Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).
(9) The radical pair spectra derived from **1** and **2** were not identical, which is consistent with previous observations by M. Trifunac; cf. M. Trifunac, Ph.D. Thesis, The University of Chicago, 1974.
(10) H. Kristinsson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind. (London)*, 1562 (1966).
(11) C. G. Overberger and J.-P. Anselme, *J. Am. Chem. Soc.*, **86**, 658 (1968).
(12) J.-P. Anselme, *Org. Prep. Proced.*, **1**, 73 (1969).
(13) P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958).

Synthesis of 7-Azanorbornene and *N*-Methyl-7-azanorbornene

Alan P. Marchand* and Robert W. Allen

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069

Received March 19, 1975

A number of substituted 7-azanorbornanes,[1] 7-azabenzonorbornenes,[2,3] and 7-azanorbornadienes[4-8] have been reported. However, only one fully characterized *non*-ring-substituted 7-azanorbornene, *N*-phthalimido-7-azanorbornene, has been synthesized.[9] We now describe syntheses of 7-azanorbornene (**1**) and of the corresponding N-methylated amine (**2**).

In an earlier communication,[10] we reported the anomalous reduction of isolated carbon–carbon double bonds in *N*-carbethoxy-7-azanorbornene and in *N*-carbethoxy-2,3-benzo-7-azanorbornadiene by lithium aluminum hydride (or Vitride). In the present study, the successful synthesis of *N*-methyl-7-azanorbornene (**2**) was accomplished by diisobutylaluminum hydride reduction of *N*-carbethoxy-7-azanorbornene. The syntheses of **2** and of the parent (unsubstituted) amine (**1**), outlined in Scheme I, provide the first practical routes to the 7-azanorbornenyl system.

The starting material, *N*-benzyl-7-azanorbornadiene-2,3-dicarboxylic acid (**3**),[11] is obtained in 15–20% yield by Diels–Alder addition of acetylenedicarboxylic acid to *N*-benzylpyrrole.[12] Hydrogenation–hydrogenolysis of **3** affords **4**, which is then converted to the *N*-tosyl or *N*-carbethoxy derivative **5** and **6**. Electrolytic oxidative bisdecarboxylation of **5** and **6** gave the corresponding olefins **7** and **8**, which were further reduced to **1** and **2**, respectively.

Experimental Section

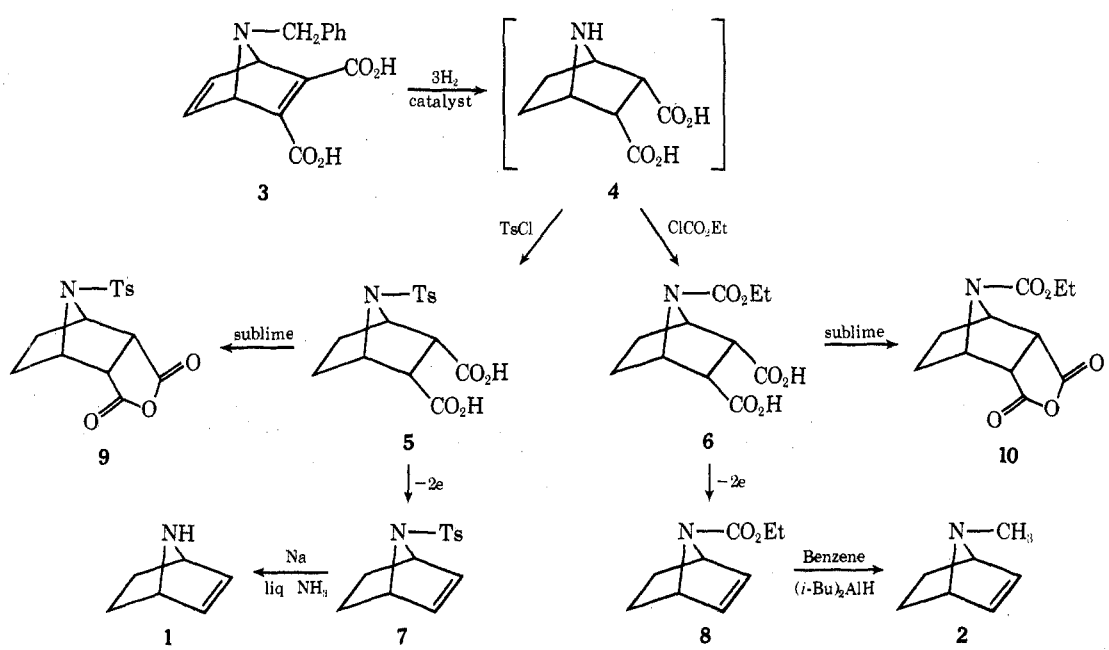
Melting points are uncorrected. NMR spectra were obtained on a Varian T-60 NMR spectrometer (Me_4Si internal standard). Ir spectra were obtained on a Perkin-Elmer Model IR-8 infrared spectrophotometer. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-7E mass spectrometer (70 eV); in order to obtain the molecular ion for compounds **1**, **2**, **7**, and **8**, it was necessary to cool the filament chamber to ambient temperature.

***N*-Carbethoxy-7-azanorbornane-*endo,endo*-2,3-dicarboxylic Acid (6).** *N*-Benzyl-7-azanorbornadiene-2,3-dicarboxylic acid[11] (**3**, 10.0 g, 36.9 mmol) was dissolved in excess aqueous sodium carbonate solution (100 ml). The resulting solution was hydrogenated (45 psig) over 10% palladized charcoal catalyst on a Parr apparatus. After 3 equiv of hydrogen had been taken up, the catalyst was removed by filtration. To the filtrate containing the hydrogenation product (**4**) was added excess ethyl chloroformate, and the resulting solution was stirred overnight at room temperature. The solution was then acidified with dilute aqueous hydrochloric acid and extracted with chloroform. The combined chloroform extracts were dried (Na_2SO_4), filtered, and then concentrated, affording **6** as a colorless syrup (8.20 g, 86.4%). Diacid **6** was characterized via the corresponding anhydride, **10**, which could be obtained via sublimation of syrupy **6** at 110° (0.1 mm). This procedure afforded **10** (5.80 g, 65.8%), which recrystallized from ether–hexane to afford colorless crystals: mp 111.5–112.8°; NMR ($CDCl_3$) δ 1.30 (t, J = 6 Hz, 3 H, $-OCH_2CH_3$), 1.61–2.1 (complex m, 4 H, 5,6-exo and endo ring protons), 3.73 (m, 2 H, 2,3-exo ring protons), 4.15 (q, J = 6 Hz, 2 H, $-OCH_2CH_3$), 4.70 [m, 2 H, 1,4 (bridgehead) protons]; ir (KBr) 2980 (w), 1860 (s), 1785 (s), 1690 (s), 900 cm^{-1} (s); mass spectrum *m/e* 239 (molecular ion), 141 (base peak), 140, 139, 122, 68.

Anal. Calcd for $C_{11}H_{13}NO_5$: C, 55.23; H, 5.48. Found: C, 55.30; H, 5.35.

***N*-Carbethoxy-7-azanorbornene (8).** Compound **6** (5.00 g, 19.5 mmol) was dissolved in an electrolysis solution which consisted of water (20 ml), triethylamine (2.5 ml), and pyridine (175 ml). A direct current (80 V, initial current 350 mA, Pt wire electrodes) was passed through this solution for 15 hr while the solution was maintained at 20° via external cooling. At the conclusion of the electrolysis, the current had dropped to 40 mA. The solution was then quenched with dilute, aqueous hydrochloric acid, and the resulting solution was extracted with diethyl ether (500 ml). The ether layer was then extracted with 10% aqueous sodium hydroxide solution to recover unreacted **6** (0.60 g). The ether layer was dried (Na_2SO_4), filtered, and then concentrated to afford crude **8**.

Scheme I



The crude product was further purified via column chromatography on neutral alumina (hexane eluent); this procedure afforded pure 8 [749 mg, 26.2% based on consumed (unrecovered) 6] as a colorless, sweet-smelling oil, bp ca. 50° (0.14 mm, microdistillation). An analytical sample of 8 was obtained via preparative VPC [0.25 in. × 10 ft column, 20% FFAP on Chromasorb W, all VPC components (injector, column, and detector) at 140°, He flow rate 100–110 ml/min]: NMR ($CDCl_3$) δ 1.13 (m, 2 H, 5,6-endo ring protons), 1.26 (t, $J \approx 6$ Hz, 3 H, $-OCH_2CH_3$), 1.90 (m, 2 H, 5,6-exo ring protons), 4.07 (q, $J = 6$ Hz, 2 H, $-OCH_2CH_3$), 4.74 [m, 2 H, 1,4 (bridgehead) protons], 6.24 [unsymmetrical t, 2 H, 2,3 (vinyl) protons]; ir (film) 3020 (w), 2995 (w), 1710 (s, br), 1270 (m), 690 cm^{-1} (m); mass spectrum *m/e* 167 (molecular ion), 139, 94, 80, 66, 41, 39 (base peak).

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84. Found: C, 64.88; H, 7.87.

***N*-Methyl-7-azanorbornene (2).** *N*-Carbethoxy-7-azanorbornene (8, 749 mg, 4.49 mmol) was dissolved in benzene (30 ml). To the resulting solution was added a benzene solution (23 ml) of diisobutylaluminum hydride (0.61 mmol/ml). After stirring for 4 hr at room temperature, an additional 5 ml of the benzene solution of diisobutylaluminum hydride was added (total 28 ml, 17.1 mmol of diisobutylaluminum hydride). After stirring for an additional 4 hr at room temperature, the reaction was quenched with excess methanol until precipitation of aluminum methoxide was complete. The reaction mixture was then filtered and combined with an equal volume of a saturated solution of picric acid in 95% ethanol, whereupon yellow crystals of *N*-methyl-7-azanorbornene picrate precipitated almost immediately. Recrystallization from 95% ethanol afforded the pure picrate (1.30 g, 85.6%) as yellow needles, mp 225° dec.

Anal. Calcd for $C_{13}H_{14}N_4O_7$: C, 46.16; H, 4.17. Found: C, 45.93; H, 3.98.

The free base (2) was obtained by treating the above picrate with concentrated, aqueous KOH solution. The resulting mixture was extracted with chloroform, and the free amine (2) was isolated via preparative VPC [0.25 in. × 4 ft column, 28% Pennwalt 223 on 80/100 mesh Gas-Chrom R containing 4% KOH, all VPC components (injector, column, and detector) at 100–110°, *nitrogen* carrier gas, N_2 flow rate ca. 100–110 ml/min]: NMR ($CDCl_3$) δ 0.98 (m, 2 H, 5,6-endo ring protons), 1.87 (m, 2 H, 5,6-exo ring protons), 2.05 (s, 3 H, NCH_3), 3.70 [m, 2 H, 1,4 (bridgehead) protons], 5.98 [br s, 2 H, 2,3 (vinyl) protons]; ir (film) 3080 (w), 2990 (w), 690 cm^{-1} (m); mass spectrum *m/e* 109 (molecular ion), 94, 81, 80, 66, 53, 42, 39 (base peak).

***N*-Tosyl-7-azanorbornane-*endo,endo*-2,3-dicarboxylic Acid (5).** Compound 5 was prepared using the same procedure which was previously employed for the synthesis of 6. Hydrogenation–hydrogenolysis of 3 (10.0 g, 36.9 mmol) followed by treatment of the resulting solution with excess *p*-toluenesulfonyl chloride afforded crude 5 (12.0 g, 95.5%). The crude product was further purified by sublimation at 150° (0.05 mm), which afforded the corresponding acid anhydride (9). Compound 9 recrystallized from acetone to afford a colorless, microcrystalline solid, mp 230–232°. Hydrolysis of 9 afforded pure 5: NMR (pyridine-d_5) δ 1.53–2.50 (m, 4 H, 5,6-exo and endo ring protons), 2.30 (s, 3 H, $ArCH_3$), 3.90 (m, 2 H, 2,3-exo ring protons), 4.70 [m, 2 H, 1,4 (bridgehead) protons], 5.50 (s, 2 H, –COOH), 7.63 (AA′BB′ pattern, 4 H, aryl ring protons). Compound 5 was further characterized via the corresponding anhydride (9); ir of 9 (KBr) 3070 (w), 2980 (w), 1865 (s), 1785 (s), 1335 (sh), 1140 (sh), 1590 (w), 905 cm^{-1} (s); mass spectrum *m/e* 321 (molecular ion), 223, 166, 155, 122, 91, 68 (base peak).

Anal. Calcd for $C_{15}H_{15}NO_5S$: C, 56.06; H, 4.70. Found: C, 56.16; H, 4.92.

***N*-Tosyl-7-azanorbornene (7).** Compound 5 (2.3 g, 6.8 mmol) was dissolved in an electrolyte solution (100 ml) which was prepared as described previously for the synthesis of 8 from 6. A direct current (80 V, initial current 160 mA) was passed through this solution for 12 hr while the solution temperature was maintained at 20° via external cooling. At the conclusion of the electrolysis, the current had dropped to 50 mA. Work-up of the reaction was carried out as described for the synthesis of 8 from 6. The crude product was purified via elution chromatography on neutral alumina (hexane eluent). Compound 7 (204 mg, 12.1%) was thereby obtained. Recrystallization of 7 from hexane afforded an analytical sample as colorless needles: mp 91.5–92.0°; NMR ($CDCl_3$) δ 1.07 (m, 2 H, 5,6-endo ring protons), 2.03 (m, 2 H, 5,6-exo ring protons), 2.42 (s, 3 H, $ArCH_3$), 4.64 [m, 2 H, 1,4 (bridgehead) protons], 5.73 [unsymmetrical t, 2 H, 2,3 (vinyl) protons], 7.41 (AA′BB′ pattern, 4 H, aryl ring protons); ir (KBr) 3090 (w), 2995 (w), 2960 (w), 1590 (w), 1335 (s), 1150 (s), 690 cm^{-1} (s); mass spectrum *m/e* 249 (molecular ion), 221, 155, 106, 91 (base peak), 65, 58.

Anal. Calcd for $C_{13}H_{15}NO_2S$: C, 62.62; H, 6.06. Found: C, 62.50; H, 5.99.

7-Azanorbornene (1). Compound 7 (204 mg, 0.82 mmol) was dissolved in a solution of diethyl ether (10 ml) in liquid ammonia (20 ml). Excess, clean sodium metal was added portionwise until the blue color of solvated electrons persisted for 1 min. The reaction mixture was then concentrated, and the residue was dissolved in diethyl ether and extracted with dilute aqueous hydrochloric acid. The aqueous phase was rendered strongly basic (KOH) and the resulting solution was extracted with chloroform (10 ml). The chloroform extracts were dried and carefully concentrated, affording 1 as a colorless liquid (70 mg, 90%): NMR ($CDCl_3$) δ 1.02 (m, 2 H, 5,6-endo ring protons), 1.75 (m, 2 H, 5,6-exo ring protons), 1.76 (s, 1 H, –NH, disappears upon addition of D_2O), 4.12 [m, 2 H, 1,4 (bridgehead) protons], 6.23 [unsymmetrical t, 2 H, 2,3 (vinyl) protons]; ir (film) 3250 (br), 3070 (w), 2960 (s), 1650 (br), 1260 (m), 790 cm^{-1} (s); mass spectrum *m/e* 95 (molecular ion), 80, 67, 66, 51, 42, 39 (base peak), 28. Compound 1 was further characterized via its picrate. When 1 was added to a solution of picric acid (excess) in 95% ethanol, precipitation of 7-azanorbornene picrate occurred almost immediately. Recrystallization of the picrate from 95% ethanol afforded yellow needles, mp 208–210° dec.

Anal. Calcd for $C_{12}H_{12}N_4O_7$: C, 44.45; H, 3.73; N, 17.28. Found: C, 44.21; H, 3.85; N, 17.30.

Acknowledgments. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Financial support of this study by the Research Council, University of Oklahoma, is also gratefully acknowledged.

Registry No.—1, 55590-24-4; 1 picrate, 55590-25-5; 2, 55590-26-6; 2 picrate, 55590-27-7; 3, 34354-00-2; 4, 55658-14-5; 5, 55658-15-6; 6, 55590-28-8; 7, 55590-29-9; 8, 55258-01-0; 9, 17037-46-6; 10, 55590-30-2.

References and Notes

(1) R. R. Fraser and R. B. Swingle, *Can. J. Chem.*, **48**, 2065 (1970).
(2) V. Rautenstrauch, *Chem. Commun.*, 1122 (1969).
(3) P. Rosso, J. Oberdier, and J. Sweeton, *Tetrahedron Lett.*, 3947 (1971).
(4) R. Kitzing, R. Fuchs, M. Joyeux, and H. Prinzbach, *Helv. Chim. Acta*, **51**, 888 (1968).
(5) R. C. Bansal, A. W. McCulloch, and A. G. McInnes, *Can. J. Chem.*, **47**, 2391 (1969).
(6) L. Mandell and W. A. Blanchard, *J. Am. Chem. Soc.*, **79**, 2343 (1957).
(7) J. C. Blazejewski, D. Cantacuzene, and C. Wakselman, *Tetrahedron Lett.*, 363 (1975).
(8) G. W. Gribble, N. R. Easton, Jr., and T. Eaton, *Tetrahedron Lett.*, 1075 (1970).
(9) L. Hoesch and A. S. Dreiding, *Chimia*, **26**, 629 (1972).
(10) A. P. Marchand and R. W. Allen, *Tetrahedron Lett.*, 67 (1975).
(11) A. Shafi'ee and G. Hite, *J. Org. Chem.*, **33**, 3435 (1968).
(12) A. D. Josey, R. J. Tuite, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 1597 (1960).

Addition of *tert*-Butylcyanoketene to Imino Ethers. Steric Effects on Product Formation

Donald H. Aue* and Darryl Thomas

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

Received October 7, 1974

In connection with a series of studies on additions to imino ethers,[1] we have investigated ketene additions to cyclic and acyclic imino ethers here. Ketenes were first shown by Staudinger to add to imines to give β-lactams A in 1907.[2] In many cases 2:1 adducts are formed at the expense of the β-lactam, however.[3-17] Although originally assigned the piperidinedione structure D,[4-9] most 2:1 adducts have since been shown to be oxazinones B.[3,10-13] In a few cases the dioxazines C have been formed too.[14-17] Compounds of structure E are known,[18-26] but not from 1,4-dipolar addi-