ca. 1 cm from the exit of the pyrolysis tube, or trapped on a KBr window at 77 K as the neat solid for IR spectroscopy. For UV spectroscopy the nitrile imine was co-condensed with isopentane on a quartz window at 77 K.

The molecular ion from **1** disappeared as a result of the pyrolysis, leaving an intense signal of the molecular ion of **2** (m/z 190). The collisionally induced dissociation (CID) mass spectrum of the latter ion was significantly different

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