Bridgehead Substitution *vs.* Ring Contraction in the Deamination of 1-Aminobicyclo[2.2.1]hept-5-en-2-ol

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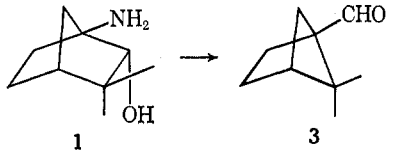
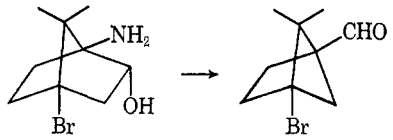
Received October 31, 1969

The synthesis of *endo*-1-aminobicyclo[2.2.1]hept-5-en-2-ol (**13**) is described. Deamination reactions resulted in bridgehead substitution rather than the ring contraction characteristic of the corresponding saturated amines. This result can be rationalized on the basis of the increase in steric strain which would be encountered in the rearrangement process, but not in the competing substitution.

The deamination of vicinal aliphatic amino alcohols provides many examples of molecular rearrangement.[2] Recently, Larson and coworkers[3] observed that the nitrous acid deamination of amino alcohols **1** and **2** led, *via* semipinacolic rearrangement, to the aldehydes **3** and **4** as the sole isolable products in *ca.* 70% yield.



1 **3**



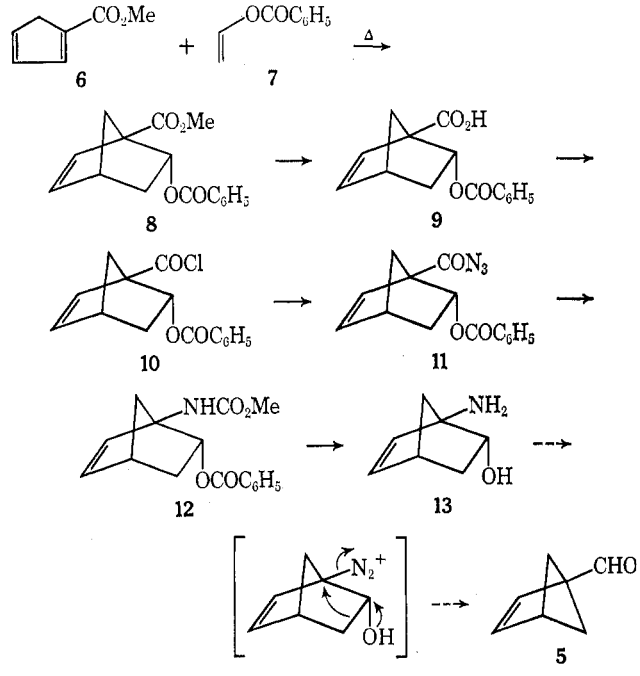
2 **4**

This observation is compatible with the proposal of Pollak and Curtin[4] that the nature of the rearranged product in these reactions is dependent on the *trans*-coplanar relationship between the migrating group and the departing nitrogen. The present investigation describes an attempt to prepare a bridgehead-substituted bicyclo[2.1.1]hex-2-ene (**5**) based on this type of rearrangement. Toward this end, a desirable compound for study appeared to be 1-aminobicyclo[2.2.1]-hept-5-en-2-ol (**13**), the synthesis of which is outlined in Chart I.

The initial step involved the Diels–Alder reaction between "Thiele's ester" **6** and vinyl benzoate **7**. The desired diester **8** could be isolated in 14% yield from the resultant mixture of adducts. Selective cleavage of the methyl ester of **8** with anhydrous lithium iodide in refluxing pyridine[5] gave the acid benzoate **9** in 92% yield. The Curtius reaction[6] provided an efficient method of degrading this bridgehead carboxylic acid to the corresponding carbamate **12**, obtained as a white, crystalline solid in 81% overall yield from **9** after recrystallization from hexane–ether.

The nuclear magnetic resonance (nmr) spectrum of **12** provides strong support for its assigned structure and

CHART I



6 **7** **8** **9** **10** **11** **12** **13** **5**

stereochemistry. It shows a one-proton pair of doublets (J_1 = 8 cps, J_2 = 3 cps) centered at τ 4.4, assigned to the proton on the carbon bearing an oxygen, a broad one-proton singlet at τ 7.26 (H-4), and a one-proton septet at τ 7.65 (*exo* H-3), along with other characteristic absorption signals. Proof that the carbamate group is adjacent to the benzoate group was obtained in conducting double-resonance experiments. If the benzoate group is in fact located at the C-2 position, irradiation at the H-4 should have no effect on the τ 4.4 splitting pattern. This is indeed the case. The τ 4.4 (H-2) absorption remains a pair of doublets, while the τ 7.65 (*exo* H-3) absorption collapses to an overlapping pair of doublets (J_3 = 8 cps, J_4 = 12 cps). That the benzoate group was *endo* was verified by the absence of long-range *anti*-H-7–*endo*-H-2 coupling.[7] Basic hydrolysis of **12** gave the desired amino alcohol **13** in 96% yield.

When the nitrous acid deamination of **13** was carried out under conditions reported to give maximum rearrangement,[2a,3] a mixture containing two major com-

(1) National Institutes of Health Predoctoral Fellow, 1966–1969.

(2) (a) M. Cherest, H. Felkin, J. Sicher, F. Sipos, and M. Tichy, *J. Chem. Soc.*, 2513 (1965); (b) G. E. McCasland, *J. Amer. Chem. Soc.*, **73**, 2293 (1951); (c) J. W. Huffman and J. E. Engle, *J. Org. Chem.*, **24**, 1844 (1959); (d) J. G. Traynham and M. T. Yang, *J. Amer. Chem. Soc.*, **87**, 2394 (1965).

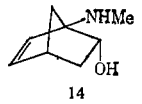
(3) (a) K. Ebisu, L. B. Batty, J. M. Higaki, and H. O. Larson, *ibid.*, **88**, 1995 (1966); (b) H. O. Larson, T. Ooi, W. Luke, and K. Ebisu, *J. Org. Chem.*, **34**, 525 (1969).

(4) P. I. Pollak and D. Y. Curtin, *J. Amer. Chem. Soc.*, **72**, 961 (1950).

(5) F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **43**, 113 (1960).

(6) P. A. S. Smith, *Org. React.*, **3**, Chapter 9 (1946).

(7) Compounds **12** and **14** show long-range *endo*-H-3–*anti*-H-7 coupling constants of 4.0 and 3.5 cps, respectively; *cf.* J. Meinwald and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **85**, 2514 (1963).



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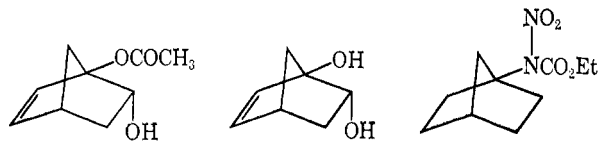
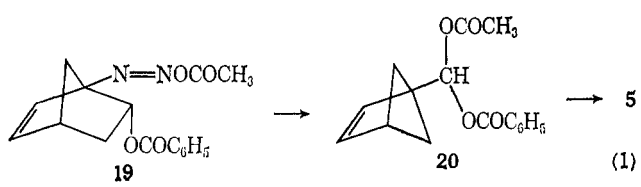
ponents could be isolated in good yield. Neither proved to be the desired ring-contracted aldehyde. The mixture was separated by preparative tlc, and the faster moving component (*ca.* 27% of mixture) was assigned structure **15** on the basis of its infrared and nmr spectra. Vacuum sublimation of the second major component (*ca.* 66% of mixture) gave a crystalline diol, assigned structure **16**, the nmr spectrum of which exhibited the same characteristic bicyclo[2.2.1]hept-5-ene absorption as **15**, as well as a two-proton singlet at τ 7.0 exchangeable with deuterium oxide. The mass spectrum of **16** shows an intense *m/e* 82 peak which is compatible with fragmentation *via* a retro Diels–Alder reaction.[8,9]

When it became apparent that unrearranged bridgehead substitution products were being formed in preference to ring contraction, an alternative deamination technique was sought. Recently, White and coworkers[10] have observed the formation of a relatively



15 16 17

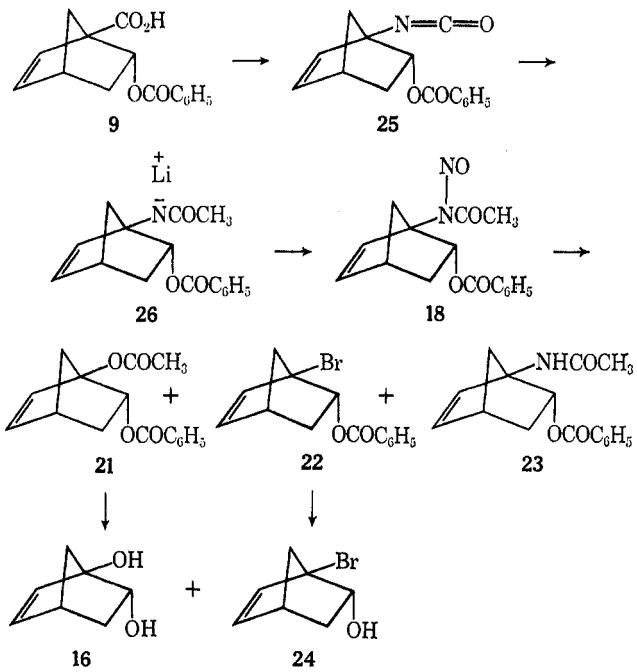
large percentage of solvent-derived products in the thermal decomposition of the N-nitrourethan **17**, derived from 1-norbornylamine, in nonpolar solvents. In their explanation of these results, the authors concluded that a large fraction of relatively "free" carbonium ions were being formed. If this were correct, a hydroxyl group at the 2 position might be expected to facilitate ring contraction during decomposition. With this in mind, a study of the thermolysis of N-nitroso-1-acetamidobicyclo[2.2.1]hept-5-en-2-yl benzoate (**18**) wasun dertaken, with the hope that the intermediate diazo ester **19** would undergo rearrangement upon dissociation to give the diester **20**, which on hydrolysis would give the desired aldehyde **5** (eq 1).



19 20 (1)

In fact, thermal decomposition of a carbon tetrachloride solution of **18**, prepared as shown in Chart II, led to formation of a product shown to be a mixture of the bridgehead acetate **21** (*ca.* 28%) and bromide **22** (*ca.* 42%).[11] In addition, 26% of the amide benzoate **23** could be recovered. No trace of the desired rearrangement product was observed in the nmr spectrum of the crude reaction mixture. The structures **21** and **22** were assigned on the basis of the similarity of their nmr and mass spectra to those of other bicyclo[2.2.1]hept-5-enes encountered in this work. In each case a major

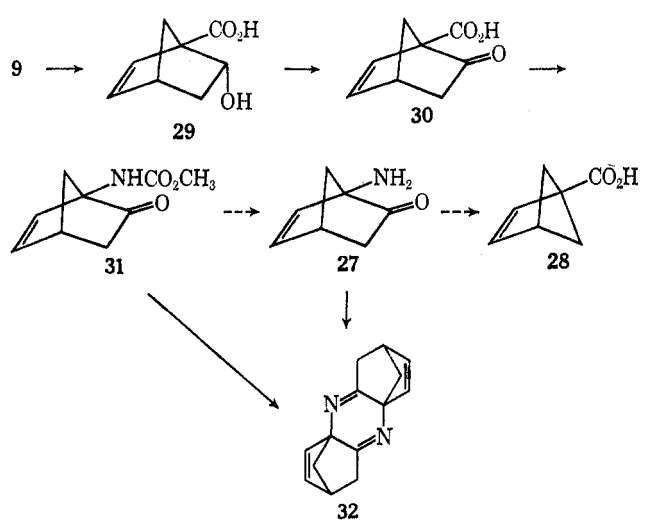
CHART II



fragment ion in the mass spectrum was the result of a retro Diels–Alder reaction. Supporting spectral evidence was obtained from the corresponding alcohols **16** and **24**. Apparently, if any "free" carbonium ions were formed in the thermolysis of **18**, bridgehead substitution to give unrearranged product was energetically more favorable than the desired ring contraction.

During the course of this investigation an attempt was made to prepare the amino ketone **27**, as summarized in Chart III, with the hope that nitrous acid deam-

CHART III



ination of **27** might lead, *via* the appropriate rearrangement, to the bridgehead carboxylic acid **28**. Unfortunately, basic hydrolysis of the carbamate **31** led to the dihydropyrazine **32** rather than the expected amino ketone. The assignment of structure **32** is based on its characteristic infrared, nmr, and mass spectra, and finds analogy in a report by Applequist[12]

(8) T. Goto, A. Tatamatsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, **22**, 2213 (1966).

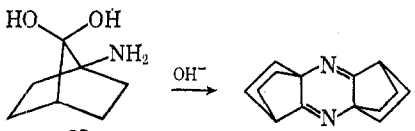
(9) S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966).

(10) E. H. White, H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, **90**, 4734 (1968).

(11) The bromide ion was presumably supplied by the lithium bromide present in the methyllithium used in the synthesis of the nitroso amide.

(12) D. E. Applequist and J. P. Klieman, *J. Org. Chem.*, **26**, 2178 (1961).

of the formation of a similar dihydropyrazine **34** on treatment of **33** with aqueous sodium hydroxide.



33 34

In rationalizing the failure of **13** to undergo the desired semipinacolic ring contraction,[13] we conclude that the 5,6 double bond raises the transition-state energy associated with ring contraction such that ion-pair collapse to solvent-derived products is favored. This is not unreasonable, since bridgehead substitution does not change the environment of the double bond, while rearrangement would force the double bond into a more strained ring system. This steric factor apparently renders Larson's elegant synthesis of bicyclo[2.1.1]hexanes inapplicable to the corresponding olefins.

Experimental Section

Diels–Alder Reaction between Vinyl Benzoate and Thiele's Ester. 1-Carbomethoxybicyclo[2.2.1]hept-5-en-2-yl Benzoate (8).[14]—A mixture of 112 g (0.758 mol) of freshly distilled vinyl benzoate, 28.2 g (0.228 mol) of freshly distilled Thiele's ester, bp 87–90° (16 mm), and 400 mg of hydroquinone was heated at 180° under nitrogen for 48 hr. Fractional distillation gave 57.1 g (92%) of a mixture of adducts, bp 144–154° (0.5 mm). This mixture was dissolved in 120 ml (2.7 mol) of dimethylamine and stored at 0° for 18 hr. The excess amine was removed with little or no heating. The residue was dissolved in ether, and the ether was extracted with 250 ml of 1.0 *N* HCl, washed with saturated NaCl solution, dried ($MgSO_4$), and evaporated to give 25 g (44%) of an oil. Vacuum distillation gave 21.7 g of a mixture, bp 144–154° (0.5 mm), which showed two methoxyl peaks at τ 6.25 and 6.3 in the nmr. Silica gel column chromatography gave 7.4 g of a mixture highly enriched in the desired adduct **8**: ir ($CHCl_3$) 1728 (COOMe), 1603, 1440, 1310, 1280–1180, and 1110 cm^{-1}; nmr (CCl_4) τ 2.0 (m, 2) and 2.6 (m, 3, aromatic), 3.62 (m, 2, olefinic), 4.17 (q, 1, J_1 = 8 cps, J_2 = 3 cps, H-2), 6.25 (s, 3, COOMe), 7.0 (s, 1, H-4), 7.48 (septet, 1, *exo* H-3), 8.12 (m, 2, *syn* and *anti* H-7), and 8.8 (m, 1, *endo* H-7).

1-Carboxybicyclo[2.2.1]hept-5-en-2-yl Benzoate (9).—A solution of 56.5 g (421 mmol) of anhydrous lithium iodide and 11.4 g (42.1 mmol) of **8** in 1200 ml of anhydrous pyridine was refluxed under nitrogen for 3 days, poured over crushed ice, neutralized (concentrated HCl) with external cooling, and extracted with ether. The ether extract was concentrated under reduced pressure and extracted with 40 ml of 1 *N* NaOH solution. Ether extraction of the reacidified solution gave 9.9 g (91%) of product, which when recrystallized from hexane–ether gave 5.36 g (49%) of crystalline acid benzoate **9**: mp 138–141°; ir ($CHCl_3$) 3500–2500, 1715, 1605, 1588, 1450, 1315, 1275–1195, and 1110 cm^{-1}; nmr ($CDCl_3$) τ −2.0 (s, 1, COOH), 1.6–2.74 (m, 5, aromatic), 3.23–3.60 (m, 2, H-5, H-6), 3.95 (q, 1, J_1 = 8 cps, J_2 = 3 cps, H-2), 6.8 (s, 1, H-4), 7.29 (septet, 1, *exo* H-3), 8.0 (m, 2, *syn* and *anti* H-7) and 8.5 (m, 1, *endo* H-3).

Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.42. Found: C, 69.60; H, 5.41.

N-Carbomethoxy-1-aminobicyclo[2.2.1]hept-5-en-2-yl Benzoate (12).—A 2.9-g (11.2 mmol) sample of **9** was dissolved in 23 ml of 0.5 *N* NaOH and evaporated under reduced pressure (30°). The residue was dried overnight at 100° in a vacuum oven, suspended in 100 ml of anhydrous benzene, and cooled to 0°. To the vigorously stirred suspension was added 5 drops of pyridine and 4.27 g (34 mmol) of oxalyl chloride. After 15 min at 0° and 30 min at room temperature excess oxalyl chloride and solvent were removed under reduced pressure and the residue was dissolved in anhydrous benzene, filtered, and evaporated to give **10**, which had infrared (neat) absorption at 1790, 1723, 1605, 1585, 1452, 1272, 1111, 790, 740, and 700 cm^{-1}. A solution of 2.21 g (34 mmol) of sodium azide in 5.5 ml of water was added with stirring under nitrogen to a chilled solution of **10** in 125 ml of acetone. After 30 min at 0° an equal volume of water was added and the solution was extracted with ether. Evaporation of the dried ($MgSO_4$) extract gave **11**, which showed infrared ($CHCl_3$) absorption at 2139, 1712, 1603, 1585, 1450, 1310 (d), 1275, 1160, 1113, 968, and 950 cm^{-1}. The azide was refluxed in equal volumes of anhydrous methanol and benzene (20 ml) for 12 hr under nitrogen. Evaporation of solvent gave **12**, which on recrystallization from hexane–ether gave 2.59 g (81%) of white needles: mp 131–133°; ir ($CHCl_3$) 3440, 1723, 1604, 1588, 1500, 1450, 1342, 1270–1180, and 1110 cm^{-1}; nmr ($CDCl_3$) τ 2.0–2.9 (m, 5, aromatic), 3.75 (q, 1, J_1 = 6 cps, J_2 = 4 cps, H-5), 3.87 (s, 1, NH), 3.98 (br d, 1, J_1 = 6 cps), 4.4 (qt, 1, J_3 = 8 cps, J_4 = 3 cps, H-2), 6.47 (s, 3, COOMe), 7.26 (m, 1, H-4), 7.65 (septet, 1, *exo* H-3), 7.95 (m, 1, *syn* H-7), 8.3 (d, 1, J_5 = 8.5 cps, *anti* H-7), and 8.8 (pair of overlapping doublets, 1, J_6 = 12 cps, *endo* H-3). Double irradiation at 277.4 cps downfield from TMS caused the following changes: H-5 absorption collapsed to a doublet (J_1 = 6 cps), *exo* H-3 collapsed to overlapping pair of doublets (J_3 = 8 cps, J_6 = 12 cps), and the *syn* H-7 collapsed to a doublet of doublets (J_5 = 8.5 cps, J_7 = 4 cps).

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.90; H, 5.97; N, 4.88. Found: C, 66.96; H, 5.99; N, 5.02.

1-Aminobicyclo[2.2.1]hept-5-en-2-ol (13).—A suspension of 958 mg (3.33 mmol) of **12** in a tenfold excess of alcoholic aqueous potassium hydroxide was refluxed under nitrogen for 40 hr. The methanol was removed under vacuum and the residual aqueous solution was continuously extracted with ether to give 400 mg (96%) of **13**: ir ($CHCl_3$) 3570–3080, 3370, 1650, 1580, 1460, 1400, 1350, 1260, 1110, 1080, 1050, and 990 cm^{-1}; nmr ($CDCl_3$) τ 3.67 (q, 1, J_1 = 5.5 cps, J_2 = 3.4 cps, H-5), 4.2 (d, 1, J_1 = 5.5 cps, H-6), 5.93 (q, 1, J_3 = 8 cps, J_4 = 3 cps, H-2), 7.36 (m, 1, H-4), 7.53 (s, 3, NH_2, OH), 7.78 (septet, 1, *exo* H-3), 8.64 (m, 2, *syn* and *anti* H-7), and 9.07 (m, 1, *endo* H-3).

Deamination of 1-Aminobicyclo[2.2.1]hept-5-en-2-ol (13).—To an ice-cold solution of 351 mg (2.81 mmol) of amine **13** in 12 ml of 50% acetic acid was added 776 mg (11.2 mmol) of sodium nitrite in 4 ml of water. The solution was stirred for 1 hr at 0° and 1 hr at room temperature, neutralized (Na_2CO_3), and continuously extracted with ether to give 265 mg of product: ir ($CHCl_3$) 3580, 3420, 1723, 1650, 1540, 1375, 1350, 1270, 1180, 1160, 1000, and 905 cm^{-1}; nmr ($CDCl_3$) τ −0.4 (s), −0.1 (s), 3.55–4.16 (m, 2, olefinic), 5.67 (m, 1, H-2), 5.95 (s, *ca.* 2.3), 7.0 (m, *ca.* 0.43), 7.36 (m, 1, H-4), 7.88 (s, *ca.* 0.86, COOMe), 7.73 (m, 2), 8.21 (m, 1), 8.47 (m, 2), and 8.93 (m, 2). Preparative thin layer chromatography of 150 mg of this product gave 41 mg of **15** (contaminated with some **16**): ir ($CHCl_3$) 3580, 3400, 1723, 1375, and 1270 cm^{-1}; nmr ($CDCl_3$) τ 3.63 (q, 1, J_1 = 6 cps, J_2 = 3 cps, H-5), 3.83 (d, 1, J_1 = 6 cps, H-6), 5.58 (q, 1, J_3 = 8 cps, J_4 = 2.5 cps, H-2), 6.53 (s, 1, OH), 7.25 (m, 1, H-4), 7.87 (s, 3, COOMe), 7.71 (septet, 1, *exo* H-3), and 8.0–9.2 (m, 3, *syn* and *anti* H-7, *endo* H-3). Vacuum sublimation at 100° (0.5 mm) of the second fraction gave 46 mg of crystalline diol **16**: mp 173–175° dec (sealed tube); ir ($CHCl_3$) 3580, 3400, 1605, 1580, 1460, 1400, 1350, 1160, 1085, 1040, 990, and 910 cm^{-1}; nmr ($CDCl_3$) τ 3.65 (q, 1, J_1 = 5.8 cps, J_2 = 3.2 cps, H-5), 4.11 (d, 1, J_1 = 5.8 cps, H-6), 5.86 (q, 1, J_3 = 8 cps, J_4 = 3 cps, H-2), 7.0 (s, 2, OH), 7.3 (m, 1, H-4), 7.73 (septet, 1, *exo* H-3), 8.57 (m, 2, *syn* and *anti* H-7), and 8.97 (m, 1, *endo* H-3); mass spectrum (70 eV) *m/e* (rel intensity) 107 (0.4), 105 (0.4), 95 (1), 83 (8), 82 (100), 81 (9), 79 (2), 77 (3), 67 (0.9), 65 (1), 63 (0.9), 54 (5), 53 (9), 52 (2), and 51 (3).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.87; H, 8.17.

Thermal Decomposition of N-Nitroso-1-acetamidobicyclo[2.2.1]hept-5-en-2-yl Benzoate (18).—A benzene solution of acid azide **11**, obtained from 1.5 g of **9**, was refluxed under nitrogen for 36 hr to give 1.5 g of isocyanate **25**: ir (CCl_4) 2260, 1730, 1605, 1580, 1455, 1270, and 1110 cm^{-1}. An ether solution

(13) During the course of this study the aminodiol **35** and the quaternary salt **36** were also synthesized. Subsequent reactions of these compounds led to uncharacterizable tars and are therefore not discussed in detail.

35 36

(14) D. Peters, *J. Chem. Soc.*, 1042 (1961).

of **25** was added to a 100-ml, three-neck flask, the flask was flushed with nitrogen and cooled to −78°, and 2.9 ml (5.8 mmol) of 2 *M* ethereal methyllithium solution was added with vigorous stirring. After 2 hr at −78° the solution was gradually warmed to room temperature, the ether was evaporated under a stream of nitrogen, and 25 ml of CCl_4 was added. The solution was cooled to −50° and then 1.43 g (17.5 mmol) of fused sodium acetate and 7 ml of a 0.0185 *M* solution of N_2O_4 in CCl_4 were added with stirring. The solution was slowly warmed to room temperature and then heated at 70° for 16 hr. The suspended solid was filtered and the filtrate was evaporated to give 1.12 g of product. Ether extraction of an aqueous solution of the filtered solid gave 435 mg of amide **23** (26%). Preparative tlc followed by sublimation at 110° (0.5 mm) gave a white, crystalline solid: mp 156–158°; ir ($CHCl_3$) 3390, 3060, 1715, 1675, 1588, 1502, 1455, 1345, 1280, and 1115 cm^{-1}; nmr ($CDCl_3$) τ 1.85–2.6 (m, 5, aromatic), 3.08 (br, 1, NH), 3.6 (q, 1, J_1 = 6 cps, J_2 = 3.5 cps, H-5), 3.9 (d, 1, J_1 = 6 cps, H-6), 4.25 (q, 1, J_3 = 8 cps, J_4 = 2.5 cps, H-2), 7.1 (m, 1, H-4), 7.5 (m, 2, *exo* H-3, *syn* H-7), 8.0 (s, 3, COMe), 8.28 (d, 1, J_5 = 8 cps, *anti* H-7) and 8.7 (m, 1, *endo* H-3); mass spectrum (70 eV) *m/e* (rel intensity) 167 (2.5), 166 (17.3), 149 (3.1), 124 (37.8), 123 (100), 107 (5.3), 105 (33.3), 81 (66.7), 80 (12.6), 77 (22.8), 66 (1.0), 65 (1.5), 53 (3.6), 51 (6.4), and 43 (17.3), metastable peaks at *m/e* 79.5 (149–107), 56.5 (105–77), 53.4 (123–81), 51.5, 35.2 (81–53), and 33.8 (77–51).

Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.85; H, 6.27; N, 5.17. Found: C, 71.17; H, 6.42; N, 4.94.

Two major components could be isolated from the 1.12 g of product by repeated Florisil column chromatography. Vacuum sublimation at 60° (0.5 mm) of the faster moving component (*ca.* 57% of mixture) gave a white, crystalline solid, **22**: mp 74–75°; ir (CCl_4) 3060, 1730, 1605, 1585, 1455, 1330, 1315, 1285, 1275, 1115, and 1105 cm^{-1}; nmr (CCl_4) τ 1.9–2.9 (m, 5, aromatic), 3.75 (m, 2, olefinic), 4.5 (q, 1, J_1 = 8 cps, J_2 = 3 cps, H-2), 7.15 (m, 1, H-4), 7.5 (m, 1, *exo* H-3), 8.0 (m, 2, *syn* and *anti* H-7), and 8.67 (m, 1, *endo* H-3); mass spectrum (70 eV) *m/e* (rel intensity) 294 (3.0), 292 (3.0), 248 (0.4), 213 (0.2), 189 (0.3), 187 (0.3), 149 (4.5), 146 (7.7), 106 (7.7), 105 (100), 77 (28.6), 65 (6.5), and 51 (8.3), metastable peaks at *m/e* 56.5 (105–77) and 29.1 (144/146–65). Basic hydrolysis of **22** gave, after preparative tlc, 12 mg of **24**: ir (CCl_4) 3590, 3460, 3138, 3060, 1338, 1305, 1275, 1235, 1130, 1110, 1070, 1040, 995, 975, and 875 cm^{-1}; nmr ($CDCl_3$) τ 3.38 (q, 1, J_1 = 6 cps, J_2 = 3 cps, H-5), 3.67 (d, 1, J_1 = 6 cps, H-6), 5.26 (q, 1, J_3 = 8 cps, J_4 = 3 cps, H-2), 6.8 (s, 1, OH), 7.0 (m, 1, H-4), 7.48 (septet, 1, *exo* H-3), 7.86 (m, 2, *syn* and *anti* H-7), and 8.67 (m, 1, *endo* H-3); mass spectrum (70 eV) *m/e* (rel intensity) 146 (100), 144 (100), 125 (9), 123 (11), 111 (15), 97 (24), 83 (22), 81 (27), 65 (83), and 55 (40). Preparative tlc of the second major component (*ca.* 38% of mixture) gave essentially pure **21**: ir (CCl_4) 3060, 1755, 1730, 1655, 1605, 1585, 1455, 1370, 1340, 1315, 1275, 1235, 1175, and 1110 cm^{-1}; nmr (CCl_4) τ 2.0–2.9 (m, 5, aromatic), 3.78 (m, 2, olefinic), 4.2 (q, 1, J_1 = 8 cps, J_2 = 3 cps, H-2), 7.2 (m, 1, H-4), 7.53 (m, 1, *exo* H-3), 7.98 (m, 2, *syn* and *anti* H-7), 8.0 (s, 3, COOMe), and 8.7 (m, 1, *endo* H-3); mass spectrum (70 eV) *m/e* (rel intensity) 272 (0.2), 258 (0.2), 230 (0.7), 168 (1.0), 167 (8), 149 (1.0), 126 (4), 125 (44), 124 (44), 107 (4), 106 (8), 105 (100), 82 (59), 81 (7), 77 (52), 67 (4), 65 (3), and 43 (48). Basic hydrolysis of **21** followed by vacuum sublimation of the product at 100° (0.5 mm) gave 20 mg of diol **16**.

1-Carboxybicyclo[2.2.1]hept-5-en-2-ol (29).—A solution of 3.91 g (15.2 mmol) of **9** in 60.8 ml of 0.5 *N* sodium hydroxide was stirred at room temperature under nitrogen for 12 hr. The solution was acidified (1.0 *N* HCl) and extracted with ether, and the ether was dried ($MgSO_4$) and evaporated to give 4.19 g of a mixture of benzoic acid and **29**. This mixture was digested in 75 ml of hexane and cooled, and the suspended solid was filtered to give, after recrystallization from acetone, 1.45 g (62%) of crystalline **29**: mp 162–164° dec; ir (KBr) 3600–2500, 3320, 1700, 1340, 1313, 1270, 1258, 1068, 1055, 930, 820, and 705 cm^{-1}; nmr (CD_3COCD_3) τ 3.6 (q, 1, J_1 = 6 cps, J_2 = 3 cps, H-5), 3.84 (d, 1, J_1 = 6 cps, J_2 = 3 cps, H-5), 3.84 (d, 1, J_1 = 6 cps, H-6), 1.8–4.63 (br, 2, COOH, OH), 5.2 (q, 1, J_3 = 8 cps, J_4 = 3 cps, H-2), 7.15 (m, 1, H-4), 7.73 (septet, 1, *exo* H-3), 8.37 (m, 2, *syn* and *anti* H-7), and 9.0 (m, 1, *endo* H-3).

Anal. Calcd for $C_8H_{10}O_3$: C, 62.34; H, 6.49. Found: C, 62.58; H, 6.69.

1-Carboxybicyclo[2.2.1]hept-5-en-2-one (30).—A solution of 700 mg (4.53 mmol) of **29** in 5 ml of anhydrous pyridine was added to a stirred solution of 7 g (27.2 mmol) of Collins reagent[15] in 95 ml of pyridine. After 12 hr at room temperature the suspension was poured over ice, neutralized (concentrated HCl) with external cooling, and extracted repeatedly with ether. The ether was dried ($MgSO_4$) and evaporated and the residue was vacuum sublimed twice at 70° (0.5 mm) to give 457 mg (66%) of crystalline **30**: mp 119–121°; ir ($CHCl_3$) 3600–2500, 1790 (sh), 1770, 1760, 1720, 1310, 1100, 990, and 970 cm^{-1}; nmr ($CDCl_3$) τ −1.5 (s, 1, COOH), 3.3 (q, 1, J_1 = 6 cps, J_2 = 3 cps, H-5), 3.6 (d, 1, J_1 = 6 cps, H-6), 6.74 (m, 1, H-4), and 7.55–7.87 (m, 4, *syn* and *anti* H-7, *exo* and *endo* H-3); mass spectrum (70 eV) *m/e* (rel intensity) 153 (2.3), 152 (2.5), 135 (0.4), 124 (8.4), 110 (100), 105 (1.2), 93 (9.6), 82 (55.8), 79 (15.4), 77 (15.4), 66 (82.8), 65 (21.2), 51 (11.5), and 45 (6), metastable peaks at *m/e* 101.5, 64.5 (135–93), 61.5 (110–82), and 39.6 (110–66).

Anal. Calcd for $C_8H_8O_3$: C, 63.16; H, 5.26. Found: C, 63.13; H, 5.10.

Attempted Preparation of 1-Aminobicyclo[2.2.1]hept-5-en-2-one (27).—A suspension of the sodium salt of the keto acid **30**, when treated with 1 equiv of oxalyl chloride as described above, gave an acid chloride: ir (CCl_4) 1818, 1789, 1757, 1480, 1232, 1175, 1085, 1036, and 870 cm^{-1}. The acid chloride was dissolved in acetone, cooled to 0°, and treated with 1 equiv of sodium azide to give an acid azide: ir 2130, 1770, 1715, 1298, 1256, 1175, and 945 cm^{-1}. The crude carbamate obtained by methanolysis of the azide was chromatographed through Florisil to give 307 mg (49%) of crystalline keto carbamate **31**: mp 80–81°; ir ($CHCl_3$) 3403, 1755, 1731, 1605, 1580, 1504, 1455, 1260, 1085, and 1000 cm^{-1}; nmr ($CDCl_3$) 3.45 (q, 1, J_1 = 5.5 cps, J_2 = 3.2 cps, H-5), 4.0 (q, 1, J_1 = 5.5 cps, J_3 = 1 cps, H-6), 4.18 (s, 1, NH), 6.33 (s, 3, COOMe), 6.86 (m, 1, H-4), 7.1 (m, 1, *exo* H-3), and 7.92 (m, 3, *syn* and *anti* H-7, *endo* H-3); mass spectrum (70 eV) *m/e* (rel intensity) 181 (0.3), 153 (100), 150 (2.4), 139 (29.2), 121 (12.1), 120 (19.1), 108 (5), 107 (32.1), 94 (23.1), 80 (13.6), 79 (12.1), 78 (29.2), 67 (15.5), 66 (8.5), 65 (5.6), 59 (14.6), and 53 (19.1), metastable peaks at *m/e* 104.3, 94.8 (153–120), 82.7 (139–107), and 39.8 (107–65).

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.76; H, 6.08; N, 7.73. Found: C, 60.05; H, 6.17; N, 7.84.

A solution of 265 mg (1.46 mmol) of **31** and 818 mg (14.6 mmol) of potassium hydroxide in equal volumes of methanol and water (5 ml) was refluxed for 12 hr under nitrogen. The methanol was evaporated and the residue was continuously extracted with ether to give 112 mg of **32** (73%). Vacuum sublimation at 80° (0.5 mm) gave 70 mg of a waxy solid: ir (CCl_4) 3060, 1678, 1430, 1328, 1240, 1125, 1105, 1045, and 900 cm^{-1}; nmr (CCl_4) 3.66 (q, 2, J_1 = 5.5 cps, J_2 = 3 cps, H-5, H-5′), 4.36 (d, 2, J_1 = 5.5 cps, H-6, H-6′), 7.01 (m, 2, H-4, H-4′), and 7.43–9.26 (m, 8); mass spectrum (70 eV) *m/e* (rel intensity) 210 (27), 209 (27), 195 (14), 183 (3.6), 168 (6.7), 145 (6.1), 132 (18), 105 (100), 91 (14), 78 (12), 77 (14), and 65 (60); high resolution (measured *m/e*, elemental composition, calculated mass) 210.1160, $C_{14}H_{14}N_2$, 210.1160; 145.0765, $C_9H_9N_2$, 145.0766; 105.0578, C_7H_7N, 105.0578; 91.0547, C_7H_7, 91.0545; 78.0469, C_6H_6, 78.0462; and 65.0391, C_5H_5, 65.0383.

Registry No.—**8**, 23939-72-2; **9**, 23972-87-4; **12**, 23939-73-3; **13**, 23939-74-4; **15**, 23972-88-5; **16**, 23939-75-5; **21**, 23972-89-6; **22**, 23939-76-6; **23**, 23939-77-7; **24**, 23939-78-8; **29**, 23939-79-9; **30**, 23936-82-5; **31**, 23936-83-6; **32**, 23936-84-7.

Acknowledgment.—This work was supported in part by Grant GM 14662 from the National Institutes of Health.

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