Table I. Acylation Products of β-Aminoacrylic Esters[a]

| starting material | acylating reagent[b] | conditions[c] | products (% yield) Z isomer | E isomer |
|---|---|---|---|---|
| 3a | II | A | 1c (81) | 2c (0) |
| | | B | 1c (28) | 2c (55) |
| 3b | I | A | 1a (56) | 2a (0) |
| | | B | 1a (58) | 2a (28) |
| 3c | I | A | 1b (76) | 2b (0) |
| | | B | 1b (73) | 2b (7) |
| 3c | II | A | 1d (78) | 2d (0) |
| | | B | 1d (17) | 2d (50) |

[a] Yields shown are estimated from integrations of vinyl proton signals of the E and Z components of crude reaction mixtures. [b] Acylating agents: I, benzoyl chloride; II, o-(carbomethoxy)benzoyl chloride. [c] Reaction conditions: A, reaction mixture refluxed 15 h; B, reaction mixture stirred 20 h at 25 °C in the dark.

Similar treatment of **1c** or **2c** with $D_2$ in EtOD gave **4b** or **4c**, respectively. **4b**: NMR ($CDCl_3$) δ 1.30 (3 H, s), 2.63 (1 H, br s, $W_{1/2}$ = 5 Hz), 3.67 (3 H, s), 3.83 (3 H, s), 6.57 (ca. 0.2 H, br s, $W_{1/2}$ = ~10 Hz, NH), 7.33–7.90 (4 H, m). **4c**: NMR δ 1.35 (3 H, s), 2.67 (1 H, br s, $W_{1/2}$ = 5 Hz), 3.70 (3 H, s), 3.86 (3 H, s), 6.62 (ca. 0.25 H, br s, $W_{1/2}$ = ~10 Hz), 7.36–7.93 (4 H, m).

**Conversion of Methyl 3-[o-(Carbomethoxy)benzamido]butyrates (4a–c) to Methyl 3-Phthalimidobutyrates (5a–c).** The hydrogenation product **4a** (50 mg) was heated without solvent in an oil bath at 150–160 °C under low vacuum (ca. 100–200 mmHg) for 27 h. After cooling, the products were purified by preparative TLC (silica gel HF 254 + 366, solvent 10% EtOAc–hexane) and then crystallized from EtOH to yield **5a** (38 mg, 84%), plates, mp 61–62 °C; NMR ($CDCl_3$) δ 1.54 (3 H, d, J = 7 Hz), 2.78 (1 H, dd, $J_1$ = 6 Hz, $J_2$ = 16 Hz), 3.13 (1 H, dd, $J_1$ = 8 Hz, $J_2$ = 16 Hz), 3.60 (3 H, s), 4.84 (1 H, m), 7.57–7.90 (4 H, m).

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30. Found: C, 63.15; H, 5.36.

Similar treatment of **4b** gave **5b**: NMR δ 1.53 (3 H, s), 3.13 (1 H, br s, $W_{1/2}$ = 6 Hz), 3.63 (3 H, s), 7.57–7.90 (4 H, m).

Similarly, **4c** was converted to **5c**: NMR δ 1.53 (3 H, s), 2.80 (1 H, br s, $W_{1/2}$ = 6 Hz), 3.63 (3 H, s), 7.57–7.90 (4 H, m).

**Photochemical Isomerization of 2c to 1c.** A solution of **2c** (500 mg) in $CHCl_3$ (50 mL) containing a small drop of $Br_2$ in a Pyrex flask was irradiated at 25 °C (with cooling by a cold-finger condenser) using a 275-W sunlamp at a distance of 2 in. for 50 min. The solvent was then evaporated to give **1c**, needles mp 82–84 °C; NMR spectrum identical with spectrum of previously prepared **1c**.

**Solvent-Induced Isomerizations of 2a to 1a and 2c to 1c.** A 50-mg sample of the substrate, **2a** or **2c**, was dissolved in a mixture of $CDCl_3$ (0.3 mL) and pyridine-$d_5$ (0.15 mL), and the NMR spectrum was recorded at intervals after the mixture stood in total darkness first at 25 °C and then at 65 °C. No changes were observed after 24 h at 25 °C. After the mixture was heated at 65 °C for 27 h, a ~50% conversion of **2a** to **1a** was observed, whereas 5 days were required for a 50% conversion of **2c** to **1c**. No isomers other than the E + Z isomers **1a** + **2a** or **1c** + **2c** were detectable by NMR.

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**Registry No.** **1a**, 78120-34-0; **1b**, 78168-75-9; **1c**, 78168-76-0; **1d**, 78168-77-1; **2a**, 78168-78-2; **2b**, 78168-79-3; **2c**, 78168-80-6; **2d**, 78168-81-7; **3a**, 21731-17-9; **3b**, 626-34-6; **3c**, 78168-82-8; **4a**, 78168-83-9; **4b**, 78168-84-0; **4c**, 78168-85-1; **5a**, 78168-86-2; **5b**, 78168-87-3; **5c**, 78168-88-4; benzoyl chloride, 98-88-4; o-(carbomethoxy)benzoyl chloride, 4397-55-1; ethyl 4-methyl-3-oxopentanoate, 7152-15-0.

# The Purported 2-Methylbicyclo[3.2.2]nonatrienyl Cation

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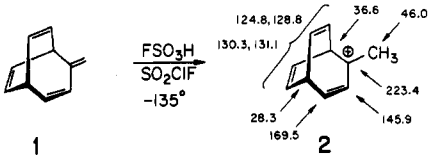
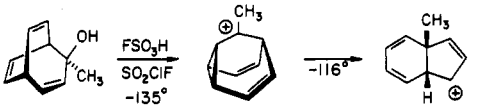
Some time ago, treatment of 2-methylenebicyclo[3.2.2]nona-3,6,8-triene (**1**) with fluorosulfonic acid in sulfuryl chlorofluoride at −135 °C provided $^1H$ and $^{13}C$ NMR spectra that were attributed to the 2-methylbicyclo[3.2.2]nonatrienyl cation (**2**).[1] The original $^{13}C$ NMR assignments are reproduced in eq 1.




1 2 (1)

This solution was also reported to be stable at −80 °C for days. Such results were astonishing for three different reasons.

1. One of the current authors (P.A., in collaboration with the Winstein group) had earlier reported that the corresponding tertiary alcohol (**3**) provided only the rearranged 9-methyl-9-barbaralyl cation (**4**) under identical conditions.[2] Apart from its $^1H$ NMR spectrum, the barbaralyl cation (**4**) could be characterized by its facile rearrangement to the more stable 1-methylbicyclo[4.3.0]nonatrienyl cation (**5**); $k_{-116°} = 2.2 \times 10^{-3}$ s$^{-1}$.[3]




3 4 5

If both reports were correct, this would mark the first time that an exomethylene derivative had provided a cation different from that which was provided by the corresponding tertiary methyl carbinol.

2. The generalized cationic transformation—bicyclo[3.2.2]nonatrienyl → barbaralyl → bicyclo[4.3.0]nonatrienyl (exemplified by **3** → **4** → **5**)—had earlier[4] and later[5] been used to illustrate the power of two different theo-

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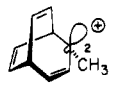
Table I. $^1$H NMR Spectrum Data of the 9-Methyl-9-barbaralyl Cation[a]

| δ, prepared from alcohol 3[b] | δ, from tetraene 1 |
|---|---|
| 6.18 | 6.18 |
| 5.93 | 5.95 |
| 5.80 | 5.80 |
| 5.21 | 5.20 |
| 4.77 | 4.75 |
| 2.94 | 2.92 |

[a] Reference: internal $CHDCl_2$ at δ 5.30. [b] Reference 2.

retical models. The stability of the bicyclo[4.3.0]nonatrienyl cation was attributed to its bishomoaromaticity.[2,3,6] The instability of the 2-bicyclo[3.2.2]nonatrienyl cation was attributed to its antibicycloaromaticity.[4] If, instead, the 2-methylbicyclo[3.2.2]nonatrienyl cation (2) were as stable as had originally been reported,[1] the power of the bicycloaromatic model would seriously have been compromised.

3. The apparent conflict, between prediction and reality, might yet be resolved by the $^{13}$C NMR spectrum that was reported for this cation. The observation of *ten* distinct signals would exclude any element of symmetry. Structure 6 accommodates this constraint by representing a 2-methylbicyclo[3.2.2]nonatrienyl cation that is pyramidal rather than trigonal at C2. However unprecedented, this




6

structural possibility might yet allow adjacent allylic stabilization, while also inhibiting antibicycloaromatic interaction with the other two bridges.

For all these reasons, it seemed important to repeat the preparation of the cation, to obtain a more thorough NMR analysis, and to confirm the original structural assignment by nucleophilic quenching experiments.

## Results

The tetraene 1 was prepared at Cornell University according to procedures that had earlier been developed at The Ohio State University.[7] Samples were then sent to the investigators at Uppsala (92 mg) and at the University of Southern California (217 mg). In none of the three laboratories, however, could the originally reported $^1$H NMR spectrum of the purported 2-methylbicyclo[3.2.2]-nonatrienyl cation (2) be duplicated.

The best resolved $^1$H NMR spectrum was obtained at the University of Uppsala (Table I). It leaves no doubt but that the only cation which the tetraene 1 provides is the 9-methyl-9-barbaralyl cation (4). (The spectrum obtained at Cornell University differs only marginally; it fails to resolve the broadened singlets at δ 5.80 and 5.95.) In none of the three laboratories could a second characteristically sharp methyl signal (reported[1] at δ ≈3.8) be detected above the base-line noise.

## Conclusions

The 2-methylbicyclo[3.2.2]nonatrienyl cation (2) can *not* be prepared from the tetraene 1. The instability of that hydrocarbon was not fully appreciated when the original spectra were taken. As a result, it might well have been transformed into the precursor of an apparent allylic cation, either during transit or storage. Tertiary methyl carbinols clearly do produce the same cations as do the corresponding exo methylene derivatives.

Whatever other limitations the bicycloaromatic model might possess,[8] there is now no reason to doubt but that it correctly anticipated the instability of the bicyclo-[3.2.2]nonatrienyl cation.

## Experimental Section

$^1$H NMR spectra at the University of Uppsala were obtained with a JEOL-FX 100 spectrometer, at Cornell University with a Varian Associates CFT-20 spectrometer operating at 79.56 MHz, and at the University of Southern California with a Varian Associates HA-100 spectrometer.

**2-Methylenebicyclo[3.2.2]nona-3,6,8-triene (1)** was obtained as described:[7] NMR ($CDCl_3$) δ 6.59 (t), 6.27 (t), 6.02 (d, 5.09 H), 5.49 (d, $J$ = 10 Hz, 1.08 H), 5.06 (s, 0.96 H), 4.70 (s, 1.03 H), 3.71 (t), and 3.43 (q, 1.85 H). Reported:[7] NMR ($CDCl_3$) δ 6.75–5.90 (m, 5 H), 5.48 (d, $J$ = 10 Hz, 1 H), 5.05 (s, 1 H), 4.7 (s, 1 H), and 3.87–3.20 (m, 2 H).

**Sample Preparation.** At the University of Uppsala, 3 μL of 1 in 60 μL of $CD_2Cl_2$ was mixed into ca. 0.4 mL of $FSO_3H$–$SO_2ClF$–$SO_2F_2$ (1:14:5, by volume) at ca. −136 °C, using the apparatus described elsewhere.[9] At Cornell University, 14 mg of 1 and 205 mg of $FSO_3H$ were concurrently condensed from the vapor phase at −198 °C onto a surface of 2.4 mL of $SO_2ClF$ and 1.0 mL of $SO_2F_2$. The apparatus was a modified version of that described by Saunders.[10] The condensed material was thawed at −136 °C and poured into an attached NMR tube, which was then sealed.

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**Registry No.** 1, 38898-40-7; 2, 78217-65-9; 3, 38694-37-0; 4, 28830-19-5; 5, 78217-66-0.

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# Air Oxidation of an Isoindene: Formation of Isobenzofuran and Acetone

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In connection with work on addition reactions of selected dienes, we required an isoindene (2*H*-indene). The only isoindene which is claimed to be stable enough for isolation is the 2,2-dimethyl-1,3-diphenyl derivative (1).[1] Even

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