^{13}C NMR Spectroscopic Investigation of Tertiary Spiro[cyclopropane-3'-norbornan]-2'-yl Cations and Their Rearrangements[1]

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2'-Methylspiro[cyclopropane-3'-norbornan]-2'-yl (9), 2'-phenylspiro[cyclopropane-3'-norbornan]-2'-yl (10), and 2-cyclopropylspiro[cyclopropane-3'-norbornan]-2'-yl (11) cations were prepared from the corresponding alcohols with Magic Acid (1:1 SbF_5 + FSO_3H) at low temperatures and characterized by ^{13}C NMR spectroscopy. Cation 11 is extremely stable up to -20 °C. Cation 10 rearranges to the 2-phenyl-4-methylbicyclo[3.2.1]oct-3-en-2-yl cation (13) at about -70 °C. The cation 9, and its rearranged isomer 2,4-dimethylbicyclo[3.2.1]oct-3-en-2-yl cation (12), exist in an 1:1 ratio even at -90 °C. The chemical shift assignments were aided by ab initio IGLO calculations. The study shows the overwhelming delocalizing ability of the 3-spirocyclopropyl group over C1-C6 σ-bond participation. The latter nonclassical σ-participation, however, was shown to persist to some extent even in the tertiary 2-norbornyl cations.

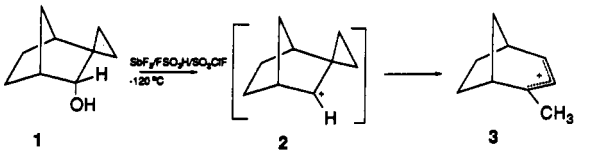
Introduction

The 2-norbornyl cation has been one of the most extensively explored carbocations. Winstein and co-workers[2] originally determined that *exo*-2-norbornyl brosylate solvolyzes 350 times faster than the corresponding endo isomer in acetic acid. They also observed the almost exclusive formation of exo products from the acetolysis of either the exo or endo brosylates.[2] Based on these observations, they suggested C1-C6 bond participation during the solvolysis, resulting in a σ-bridged, nonclassical cation. The 2-norbornyl cation was subsequently prepared at low temperature in superacidic, low nucleophilicity media by Olah and associates and was well characterized by solution NMR (^1H, ^{13}C), ESCA, and Raman spectral studies. Yannoni and co-workers[3a,b] were also successful in obtaining a solid-state magic angle spinning ^{13}C NMR spectra of ^{13}C-enriched 2-norbornyl cation in SbF_5 solid matrix from -144 to -268 °C. The absorption for C1 and C2 at $\delta(^{13}C)$ 125 remained unchanged even at -268 °C (5 K), based on which the authors estimated a barrier of 0.2 kcal/mol for the 1,2-Wagner-Meerwein rearrangement of the hypothetical structures. The topic has been well reviewed.[3c-e] Brown and co-workers, on the other hand, maintained that the high exo/endo rate ratio could be explained alternatively as due to the normal solvolysis rate of the exo isomer and the decreased reactivity of the endo isomer as due to the steric interaction of the leaving group and the endo C6 hydrogen.[4]

Wilcox and Jesaitis found that the exo/endo rate ratio approaches a value of 3 in the solvolysis of spiro[cyclopropane-3'-norbornan]-2'-yl 3,5-dinitrobenzoates.[5] They have accounted for the diminished exo/endo ratios by proposing neighboring cyclopropyl group participation in the stabilization of the 2-norbornyl cation, which thus requires no further stabilization by C1,C6 σ-bond participation. Similar behavior was also observed in the solvolyses of 3-methylene-2-norbornyl derivatives, where the allyl participation effectively overrides the C1-C6 bond participation.[6]

Lenoir and Schleyer similarly found a low exo/endo rate ratio of 12 for the solvolysis of spiro[cyclopropane-3'-benzonorbornen]-2'-yl *p*-nitrobenzoates,[7] but the corresponding tertiary 2-methyl system, although significantly more reactive due to the cyclopropyl participation, exhibited high exo/endo rate ratios. They suggested the involvement of steric factors in the tertiary system.[8] Involvement of steric factors in the tertiary 2-aryl-3-methylene-2-norbornyl and 2'-arylspiro[cyclopropane-3'-norbornan]-2'-yl systems was also shown by Brown and co-workers.[9] However, Brown's subsequent application of the "tool of increasing electron demand" that had been originally adopted by Farnum and co-workers[10a,b] to the 3-methylene-2-norbornyl system under stable ion conditions showed that C1-C6 σ-bond participation, besides the allylic stabilization, was important for the deactivated cations.[10c]

Direct observation of secondary spiro[cyclopropane-3'-norbornan]-2'-yl cation (2) by Olah and co-workers was unsuccessful because the ion spontaneously rearranged to the allylic 2-methylbicyclo[3.2.1]oct-3-en-2-yl cation (3).[11]



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Tertiary spiro[cyclopropane-3'-norbornan]-2'-yl cations are expected to be more stable than the secondary cation 2. Although the substituents at the 2-position in the tertiary cation also stabilize the cationic center, by choosing substituents of known electronic behavior, we hoped to

(1) Stable Carbocations. 283. For part 282, see: Olah, G. A.; Reddy, V. P.; Rasul, G.; Prakash, G. K. S. *Croatica Chemica Acta (Sunko Issue)*. In press.

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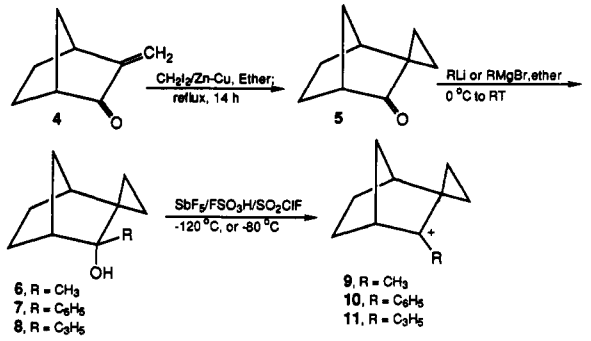
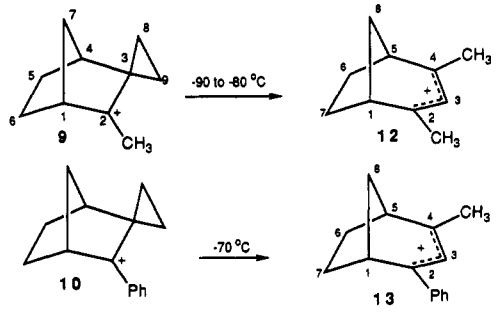
Scheme I. Synthesis of Tertiary Spiro[cyclopropane-3′-norbornan]-2′-yl Cations



Scheme II. Rearrangement of the Tertiary Spiro[cyclopropane-3′-norbornan]-2′-yl Cations



distinguish the relative importance of the stabilizing influence of the spirocyclopropyl group and C1–C6 bond on the cationic center. With that aim, we have now prepared the tertiary 2′-methylspiro[cyclopropane-3′-norbornan]-2′-yl, 2-phenylspiro[cyclopropane-3′-norbornan]-2′-yl, and 2′-cyclopropylspiro[cyclopropane-3′-norbornan]-2′-yl cations (**9–11**) and characterized them by ^{13}C NMR spectroscopy. Furthermore, ab initio IGLO ^{13}C NMR chemical shift calculations were also carried out to rationalize the experimental results.

Results and Discussion

3-Methylene-2-norbornanone (**4**) was cyclopropanated by using the Simmons–Smith reaction, and the resulting spiro[cyclopropane-3′-norbornan]-2′-one (**5**) was reacted separately with methylmagnesium bromide, phenylmagnesium bromide, and cyclopropyllithium to provide alcohols **6**, **7**, and **8** (Scheme I). The 2′-methylspiro[cyclopropane-3′-norbornan]-2′-yl cation (**9**) was prepared by ionizing alcohol **6** in Magic Acid (1:1 FSO_3H–SbF_5)–SO_2ClF at −120 °C. Even at this low temperature, ion **9** could not be prepared free from its rearranged cation **12**. At −90 °C, it was found that ions **9** and **12** exist approximately in a ratio of 1:1. After warming to −80 °C, rearrangement to the allylic cation **12** was complete. 2′-Phenyl[spirocyclopropane-3′-norbornan]-2′-yl cation (**10**) was prepared by ionizing the corresponding alcohol in Magic Acid at −80 or at −120 °C. Ion **10** was stable at −80 °C but rearranged to **13** even on warming to −70 °C (Scheme II). 2′-Cyclopropyl[spirocyclopropane-3′-norbornan]-2′-yl cation (**11**) was similarly prepared and was observed by NMR from −120 to −20 °C, without any change in spectral characteristics. At −20 °C, it slowly decomposed. The related 2-cyclopropylnorbornyl cation, **14**, previously prepared by Olah and co-workers,[12] exists as a mixture of two conformational isomers from −90 to −70 °C, above which it decomposes. Ion **11**, on the other hand, exists as a single species from −120 to −20 °C, suggesting that the cationic center in **11** is more effectively stabilized by the spirocyclopropyl group, and hence free rotation of the cyclopropane ring could be achieved more easily.

The ^{13}C NMR spectral multiplicity patterns and the C–H coupling constants of the cations facilitate the assignment of the chemical shifts to most of the carbons. Complete assignment of the chemical shifts was achieved by matching with the theoretically calculated chemical shifts obtained by the IGLO (Individual Gauge for Localized Orbitals) method. The performance of the IGLO method for predicting the ^{13}C NMR chemical shifts, especially using geometries from larger basis sets, has recently been high-lighted.[13] We have done IGLO calculations at the DZ level on geometries obtained from RHF/STO-3G or RHF/3-21G optimizations.[14] The structures **9**, **10**, **11**, and **13** were partly optimized by keeping the C–H bond lengths and angles (obtained from MNDO) constant. Structures **10**, **11**, and **13** could not be optimized beyond the STO-3G level because of the large number of heavy atoms involved and the lack of symmetry. At the lower level of theory used in the IGLO calculations (DZ//STO-3G or DZ//3-21G), the chemical shifts, as expected, did not very closely match the experimental values, but the agreement was close enough to assign all the carbons. As reported by Schindler, carbocations with localized charge show deviations of the cationic center's chemical shift with the IGLO-calculated values, by approximately 30 ppm.[13a] As can be seen from the data in Table II, the IGLO chemical shift values obtained from 3-21G geometry are, as expected, closer with the experimental values than those of STO-3G values. Thus, for cation **9**, the IGLO(DZ)//3-21G value for the cationic center differs from the experimental value by 29 ppm, whereas the corresponding IGLO(DZ)//STO-3G value deviates by 66 ppm. The cationic center's shift values obtained by STO-3G differ from the experimental values by 43 and 54 ppm, respectively, for cations **10** and **11**. In accordance with Schindler's observations[13a] on the allylic cations, the IGLO values of allylic cations **12** and **13** show excellent agreement with the experimental values, the cationic center's chemical shifts differing only by 4 and 12 ppm, respectively. For cation **11**, it was not possible to distinguish the spirocyclopropyl carbons from those of an α-cyclopropyl group, as they all show similar chemical shift values. The experimental and the IGLO-calculated ^{13}C NMR chemical shift data are summarized in Tables **I** and **II**, respectively. The ^{13}C NMR spectrum of the cation **11**, as a representative example, is shown in Figure 1.

The stabilizing effect of the cyclopropyl and phenyl groups varies from carbocation to carbocation, although, in general, the cyclopropyl group is expected to be slightly more stabilizing than the phenyl. Both of these groups are much more stabilizing than the methyl group.[15] The present observation that the 2′-cyclopropylspiro[cyclopropane-3′-norbornan]-2′-yl cation (**11**) is stable up to −20 °C, whereas the cations **9** and **10** rearrange to the allylic

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Table I. ^{13}C NMR Chemical Shifts of Carbocations in Magic Acid/SO_2ClF Solutions[a]

	chemical shifts									
cation	C1	C2	C3	C4	C5	C6	C7	C8	C9	others
9	63.6 (158)	288.6	69.2	51.4 (151)	22.3	22.9	44.5 (135)	51.4 (171)	45.5 (169)	27.2 (139, CH_3)
10	58.3 (153)	257.3	61.1	49.3 (153)	24.0 (135)	28.9 (140)	42.8 (139)	53.7 (173)	41.2 (171)	145.1 (164, C_p), 134.8 (171, C_o), 130.6, 167, C_m), 130.5 (C_i)
11	52.9 (150)	281.4	58.8	44.7 (160)	23.5 (134)	27.3 (137)	42.1 (139)			29.1 (177, α-CH), 39.9 (173), 34.7 (174), 33.0 (171), 28.7 (175)
12	51.4 (150)	228.7	135.1 (180)	228.7	51.4 (151)	25.9 (134)	25.9 (134)	41.6 (138)		29.1 (130, CH_3)
13	45.3 (145)	240.1	133.3 (163)	219.4	50.8 (148)	27.7	28.6	42.0 (136)		28.7 (CH_3), 142.0 (162, C_p), 133.5 (C_i), 130.6 (161, C_o), 129.2 (168, C_m)

[a] Chemical shifts are referenced to external TMS; the values in parentheses refer to the ^{13}C–H coupling constant in hertz. C_o, C_m, C_p, and C_i are the ortho, meta, para, and the quaternary carbons of the aromatic ring.

Table II. ^{13}C NMR Chemical Shifts of Carbocations Obtained by IGLO Calculation[a]

	chemical shift (ppm from TMS)									
cation	C1	C2	C3	C4	C5	C6	C7	C8	C9	others
9	62.7 (58.8)	354.6 (317.9)	59.1 (55.0)	36.8 (36.2)	21.3 (22.6)	21.2 (23.4)	40.4 (42.8)	35.5 (47.1)	29.2 (34.0)	28.5 (CH_3) (23.9)
10	53.0	300.0	44.4	38.5	21.3	21.9	37.2	34.2	29.0	153.0 (C_p), 125.8 (C_m), 136.5 (C_o), 121.3 (C_i)
11	51.7	335.6	52.0	35.4	21.4	20.7	38.3	30.5	24.8	26.7 (α-CH), 26.4, 25.6
12	43.4 (41.0)	250.4 (241.3)	132.8 (128.1)	250.4 (241.3)	43.4 (41.0)	20.7 (22.0)	20.7 (22.0)	39.5 (38.8)		29.5 (CH_3) (28.4)
13	40.9	235.6	124.1	230.8	39.8	22.6	22.6	39.1		28.2 (CH_3), 147.5 (C_p), 126.3 (C_m), 132.4 (C_o), 121.4 (C_i)

[a] At DZ//STO-3G level; values in parentheses are from DZ//3-21G level.

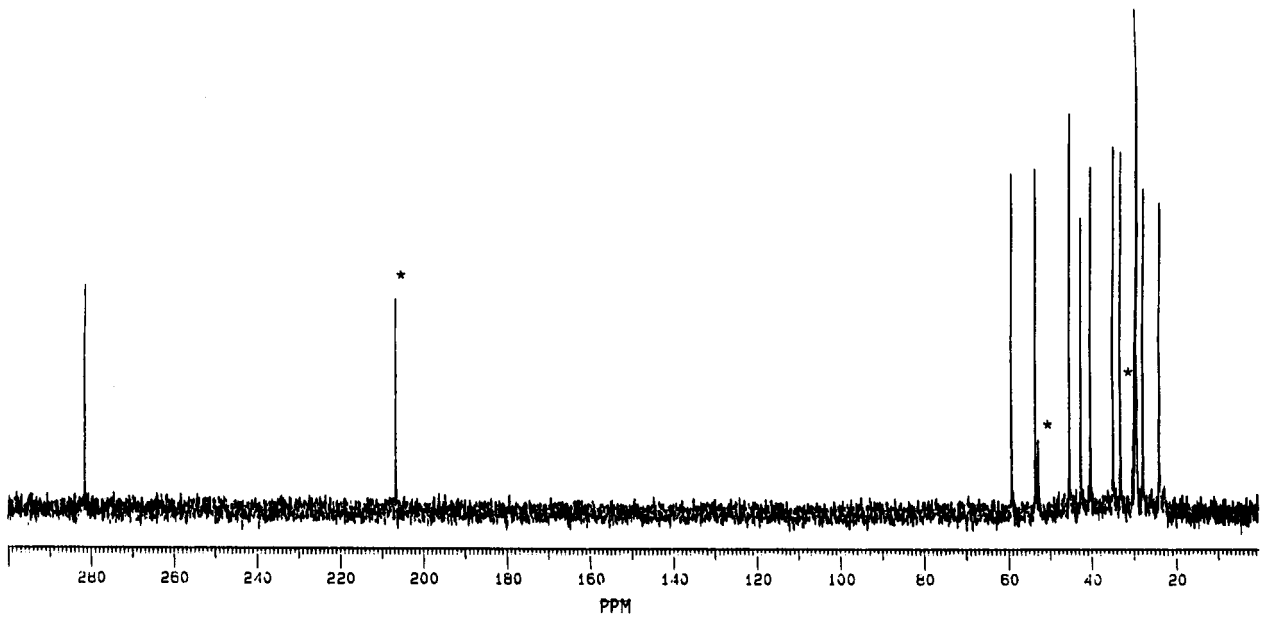
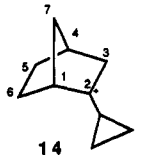


Figure 1. 90.6-MHz proton-decoupled ^{13}C NMR spectrum of 2-cyclopropylspiro[cyclopropane-3′-norbornan]-2′-yl cation (11) at −40 °C; asterisks corresponspond to absorptions due to acetone-d_6 and an impurity.

cations at temperatures as low as −90 and −70 °C, further shows the superior cation stabilizing effect of the cyclopropyl group. This order of stability is also supported by the ^{13}C NMR chemical shift values of the quarternary carbon of the spirocyclopropyl group. The charge delocalization into the spirocyclopropyl group should depend on the electron demand of the cationic center. With increase in charge delocalization into the spirocyclopropyl group, the positive character of the quaternary carbon is enhanced, resulting in more deshielding of this carbon. As the cationic center is increasingly stabilized by methyl to phenyl to cyclopropyl, the quaternary spirocyclopropyl carbon is also progressively less deshielded, i.e., $\delta(^{13}C)$ 69.2, 61.2, and 58.8 for **9**, **10**, and **11**, respectively. This observation is consistent with the relatively decreased demand for further stabilization by the spirocyclopropyl group. The relative large deshielding of the cationic center of **11** compared to the phenyl analogue **10** can be rationalized by the anisotropy effect of the cyclopropyl group. Similar effects are also observed in related nonspirocyclopropyl analogues (vide infra).

Having established spirocyclopropyl group participation, it is instructive to probe for the extent of nonclassical C1–C6 σ-participation in these cations. Certainly, the strong spirocyclopropyl group participation would lead to decreased demand for additional stabilization by the C1–C6 σ-participation. The latter participation should result in decreased charge density on C1 and C6 carbons. The parent 2-substituted 2-norbornyl cations (**14**, **15**, and **16**), as expected, show more deshielded chemical shifts for C1

and C6. Comparison of the chemical shifts of the C1 and C6 carbons of these cations[12,16] with those of spirocyclopropyl cations show this trend. The C1 and C6 carbons in cation **9** ($\delta(^{13}C)$ 63.6 and 22.9) are shielded by 16.5 and 16.6 ppm, respectively, compared to those of **16** ($\delta(^{13}C)$ 80.1 and 39.5). This clearly illustrates nonclassical C1–C6 participation in the tertiary 2-norbornyl cations. It can



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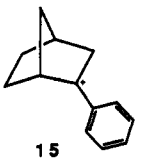
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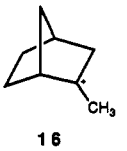

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be seen from Table I that the C1 chemical shifts for the more delocalized 2-phenyl and 2-cyclopropyl cations (**10** and **11**) are shielded by only 1 to 2 ppm compared to the corresponding chemical shifts of the nonspirocyclopropyl cations (**15** and **16**). Thus, the relatively strongly electron-releasing cyclopropyl and phenyl groups leave relatively little positive character at the cationic center, which is furthermore effectively delocalized by the cyclopropylcarbinyl group. Any C1–C6 σ-participation is therefore significantly reduced in these carbocations.

A comparison of the STO-3G-calculated C1–C6 bond lengths of cations **9**, **10**, and **11** also strengthens the supposition that phenyl and cyclopropyl groups are better stabilizing groups. The C1–C6 bond lengths of **9**, **10**, and **11** are 1.575, 1.567, and 1.571 Å, respectively. The longer bond length in **9** indicates that it is weaker and has more delocalizing character. The C3–C8 (C-exo) bond length in these structures is also longer than the C3–C9 (C-endo) bond length, suggesting that the delocalization of the spirocyclopropyl group is predominantly from the C-exo C–C bond. The C1–C8 bond lengths of **9**, **10**, and **11** are 1.550, 1.531, and 1.538 Å, respectively, again showing more delocalizing nature of the spirocyclopropyl group in **9**. The present low-level calculations, however, cannot distinguish the relative bond delocalizing stabilities in structures **10** and **11**. The HF energies of structures **9**, **10**, **12**, and **13** are −382.62133, −570.80757, −382.66490, and −570.84624 hartrees, respectively, from which it can be deduced that **12** is more stable than **9** by 27.3 kcal/mol, whereas **13** is more stable than **10** by 24.3 kcal/mol. These energy difference values, inspite of being from the STO-3G level, at least reflect the thermodynamically more favorable rearrangement pathway for **9** to **12** than from **10** to **13**.

The present data adequately account for the diminished solvolytic rate ratios for the spiro[cyclopropane-3′-norbornan]-2′-yl cations. The 3-spirocyclopropyl group effectively competes with C1–C6 σ-participation in the 2-norbornyl cation framework, resulting in comparable reactivities of the systems. The residual small C1–C6 σ-participation apparently is reflected in the observed exo/endo solvolytic rate ratios of 3–12.[5,9]

The superior stabilizing ability of the spirocyclopropyl group over C1–C6 σ-participation is also evident from the rearrangement pathways of the studied ions, leading to allylic carbocations. Carbocations **9** and **10** rearranged to the allylic bicyclo[3.2.1]oct-3-en-2-yl cations **12** and **13**, respectively, involving the neighboring group participation of the adjacent spirocyclopropyl group. Such rearrangement was also proposed earlier for the formation of the 2-methylbicyclo[3.2.1]oct-3-en-2-yl cation from spiro[cyclopropane-3′-norbornan-2′-ol in superacids at the lowest temperatures studied.[11] The intermediate spiro[cyclopropane-3′-norbornan]-2′-yl cation (**2**) was, however, too unstable to be observed even at −120 °C, and thus direct comparison of spirocyclopropyl and C1–C6 σ-bond participation in the parent secondary system was not possible.[11]

The allylic cations, **12** and **13**, hitherto unreported, have been well characterized by ^{13}C NMR spectroscopy. The chemical shifts obtained by IGLO calculations are also in close agreement with the observed chemical shift values (Table II). The 2′-cyclopropylspiro[cyclopropane-3′-norbornan]-2′-yl cation (**11**), however, did not rearrange to the expected allylic cation at the highest temperature studied (−20 °C), where it decomposed. Cation **12** has only six ^{13}C NMR peaks, expected for its C_s symmetric nature. The cationic carbon ($\delta(^{13}C)$ 228.7) is relatively less deshielded due to its allylic stabilization. Similarly, less deshielding was observed for the cationic centers of **13** ($\delta(^{13}C)$ 240.1 and 219.4). The para carbon of the phenyl group in **13** is also less deshielded ($\delta(^{13}C)$ 142.1) compared to that of **10** ($\delta(^{13}C)$ 144.9), presumably because of the more effective allylic stabilization.

In conclusion, the present study shows that the 3-spirocyclopropyl group in 2-norbornyl cations exerts a dramatic stabilizing effect and effectively competes with C1–C6 σ-participation. However, the latter "nonclassical" σ-participation persists to some extent even in highly stabilized tertiary spiro[cyclopropane-3′-norbornan]-2′-yl cations.

Experimental Section

Diethyl ether was distilled from Na-benzophenone ketyl immediately before use. 3-Methylene-2-norbornanone, methylmagnesium bromide, and phenylmagnesium bromide were obtained from Aldrich. GC/MS analyses were performed on a Finnigan-Mat/Incos-50 mass spectrometer equipped with a Varian 3400 gas chromatograph. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-200 or a Bruker-360 instrument equipped with a variable-temperature probe. ^1H and ^{13}C NMR chemical shifts for the cations are referenced to external capillary tetramethylsilane.

Spiro[cyclopropane-3′-norbornan]-2′-one (5). A 250-mL 3-necked round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser, was charged with zinc powder (9.6 g, 0.147 mol, 6 equiv), cuprous chloride (1.45 g, 14.7 mmol), and 30 mL of ether, and the reaction mixture was refluxed for 30 min. Subsequently it was cooled to room temperature, and a solution of 3-methylene-2-norbornanone (3 g, 0.0245 mol) and diiodomethane (9.2 g, 0.0343 mol, 1.4 equiv) in 5 mL of ether was added. The reaction mixture was then refluxed for 14 h. After quenching with 200 mL of water, it was extracted with ether (2 × 50 mL). The combined ether layers were washed with 10% HCl (50 mL), dried ($MgSO_4$), and filtered, and the solvents were rotary evaporated. The residue was purified by column chromatography on silica gel, eluting with methylene chloride, to obtain **5** (2.2 g, 66%).[5] MS (m/z): 136 (41.4), 121 (6.5), 108 (23.3), 93 (53), 79 (100), 77 (35.6). ^{13}C NMR: δ 219.3 (>C=O), 50.4 (C1), 42.3 (C4), 37.7, 26.4, 24.3, 16.5 (C8), 11.5 (C9).

2′-Methylspiro[cyclopropane-3′-norbornan]-2′-ol (6). Compound **5** (0.5 g, 36.7 mmol), dissolved in 10 mL of ether, was reacted with methylmagnesium bromide (1.8 mL of 3 M solution in diethyl ether; 1.5 equiv) at 0 °C. After the usual workup and purification, **6** (0.4 g, 70%) was obtained. MS (m/z) 152 (23.5 M^+), 137 (41.0), 134 (4.1), 123 (38.2), 109 (64.3), 96 (50.0), 67 (59.7), 43 (100). ^{13}C NMR: δ 50.3 (C1), 46.9 (C4), 36.9 (C7), 26.9 (C6), 26.0 (CH_3), 22.0 (C5), 11.8 and 5.8 (cyclopropyl).

2′-Phenylspiro[cyclopropane-3′-norbornan]-2′-ol (7). Compound **5** (0.5 g, 36.7 mmol), dissolved in 10 mL of ether, was reacted with phenylmagnesium bromide (1.8 mL of 3 M solution in diethyl ether; 1.5 equiv) at 0 °C and stirred for 2 h at room temperature. After the usual workup, **7** (0.6 g, 76%) was obtained. MS (m/z): 214 (28.9, M^+), 196 (2.1), 185 (17.5), 168 (7.5), 158 (16.2), 145 (21.8), 133 (17.6), 105 (100). ^{13}C NMR δ 145.9 (C_i), 129.6 (C_o), 128.7 (C_m), 125.9 (C_p), 80.3 (C2), 50.4 (C1), 46.5 (C4),

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38.1 (C7), 27.3 (C6), 22.9 (C5), 15.8 and 6.0 (cyclopropyl).

2'-Cyclopropylspiro[cyclopropane-3'-norbornan]-2'-ol (8). Lithium wire (sodium content 1%, 0.4 g, 57 mmol) was hammered into shiny plates and was placed into 50 mL of ether, contained in a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, an addition funnel, and a nitrogen inlet. The flask was cooled to 0 °C, and cyclopropyl bromide (2.3 g, 19 mmol, 1.2 equiv) was added dropwise to the contents at such a rate as to maintain gentle reflux. The solution was stirred at this temperature for 30 min. Compound 5 (2.2 g, 16 mmol), dissolved in 10 mL of ether, was then added dropwise and the reaction mixture was stirred for 2 h at room temperature. After quenching with 100 mL of water, it was extracted with ether (2 × 50 mL). The ether layers were washed with saturated sodium bicarbonate (50 mL) and dried ($MgSO_4$), and the solvents were rotary evaporated. Compound 8 (2.3 g, 81%) was obtained after purification of the residue by column chromatography (silica gel), eluting with 1:1 dichloromethane and ether. MS (m/z): 178 (6.9, M^+), 163 (10.5), 150 (32.3), 135 (17.8), 122 (29.0), 109 (30.1), 79 (32.9), 69 (100). ^{13}C NMR: δ 76.1 (C2), 49.1 (C1), 46.9 (C4), 38.0 (C3), 36.8 (C7), 26.7 (C6), 22.3 (C5), 18.1 (cyclopropyl α-CH), 11.9 (C8), 5.6 (C9), 0.51 and -0.74 (cyclopropyl β-CH_2).

Preparation of Carbocations. SbF_5 and FSO_3H were freshly distilled before use. The precursor alcohols dispersed in SO_2ClF were added to a solution of Magic Acid (1:1 SbF_5 and FSO_3H) in SO_2ClF, at -78 °C (dry ice/acetone bath) or at ca. -120 °C (pentane/liquid nitrogen slush), resulting in an approximately 10% solution of the ions. Efficient mixing of the solution was effected with a vortex stirrer.

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Proton, Electron, and Hydrogen Atom Transfers from Ions, Radicals, and Radical Ions Derived from Substituted Urazoles and Triazolinediones

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In dimethyl sulfoxide (DMSO) solution, pK_a's for the monoanion and radical derived from 4-phenylurazole have been determined to be 24.8 and 9 ± 2, respectively. The acidity constant for the 4-phenylurazolyl radical has been determined via a thermochemical cycle that incorporates proton- and electron-transfer data for ions and radicals derived from 4-phenylurazole and 4-phenyl-1,2,4-triazoline-3,5-dione. The acidity data indicate that (a) the 4-phenylurazolide monoanion is ca. 14 pK_a units less acidic than 4-phenylurazole (pK_a = 11.0) and (b) the 4-phenylurazolyl radical is slightly more acidic than 4-phenylurazole. The estimated pK_a for the 4-phenylurazolyl radical is reasonable in light of the reversible cyclic voltammetric reduction observed for 4-phenyl-1,2,4-triazoline-3,5-dione. Also in DMSO solution, the homolytic strengths of hydrazyl N-H bonds present in 4-phenylurazole, as well as for the monoanion and radical derived from 4-phenylurazole, are within 3 kcal/mol of each other. These data suggest that the 4-phenylurazolyl radical disproportionation reaction (forming 4-phenylurazole and 4-phenyl-1,2,4-triazoline-3,5-dione) is approximately thermoneutral. Similar relationships are found for ions, radicals, and radical ions derived from 4-methylurazole and 4-methyl-1,2,4-triazoline-3,5-dione.

The marriage of solution-phase proton-transfer chemistry with electrochemistry has resulted in an increased understanding of the stabilities and reactivities of several varieties of solution-phase ions, radicals, and radical ions, as well as the strengths of specific bonds contained in these species.[1] Dimethyl sulfoxide (DMSO) has proven to be a medium that is well suited for investigations of proton- and electron-transfer reactions of organic molecules.[2] The strongly basic nature of the potassium salt of the conjugate base of DMSO (the dimsyl anion) enables evaluation of proton-transfer equilibria that involve strongly basic species.[3] Kinetically stable organic dianions less basic than dimsyl can therefore be included in various thermochemical cycles provided that reliable acidity and redox data are accessible in DMSO solution.

The urazolyl[4a] moiety provides a framework that enables ready access to the equilibrium constants for proton transfers involving the neutral urazole acids, as well as the anionic and dianionic urazolide ions. A natural extension of our interest in the acidic properties of substituted urazoles and related species[5] is the investigation of the acidic nature of urazole anions in DMSO solution. The fact that the dipotassium salt of 4-phenylurazole has been dialkylated with methyl iodide, in DMSO solution, suggests

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