cooling, water (5 mL) was added followed by extraction with ethyl acetate, which was then washed with water, dried over anhydrous sodium sulfate, and evaporated. The crude product was purified by preparative TLC with ethyl acetate–cyclohexane (1:1) as the developing solvent. Recrystallization from methanol gave **6** (2 mg) as colorless needles (mp 195–197 °C) identical with the authentic material.

2-(Acetylthio)estra-1,3,5(10)-triene-3,17β-diol Diacetate (9). To a solution of **7** (66 mg) in *N,N*-dimethylformamide (0.5 mL) was added dithiothreitol (100 mg). The mixture was allowed to stand at room temperature overnight. Water was added, and the crystalline product was collected by filtration and washed well with water (50 mL) containing some β-mercaptoethanol. Attempts at recrystallization resulted in the regeneration of **7**; therefore, after being dried under vacuum, the crude product was acetylated with acetic anhydride (0.5 mL) and pyridine (1 mL) in the usual manner. The acetylated material was separated by preparative TLC with ethyl acetate–*n*-hexane (1:3) as the developing solvent into two components. Recrystallization of the less polar fraction from methanol gave **9** (25 mg) as colorless leaflets: mp 139–140 °C; $[\alpha]_D$ +61.4° (*c* 0.7); NMR ($CDCl_3$ solution) δ 0.82 (3 H, s, 18-CH_3), 2.03 (3 H, s, 17-OAc), 2.25 (3 H, s, 3-OAc), 2.38 (3 H, s, 2-SAc), 4.67 (1 H, t, J = 8 Hz, 17α-H), 6.88 (1 H, s, C_4H), 7.33 (1 H, s, C_1H). Anal. Calcd for $C_{24}H_{30}O_5S$: C, 66.95; H, 7.02. Found: C, 67.04; H, 7.02.

Recrystallization of the more polar fraction from acetone–*n*-hexane gave **8** (5 mg) as colorless needles. This product was identical in every respect with that obtained by acetylation of the starting material.

Registry No. **2**, 24513-97-1; **3**, 21147-95-5; **4**, 26788-49-8; **5**, 26362-44-7; **6**, 26788-39-6; **7**, 78109-21-4; **8**, 78109-22-5; **9**, 78109-23-6.

Synthesis of Geometrical Isomers of β-Arylamidoacrylic Esters[1]

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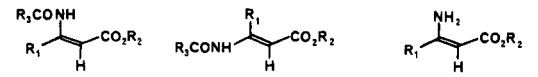
In connection with some studies on the metabolism of β-amino acids, we required several of the β-arylamidoacrylic esters (**1a–d**). Structures of this type had previously been prepared by acylation of the corresponding β-aminoacrylic esters.[2] The acylation, when carried out in a solvent mixture of pyridine and ether, was reported to yield only the *Z* isomers analogous to **1a–d**, in addition to some C-acylated byproducts. We report that under some conditions, the *E* isomers (**2a–d**) are also obtained as byproducts and are in some cases actually the major products of the reaction.



1 2 3

a R_1 = Me, R_2 = Et, R_3 = Ph
b R_1 = *i*-Pr, R_2 = Et, R_3 = Ph
c R_1 = Me, R_2 = Me, R_3 = (o-CO_2Me)Ph
d R_1 = *i*-Pr, R_2 = Et, R_3 = (o-CO_2Me)Ph

a R_1 = Me, R_2 = Me
b R_1 = Me, R_2 = Et
c R_1 = *i*-Pr, R_2 = Et

The starting β-aminoacrylic esters (**3a,b**) were obtained commercially; **3c** was prepared by treatment of ethyl isobutyrylacetate with ammonia.[3] In all cases, the β-aminoacrylic esters appeared from their ^1H NMR spectra to be single stereoisomers, presumably the *Z* isomers. Each showed in the NMR ($CDCl_3$) a single vinyl proton signal (**3a**, δ 4.50; **3b**, δ 4.49; **3c**, δ 4.56). The NH_2 proton signals in $CDCl_3$ were practically invisible but appeared in Me_2SO-d_6 solution as *two* broad bands ($W_{1/2}$ = ~20–30 Hz) at ca. δ 6.8–7.0 and ca. δ 7.6–7.7, consistent with the presence of two separate NH protons as would be expected for the *Z* isomers, **3**.

Treatment of **3a–c** with benzoyl chloride or *o*-(carbomethoxy)benzoyl chloride[4] in a mixture of pyridine and $CHCl_3$ at reflux (condition A, Table I) gave only the *Z* amides (**1a–d**), accompanied by minor unidentified byproducts (probably C-acylation products[2]). Products **1a–d** exhibited vinyl proton signals (in $CDCl_3$) in the range of δ 4.95–5.20 and prominent NH proton broadened singlets in the range of δ 11.40–12.10. However, when the acylation reactions were run in the same reagent mixture at 25 °C in the dark (condition B, Table I), each of the crude products contained a new compound having a characteristic singlet near δ 7.0. These products, isolated by preparative TLC, were identified as the *E* isomers **2a–d** primarily on the basis of their NMR spectra. These showed the expected peaks for ester grouping, alkyl side chain, and *N*-acyl function very similar to the corresponding peaks in the spectra of **1a–d**. However, the upfield vinyl proton signals of **1a–d** were replaced by 1 H singlets at substantially lower field (δ 6.78–7.07), consistent with their location proximate to the NH group.[5] Also the NH signals of **2a–d** in $CDCl_3$ were either invisible or barely detectable as an extremely broad band, e.g., in **2b** ca. δ 7.9 ($W_{1/2}$ = ~50 Hz); in Me_2SO-d_6 solution, the NH signal was clearly visible at δ 10.04 (for **2c**).

In support of the assigned structure of **2c**, hydrogenation of either **2c** or **1c** (Wilkinson's catalyst, in the dark) gave methyl 3-[*o*-(carbomethoxy)benzamido]butyrate (**4a**), which upon heating at 150 °C was converted in high yield into methyl 3-phthalimidobutyrate (**5a**).[6] Similar reduction of **1c** with D_2 in EtOD gave **4b**, which on heating gave **5b**, showing (among other bands) a broadened singlet for a single C-2 hydrogen at δ 3.13. In contrast, **2c** was converted with D_2 in EtOD to **4c**, which on heating gave **5c**, δ 2.80. Unlabeled **5a** shows for the C-2 and C-3 hydrogens a well-resolved ABX pattern, δ_A = 2.78, δ_B = 3.13, δ_X = 4.84. These facts establish that the hydrogenations proceeded stereospecifically without prior $E \rightleftarrows Z$ isomerization of the double bonds.

However, irradiation of **2c** in $CHCl_3$ plus a trace of Br_2 with a sunlamp[7] caused quantitative isomerization to **1c** in 30 min. Crude reaction mixtures containing the *E*

(1) This work was supported by Grant GM 25919 from the National Institute of General Medical Sciences.

(2) R. T. Buckler, H. E. Hartzler, and B. M. Phillips, *J. Med. Chem.*, 18, 509–513 (1975); G. D. Fallon, B. M. Gatehouse, A. Pring, I. A. Rae, and J. A. Weigold, *Can. J. Chem.*, 58, 1821–1828 (1980).

(3) S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, 67, 1017–1020 (1945).

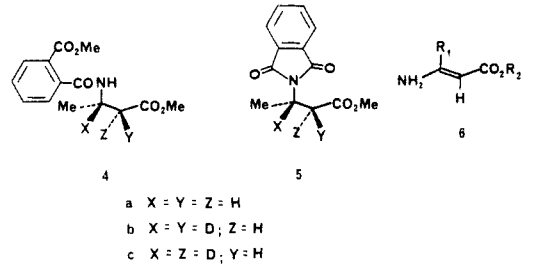
(4) E. L. Eliel and A. W. Burgstahler, *J. Am. Chem. Soc.*, 71, 2251–2252 (1949).

(5) The only previous report in the literature of the synthesis of an (*E*)-β-acylaminoacrylic ester is the formation of (*E*)-methyl β-benzamidoacrylate (2, R_1 = H; R_2 = Ph; R_3 = Me) in an electrolysis reaction: T. Iwasaki, H. Horikawa, K. Matsumoto, and M. Miyoshi, *J. Org. Chem.*, 42, 2419 (1977). The C-2 vinyl proton chemical shift of their product (δ 5.70) is not in particularly close agreement with the vinyl proton chemical shifts of our products **2a–d**.

(6) Our original reason for preparing *o*-(carbomethoxy)benzamides such as **1c** or **1d** was to use these as a hydrogenatable intermediate in the preparation of labeled β-amino acids, which could be directly converted into the phthalimido derivative without the intermediacy of the free β-amino acid.

(7) H. Kluender, C. H. Bradley, C. J. Sih, P. Fawcett, E. P. Abraham, *J. Am. Chem. Soc.*, 95, 6149–6150 (1973).

0022-3263/81/1946-3749$01.25/0



isomers (**2**) when left at room temperature in the ordinary laboratory light changed composition over a period of a few days with eventual disappearance of the *E* component. Also, heating **2a** or **2c** in a 1:2 mixture of pyridine-d_5 and $CDCl_3$ at 60 °C in the dark caused isomerization to **1a** and **1c**, respectively ($t_{1/2}$ ~27 h for **2a**, $t_{1/2}$ ~120 h for **2c**). Thus, it is understandable why *E* isomers such as **2** were not encountered in previous acylations of β-aminoacrylic esters, which apparently were all carried out in refluxing solvents.[2] The slower rate of isomerization (and higher yield in crude reaction mixtures) of *E* isomers of *o*-(carbomethoxy)benzamides (**2c,d**) is probably a result of the fact that the NH group is capable of forming an intramolecular hydrogen bond with the carbonyl oxygen of the carbomethoxy group.

It is clear that the composition of the product mixtures formed under condition B do not reflect the *Z*:*E* ratios of the starting materials, **3**/**6**. Presumably the *E* isomers **6** (which must initially be present in only trace amounts) are much more reactive toward acylating reagents than are the *Z* isomers **3** and are rapidly replaced by isomerization of **3** → **6** as the *E* isomers are acylated.

Experimental Section

NMR spectra were taken on a Varian EM-360 or EM-390 instrument. Melting points were taken on a hot-stage apparatus and are corrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. Hydrogenations were carried out in a Parr 450-mL pressure reactor. Compounds **3a** and **3b** were obtained from Aldrich Chemical Co.

Ethyl 3-Amino-4-methylpent-2-enoate (3c). Ethyl 4-methyl-3-oxobutyrate (1.3 g, 8.2 mmol) in absolute EtOH (10 mL) was treated with anhydrous NH_3 at a rate of ca. 10 mL/min at 25 °C for 42 h. After evaporation of the solvent under reduced pressure, the product was chromatographed on a column of silica gel (Fisher, 100–200 mesh), using a hexane–ethyl acetate gradient (initially 10% ethyl acetate increasing to pure ethyl acetate) to give 0.96 g of **3c** as an oil: bp 63–65 °C (0.1 mm); NMR ($CDCl_3$) δ 1.18 (d, 6, J = 6 Hz), 1.30 (t, 3, J = 6 Hz), 2.35 (heptet, 1, J = 7 Hz), 4.17 (q, 2, J = 6 Hz), 4.58 (br s, 1, $W_{1/2}$ = 2 Hz), 6.43 (br, 2, $W_{1/2}$ = ~40 Hz); NMR (Me_2SO-d_6) δ 1.08 (d, 6, J = 7 Hz), 1.15 (t, 6, J = 7 Hz), 2.31 (heptet, 1, J = 7 Hz), 3.95 (q, 2, J = 7 Hz), 4.32 (br s, 1, $W_{1/2}$ = 2 Hz), 6.90 (br, 1, $W_{1/2}$ = ~20 Hz), 7.60 (br, 1, $W_{1/2}$ = ~20 Hz).

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62. Found: C, 61.02; H, 9.53.

General Procedure for Acylation of β-Aminoacrylic Esters. Condition A. The β-aminoacrylic ester (1.2 mmol) in dry pyridine (2 mL) was treated with the acyl chloride (1.2 mmol) in $CHCl_3$ (5 mL). The mixture was refluxed for 15 h, cooled, and then poured into cold water (5 mL). The mixture was extracted with $CHCl_3$ (3 × 5 mL), and the extract was washed with 5 mL each of 6 N HCl, H_2O, 10% $NaHCO_3$, H_2O, and saturated NaCl. The $CHCl_3$ extract was then dried (Na_2SO_4) and evaporated under reduced pressure to yield the crude product mixture. The yields of *Z* and *E* products, **1** and **2**, respectively, were estimated by integration of the vinyl proton signals in the NMR spectra of this crude product.

Condition B. The β-aminoacrylic ester (1.2 mmol) in dry pyridine (2 mL) was treated with the acyl chloride (1.2 mmol) with stirring at 25 °C in the dark for 20 h. The crude product mixture was recovered as described above and examined by NMR for estimation of product yields.

The pure products were isolated by preparative TLC (silica gel HF 254 + 366, solvent ~10% EtOAc–hexane) or by column chromatography (silica gel, 100–200 mesh) using a similar solvent mixture. The products, when crystalline, were then recrystallized from the appropriate solvent.

1a: prisms from EtOH, mp 47–48 °C; NMR ($CDCl_3$) δ 1.29 (3 H, t, J = Hz), 2.49 (3 H, d, J = 1.5 Hz), 4.15 (2 H, q, J = 7 Hz), 4.95 (1 H, d, J = 1.5 Hz), 7.4 (3 H, m), 7.9 (2 H, m), 12.10 (1 H, br s, $W_{1/2}$ = 8 Hz).

Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48. Found: C, 66.88; H, 6.53.

1b: viscous oil, bp 133–135 °C (0.1 mm), which solidified on standing at room temperature, and then had a melting point of 40–41 °C; NMR ($CDCl_3$) δ 1.24 (6 H, d, J = 7 Hz), 1.34 (3 H, d, J = 7 Hz), 4.05 (1 H, heptet, J = 7 Hz), 4.20 (2 H, q, J = 7 Hz), 5.20 (1 H, s), 7.5 (3 H, m), 8.0 (2 H, m), 12.10 (1 H, br s, $W_{1/2}$ = 8 Hz).

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33. Found: C, 68.79; H, 7.41.

1c: plates from EtOH, mp 84–85 °C; NMR ($CDCl_3$) δ 2.54 (3 H, d, J = 1.5 Hz), 3.65 (3 H, s), 3.87 (3 H, s), 4.99 (1 H, d, J = 1.5 Hz), 7.5 (2 H, m), 7.8 (2 H, m), 11.40 (1 H, br s, $W_{1/2}$ = 10 Hz).

Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45. Found: C, 60.58; H, 5.55.

1d: viscous oil, bp 150–152 °C (0.25 mm); NMR ($CDCl_3$) δ 1.28 (6 *h*, d, J = 7 Hz), 1.30 (3 H, t, J = 7 Hz), 3.85 (3 H, s), 4.03 (1 H, heptet, J = 7 Hz), 4.10 (2 H, q, J = 7 Hz), 5.15 (1 H, s), 7.55 (2 H, m), 7.82 (2 H, m), 11.60 (1 H, br s, $W_{1/2}$ = 12 Hz).

Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63. Found: C, 63.73; H, 6.35.

2a: prisms from EtOH, mp 97.0–97.5 °C; NMR ($CDCl_3$) δ 1.29 (3 H, t, J = 7 Hz), 2.45 (3 H, s), 4.10 (2 H, q, J = 7 Hz), 6.90 (1 H, br s, $W_{1/2}$ = 3 Hz), 7.3–7.8 (4 H, m), ca. 7.5–8.5 (1 H, very br, $W_{1/2}$ = ~50 Hz).

Anal. Calcd for $C_{13}H_{15}NO_5$: C, 66.94; H, 6.48. Found: C, 66.84; H, 6.54.

2b: needles from EtOAc–hexane, mp 82–83 °C; NMR ($CDCl_3$) δ 1.24 (6 H, d, J = 7 Hz), 1.24 (3 H, t, J = 7 Hz), 4.13 (2 H, q, J = 7 Hz), 4.25 (1 H, heptet, J = 7 Hz), 7.07 (1 H, s), 7.3–7.8 (5 H, m), ca. 7.5–8.3 (1 H, very br, $W_{1/2}$ = ~40–50 Hz).

Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33. Found: C, 68.82; H, 7.34.

2c: needles from EtOH, mp 142–144 °C; NMR ($CDCl_3$) δ 2.46 (3 H, s, slightly broadened), 3.23 (3 H, s), 3.92 (3 H, s), 6.89 (1 H, br s, $W_{1/2}$ = ~2 Hz), 7.55 (3 H, m), 7.92 (2 H, m) (NH resonance not visible); NMR (Me_2SO-d_6) δ 2.39 (3 H, s, slightly broadened), 3.61 (3 H, s), 3.80 (3 H, s), 6.78 (1 H, s), 7.3–8.0 (4 H, m), 10.04 (1 H, br s, $W_{1/2}$ = 3 Hz).

Anal. Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45. Found: C, 60.65; H, 5.64.

2d: viscous oil; NMR ($CDCl_3$) δ 1.12 (3 H, d, J = 7 Hz), 1.27 (3 H, t, J = 7 Hz), 3.88 (3 H, s), 4.15 (2 H, q, J = 7 Hz), 4.23 (1 H, heptet, J = 7 Hz), 7.02 (1 H, s), 7.6 (2 H, m), 8.0 (2 H, m) (NH signal not visible); mass spectrum, m/e 319.14445 (M^+) ($C_{17}H_{21}NO_5$ requires 319.14197).

Hydrogenation (Deuteration) of β-Arylamidoacrylic Esters (1c or 2c). A solution of **1c** or **2c** (3.0 g, 10.8 mmol) in EtOH (60 mL) containing $ClRh(Ph_3P)_3$ (0.3 g, 0.32 mmol) was hydrogenated at 550 psi and 27 °C for 19 h. After evaporation of the solvent under reduced pressure, the resultant syrup was chromatographed on a column of silica gel (100–200 mesh, 50 g). Elution with ca. 50% EtOAc–hexane gave **4a** (2.1 g) as a viscous glass: NMR ($CDCl_3$) δ 1.30 (3 H, d, J = 6 Hz), 2.62 (2 H, d, J = 6 Hz), 3.65 (3 H, s), 3.82 (3 H, s), 4.43 (1 H, m), 6.66 (ca. 0.5 H, br s, $W_{1/2}$ = 5 Hz, NH), 6.82 (ca. 0.5 H, br s, $W_{1/2}$ = 5 Hz, NH), and 7.30–7.88 (4 H, m); mass spectrum, m/e 279.10792 (M^+) ($C_{14}H_{17}NO_5$ requires 279.11067).

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.

Acknowledgment. We thank Mr. Bruce H. Weiller for some preliminary experiments, Mr. Cliff McDonald for some of the NMR spectra, and Dr. Catherine E. Costello for the high-resolution mass spectra provided by the facility at M.I.T., supported by the National Institutes of Health (Grant RR00317; principal investigator, Professor K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources. This work was supported by Grant GM 25919 from the National Institute of General Medical Sciences.

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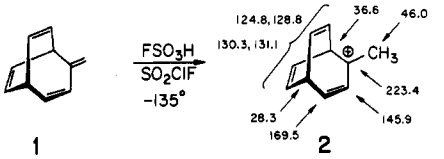
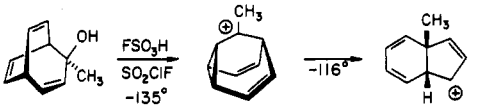
Some time ago, treatment of 2-methylenebicyclo[3.2.2]nona-3,6,8-triene (**1**) with fluorosulfonic acid in sulfuryl chlorofluoride at −135 °C provided ^1H and ^{13}C NMR spectra that were attributed to the 2-methylbicyclo[3.2.2]nonatrienyl cation (**2**).[1] The original ^{13}C NMR assignments are reproduced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