The remaining material was recrystallized from ether–benzene to yield succinic acid. The benzene-soluble fraction, upon removal of the benzene and recrystallization from petroleum ether, afforded glutaric acid. These acids gave no melting point depressions on admixture with authentic samples.

Vinyl Allyl Ketone (1,5-Hexadien-3-one) (1).—The lower boiling fraction of the thermolysis product mixture was isolated by fractional distillation under reduced pressure. The material obtained appeared homogeneous on vpc using both Triton X-305 and silicone grease columns: bp 125–126° (776 mm); d^{23}_4 0.8717; $n^{20}D$ 1.4460. Previously reported[10] literature values are bp 30–31° (8 mm), d^{20}_4 0.8907, $n^{20}D$ 1.4725. Spectral data follow: Uv max 337 mμ (ε 33), 213 (6500); ir bands at (cm^{-1}) 3080 (w), 3030 (w), 2960 (w), 2910 (w) 1700 (sh), 1680 (s), 1640 (m), 1620 (s), 1405 (s), 1330 (m), 1190 (m), 1075 (m) 995 (s), 965 (m), and 915 (s). The nmr spectrum is discussed above.

Anal. Calcd for C_6H_8O: C, 74.96; H, 8.39. Found: C, 74.65; H, 8.56.

Hydrogenation of 1 with Pd–C led to the absorption of 102% of the amount of hydrogen required to saturate two double bonds and afforded 3-hexanone, shown to be identical with an authentic sample by comparison of ir spectra, vpc retention times, and 2,4-dinitrophenylhydrazone derivatives.

Registry No.—**1**, 6857-93-8; **2**, 22922-45-8; **3**, 22922-46-9.

The Synthesis of Bicyclo[5.4.0]undecanones *via* Olefin Cyclization

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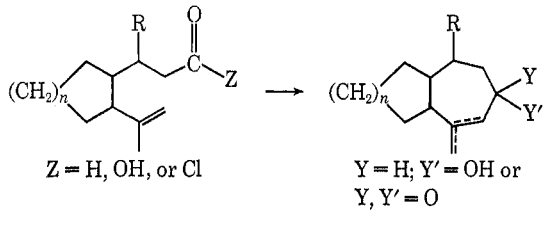
Received July 25, 1969

During the course of a project aimed at the development of methods for the stereoselective synthesis of fused-ring cycloheptane derivatives, we examined a number of cyclization reactions of the type illustrated in Scheme I.[3] Our findings to date indicate that such

SCHEME I



olefin cyclizations[4] can be usefully employed for the construction of cycloheptane rings.[5] This report summarizes our synthetic endeavors along these lines leading to bicyclo[5.4.0]undecanones.

CHART I

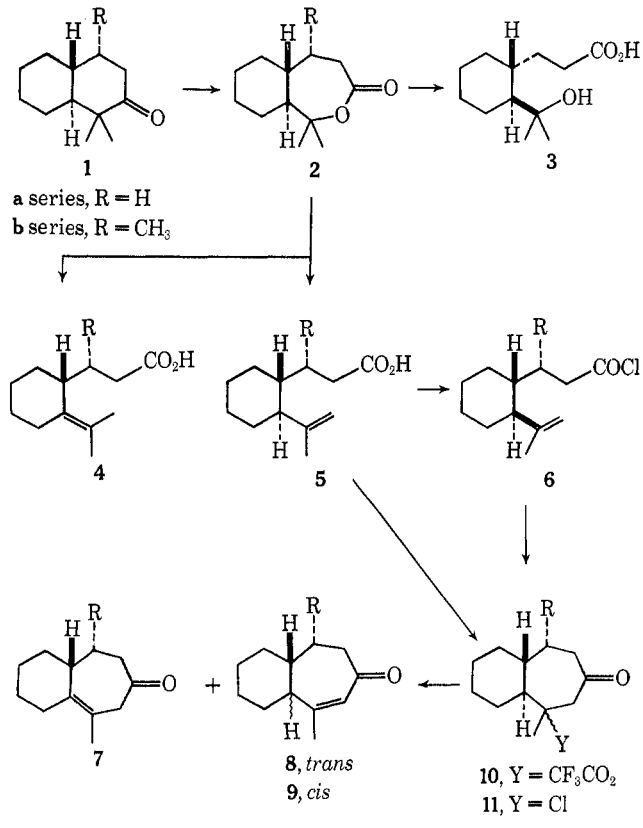
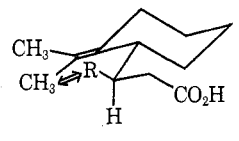
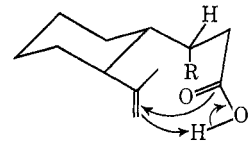


Chart I outlines our first approach starting with the known decalones **1a** and **1b**[6] which yielded the lactones **2a** and **2b**, respectively, upon treatment with *m*-chloroperoxybenzoic acid. Pyrolysis of these lactones gave the expected unsaturated acids **5a** and **5b** as the major products.[7] In the former case, a small amount of the isopropylidene isomer **4a** was also formed. The relative percentage of this isomer increased with reaction time at the expense of the isopropenyl isomer **5a** (see the Experimental Section) until an apparent equilibrium state of roughly 85% **5a** and 15% **4a** was reached. In the case of lactone **2b**, none of the isopropylidene acid **4b** could be detected, even after relatively prolonged reaction times. This trend may reflect increased steric strain[8] in the isopropylidene acid **4b** *vs.* **4a**, or may simply stem from an increased barrier to relactonization on the part of the acid **5b** *vs.* **5a** (see below).



4a, R = H
b, R = CH_3



5a, R = H
b, R = CH_3

The unsaturated acid **5a** cyclized upon treatment with trifluoroacetic anhydride affording the cycloheptanone derivative **10a** (presumably a mixture of

(1) Predoctoral Fellow of the National Institutes of Health, Institute of General Medical Sciences, 1966–1967.

(2) National Science Foundation Undergraduate Research Participant, 1968–1969.

(3) An application of this scheme to bicyclo[5.3.0]decanones led to a structure revision of the vetivane class of sesquiterpenes. For a preliminary report, see J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Amer. Chem. Soc.*, **89**, 2748 (1967); J. A. Marshall and N. H. Andersen, *Tetrahedron Lett.*, 1219 (1967).

(4) For a recent review, see W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968).

(5) Prior to this work, results obtained with simple acyclic systems appeared unpromising. *Cf.* R. J. Ferrier and J. M. Tedder, *J. Chem. Soc.*, 1435 (1957). One report involving cyclization of a styrenyl nitrile leading to a benzocycloheptenone looked encouraging: R. Conley and R. Lange, *J. Org. Chem.*, **28**, 278, 210 (1963).

(6) J. A. Marshall and N. H. Andersen, *ibid.*, **31**, 667 (1966).

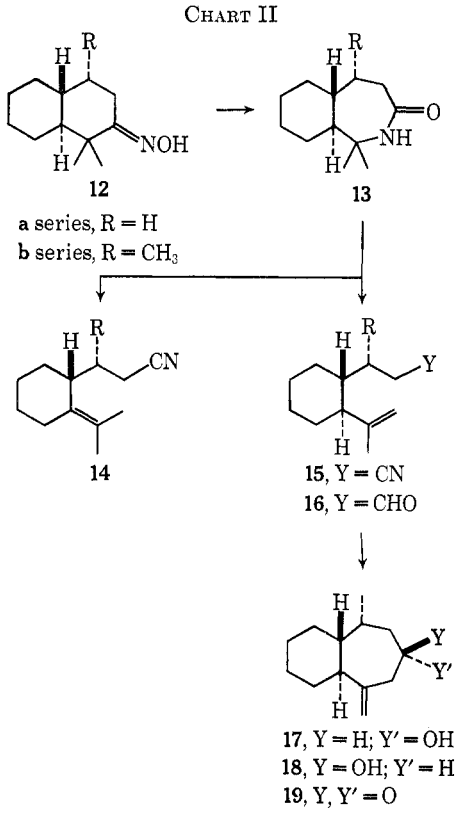
(7) *Cf.* D. Rosenthal, A. O. Niedermeyer, and J. Fried, *ibid.*, **30**, 510 (1965).

(8) *Cf.* F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

stereoisomers). Basic treatment effected the expected elimination reaction and gave the conjugated ketone **8a** as the major product, along with lesser amounts of the presumed *cis* isomer **9a**, and what appeared to be the β,γ-unsaturated ketone **7a**. The methylated unsaturated acid **5b** likewise yielded the related unsaturated ketone **8b**, but in this case the *cis* fused isomer **9b** could not be detected by gas chromatography nor was it revealed by the nmr spectrum. Nonetheless, its presence was suggested by our inability to prepare sharply melting derivatives of enone **8b**. Analogous results were obtained upon cyclization of the acid chlorides **6a** and **6b** in the presence of stannic chloride. In this case, the subsequent elimination reaction leading to unsaturated ketones **7a**, **8a**, and **9a** took place on heating as well as *via* basic treatment. Attempts to effect this elimination reaction under milder conditions, so as to prevent the isomerization to enones **7a** and **9a**, proved unsuccessful.

The above routes to enones **8a** and **8b** suffer from the fact that the cyclization reactions lead to β-substituted cycloheptanones which isomerize during removal of the β substituent. In the hope of circumventing this difficulty, we explored the sequence outlined in Chart II, wherein the unsaturated cycloheptanols **17** and **18**,

CHART II



and possibly double bond isomers thereof, would be obtained as the initial cyclization products.

Treatment of the oxime **12a** with *p*-toluenesulfonyl chloride at room temperature yielded a mixture of the lactam **13a** (36%) and the nitrile **15a** (16%). When this reaction was conducted in refluxing pyridine,[9] only the nitrile **15a**, contaminated with a trace of the isopropylidene isomer, was produced. Oxime **12b** behaved similarly. In this case, the nitrile **15b** was also prepared by treating the lactam **13b** with *p*-toluenesulfonyl chloride in pyridine at reflux.[9]

Reduction of nitriles **15a** and **15b** with lithium triethoxyaluminohydride[10] or, more effectively, with diisobutylaluminum hydride[11] followed by hydrolysis of the intermediate imines, afforded the aldehydes **16a** and **16b**. These aldehydes smoothly cyclized upon treatment with stannic chloride in benzene[12] to give the cycloheptanols **17a** and **17b**, respectively. In each case, only a small amount of the epimers **18a** and **18b** could be detected. Analysis of these mixtures by gas chromatography was complicated by the tendency of the homoallylic alcohols **17** (and/or **18**) to revert back to the corresponding unsaturated aldehydes **16** in the injection port.[13] However, we estimate that no more than 10% of the epimers **18** could have been formed in the cyclization reactions. Oxidation of the alcohol mixtures **17** and **18** with Jones reagent[14] afforded the expected ketones **19a** and **19b**, respectively. Basic treatment then gave the previously obtained enones (**7a**, **8a**, and **9a** from **19a**, and **8b** and **9b** from **19b**).

The efficient conversion of aldehydes **16a** and **16b** to the corresponding cycloheptanols **17a** and **17b** provides two further examples of the remarkable stereochemical control available to such olefin cyclizations.[15] The stereochemical assignments of these alcohols rest solely on physical data and spectral evidence,[16] and are considered tentative. Mechanistic arguments supporting these assignments in related bicyclo[5.3.0]decane systems have previously been advanced.[3,15] Finally, it should be noted that prolonged exposure of the unsaturated alcohols **17b** and **18b** to the cyclization conditions resulted in extensive isomerization of the exocyclic double bond. We therefore surmise that these alcohols represent the kinetic products of the cyclization reaction.

To summarize, olefin cyclizations of the type shown in Scheme I represent useful routes to the corresponding cycloheptane derivatives. In the case of carboxylic precursors, the cyclizations proceed in high yield, but the overall sequence leading to the unsaturated ketones **8a** and **8b** suffers owing to the tendency of these ketones to isomerize under the conditions of their formation. The aldehydes likewise cyclize in high yield to the cycloheptane derivatives and in these cases a highly selective elimination leading to the exocyclic olefins takes place as well.[3,15] Oxidation to the related ketones presents no problem, but once again isomerization occurs during base catalyzed conjugation of the double bond.

(9) *Cf.* J. Klinot and A. Vystrcil, *Collect. Czech. Chem. Commun.*, **27**, 377 (1962).

(10) H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, **86**, 1085 (1964).

(11) *Cf.* L. I. Zakharkin and I. M. Khorlina, *Dokl. Akad. Nauk SSR*, **116**, 422 (1957); *Chem. Abstr.*, **52**, 8040*f* (1958).

(12) *Cf.* D. J. Goldsmith and C. J. Cheer, *J. Org. Chem.*, **30**, 2264 (1965).

(13) *Cf.* R. T. Arnold and G. Smolinsky, *J. Amer. Chem. Soc.*, **81**, 6443 (1959).

(14) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(15) For previous examples in the bicyclo[5.3.0]decane system, see J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Org. Chem.*, **35**, 186 (1970), and ref 3.

(16) An analysis of the pertinent data and a speculative discussion of these stereochemical points can be found in the Ph.D. dissertation of Niels H. Andersen, Northwestern University, Jan 1967, pp 129–134 and 136–142.

Experimental Section[17]

2,2-Dimethyl-*trans*-3-oxabicyclo[5.4.0]undecan-4-one (2a).—A solution of 12.7 g of decalone **1a**[6] and 30 g of 85% *m*-chloroperoxybenzoic acid in 320 ml of 1:1 chloroform–methylene chloride was allowed to stand for 30 hr in the dark at room temperature. Ether was added and the solution was washed with 5% aqueous sodium hydroxide and saturated brine. After drying over anhydrous magnesium sulfate, the solution was concentrated under reduced pressure affording 13.1 g of oily lactone **2a**: λ_{max}^{film} 5.81 (CO), 8.16, 8.33, 9.01, 9.13, and 10.16 μ; $\delta_{TMS}^{CCl_4}$ 1.41 and 1.43 ppm (*gem*-dimethyl).

Attempted purification by distillation (90° at 0.1 mm) resulted in partial conversion of lactone **2a** to the unsaturated acids **4a** and **5a**. This lactone afforded the hydroxy acid **3**, mp 120.5–122°, upon brief treatment with methanolic potassium hydroxide and acidification.

2,2,6*t*-Trimethyl-1*t*-H,7*r*-H-3-oxabicyclo[5.4.0]undecan-4-one (2b).—The above procedure was followed using 4.43 g of decalone **1b**[6] and afforded 4.40 g (92%) of lactone **2b**, mp 76–84°. Recrystallization from hexane gave fine colorless needles, mp 88.5–89.5°; λ_{max}^{film} 5.85 (CO), 7.19, 7.41, 7.79, 7.89, 8.38, 8.72, 9.09, 9.90, 10.15, 12.75, and 14.06 μ; $\delta_{TMS}^{CCl_4}$ 1.42 (*gem*-dimethyl) and 0.97 ppm (C-6 CH_3, doublet, J = 7 Hz). The analytical sample, mp 88–89°, was obtained by sublimation (50° at 0.5 mm).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.23; H, 10.55. Found: C, 74.4; H, 10.4.

3-(*trans*-2-Isopropenylcyclohexyl)propanoic Acid (5a).—A 10.8-g portion of lactone **2a** was added to a flask preheated to 225° and fitted with magnetic stirring.[17a] After a contact period of 1.5 min, the material was cooled and dissolved in ether. The acidic material was extracted with 5% aqueous sodium hydroxide and isolated by acidification with cold dilute sulfuric acid under a layer of ether, followed by thorough extraction with ether.[17b] Distillation afforded 7.8 g (72%) of acid: bp 110° (0.2 mm); mp 20–40°; estimated as 85% of the isopropenyl acid **5a** and 15% of the isopropylidene acid **4a** from the integrated nmr spectrum; $\delta_{TMS}^{CCl_4}$ 12.32 (CO_2H, 1 H), 4.79 ($C{=}CH_2$, 1.7 H), and 1.68 ppm (vinyl CH_3).

The methyl ester, obtained by treating a small sample of the above acid mixture with ethereal diazomethane, showed two peaks in the ratio 87:11 upon gas chromatography.

A crystalline sample of acid **5a**, mp 50–51.5°, was obtained in poor yield upon recrystallization of the crude material from pentane. This substance was characterized as its cyclohexylammonium salt, mp 115–116.5°, after recrystallization from ethyl acetate; λ_{max}^{KBr} 2.9, 3.2–4.1 ($-NH_3^+$), 6.09, 6.11, 6.64 (CO_2^-), 7.16, 9.51, and 11.31 μ.

Anal. Calcd for $C_{18}H_{33}NO_2$: C, 73.17; H, 11.26; N, 4.74. Found: C, 73.0; H, 11.5; N, 4.7.

The variation in the relative amounts of isopropenyl and isopropylidene acids **5a** and **4a** formed at 225° from lactone **2a** at various contact times is tabulated in Table I. The yield of acidic material is indicated as % conversion. The ratio of products was determined *via* gas chromatography of the methyl esters.

TABLE I

Contact time, min	% conversion	% 5a	% 4a
0.5	34	92	7
1.5	80	87	12
6.0	87	86	13
20	88	84	15
30	90	83	16

After 30 min at 225°, a sample of acid **5a** was converted to an 88:11 mixture of **5a** and **4a**. Similar treatment of acid **4a** yielded a 30:60 mixture of **5a** and **4a** after 30 min.

syn-**3-(*trans*-2-Isopropenylcyclohexyl)butanoic Acid (5b).**—A sealed evacuated tube containing 1.06 g of lactone **2b** was plunged into an oil bath preheated to 225°. After 10 min, the acidic product was isolated as described above affording 0.96 g (91%) of acid **5b**, mp 90–92°, after sublimation at 80° (0.4 mm): λ_{max}^{KBr} 2.8–4.1 (OH), 5.87 (CO), 3.25, 6.09, 11.34 ($C{=}CH_2$), 8.03, 8.25, 8.36, and 10.5–10.6 μ; $\delta_{TMS}^{CCl_4}$ 12.09 (OH), 4.72 ($C{=}CH_2$), 1.64 (vinyl CH_3), and 0.99 ppm (CH_3, d, J = 7 Hz). The analytical sample, mp 92–92.5°, was obtained after one recrystallization from heptane.

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.23; H, 10.55. Found: C, 74.5; H, 10.4.

Cyclization of Acid 5a.—A solution of 3.80 g of acid **5a** in 50 ml of 1,2-dichloroethane was added with stirring over 5 hr at 0° to a solution of 25 ml of trifluoroacetic anhydride in 40 ml of 1,2-dichloroethane.[17a] After 6 hr at room temperature, the solution was poured onto a slurry of 45 g of potassium carbonate and 150 g of ice and the product was isolated with ether.[17b]

The resulting crude ketone **10a** was dissolved in 60 ml of 10% methanolic potassium hydroxide.[17a] After 3 hr, the product was isolated with ether [17b] and distilled, affording 2.84 g (82%) of material, bp 100° (bath temperature) at 0.2 mm, containing about 42% of the conjugated ketone **8a** which was isolated *via* preparative gas chromatography: λ_{max}^{EtOH} 243 mμ (ϵ 10,000); λ_{max}^{film} 3.32 (vinyl H), 6.01 (CO), 6.13 (C=C), 6.90, 7.25, 7.90, 8.16, 10.42, 11.15, 11.84, and 13.4 μ; $\delta_{TMS}^{CCl_4}$ 5.71 (H-3) and 1.87 ppm (vinyl CH_3, d, J = 0.8 Hz).

A sample of ketone **8a** was converted to the semicarbazone derivative, mp 188.5–190° after recrystallization from isopropyl alcohol.

Anal.[17c] Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 8.99; N, 17.86. Found: C, 66.4; H, 8.95; N, 18.0.

A sample of the minor enone **9a** was also secured *via* preparative gas chromatography; λ_{max}^{film} 6.00 (CO), 6.14 (C=C), 7.25, 7.76, 8.16, 9.36, 10.29, 10.45, 10.53, 10.78, 11.16, and 11.5–11.9 μ.

The semicarbazone derivative exhibited mp 173–178°.

Anal. Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 8.99; N, 17.86. Found: C, 65.8; H, 9.05; N, 17.5.

A more suitable analysis could not be obtained for lack of material. Under basic equilibrating conditions these ketones afforded a 1:4:9 mixture of enones **7a**, **9a**, and **8a**.

Cyclization of Acid 5b.—A 423-mg sample of acid **5b** was added with stirring to 45 ml of trifluoroacetic anhydride.[17a] After 7 hr, the mixture was poured over potassium carbonate and ice, and the product was isolated with ether.[17b] A 327-mg portion of this product was treated with methanolic potassium hydroxide, as described above, affording 222 mg (70%) of conjugated ketones (presumably **8b** and **9b**), bp 70° (bath temperature) at 0.07 mm, which showed a single peak on gas chromatography: λ_{max}^{EtOH} 246 mμ (ϵ 8,700); λ_{max}^{film} 6.01 (CO), 6.16 (C=C); $\delta_{TMS}^{CCl_4}$ 5.75 (H-3), 1.88 (vinyl CH_3, d, J = 1.1 Hz), and 0.96 ppm (CH_3, d, J = 6 Hz).

The 2,4-DNP derivative, mp 138–147°, was obtained in 74% yield. After several recrystallizations from ethanol, a sample with mp 148–155° was obtained. This material is presumably a mixture of the epimers derived from **8b** and **9b**.

Anal. Calcd for $C_{19}H_{24}N_4O_4$: C, 61.27; H, 6.50; N, 15.05. Found: C, 61.4; H, 6.4; N, 15.1.

Cyclization of Acid Chloride 6a.—A 647-mg portion of acid **5a** (~85% pure) in 10 ml of methanol was treated with 33 ml of 0.1 *N* sodium hydroxide. The resulting solution was evaporated to dryness under reduced pressure and residual water was removed by azeotropic distillation with benzene. The residual sodium salt was suspended in 40 ml of benzene and treated with 1.8 ml of oxalyl chloride.[17a] After 1 hr, the mixture was filtered and concentrated under reduced pressure affording the acid chloride **6a**.

A 552-mg sample of the acid chloride in 200 ml of 1,2-dichloroethane was cooled to 0° and 0.47 ml of stannic chloride was added with stirring.[17a] After 15 min, the crude chloro ketone **11a** was isolated with ether;[17b] λ_{max}^{film} 5.86 μ (CO); $\delta_{TMS}^{CCl_4}$ 1.12, 1.45, and 1.64 ppm [$-C(Cl)CH_3$]. Distillation at 100° (0.5 mm) effected the dehydrochlorination of this chloro ketone and afforded 453 mg (98%) of ketonic material, shown by gas chromatography to contain five components in the ratio 15:14:11:38:13 in order of increasing retention time. The three longer retention time peaks were collected and shown to be ketones **7a**, **8a**, and **9a**, on the basis of their spectral properties: **7a**, λ_{max}^{film} 5.85 (CO), 6.90, 7.95, 8.20, and 10.37μ; $\delta_{TMS}^{CCl_4}$ 3.15 ($C{=}CCH_2C{=}O$, AB quartet, J = 14 Hz, $\Delta\nu$ = 31 Hz) and 1.76 ppm (vinyl CH_3). **9a**, λ_{max}^{film} 6.00 (C=O), 6.14 (C=C), 7.25, 7.76, 8.16, 9.26, 10.29, 10.45, 10.53,

(17) (a) The apparatus described by W. S. Johnson and W. P. Schneider ("Organic Syntheses," Coll. Vol. 4, John Wiley and Sons, Inc., New York, N. Y., 1963, p 132) was used to maintain a nitrogen atmosphere. (b) The isolation procedure consisted of thorough extraction with the specified solvent, washing the combined extracts with saturated brine solution, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts under reduced pressure on a rotary evaporator; (c) Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

10.78, 11.16, and 11.5–11.9 μ; λ_{max}^{EtOH} 243 μ (ϵ 10,000); $\delta_{TMS}^{CCl_4}$ 5.71 (vinyl H) and 1.87 ppm (vinyl CH_3 d, J = 1 Hz). The spectral properties of ketone **8a** were identical with those of the material obtained in the above described experiment.

Cyclization of Acid Chloride 6b.—An 895-mg sample of acid chloride **6b**, prepared as described above for **6a**, in 40 ml of 1,2-dichloroethane, was cooled in an ice bath while 0.45 ml of stannic chloride was added with stirring.[17a] One-half of the mixture was poured onto ice and isolated with ether[17b] after 15 min affording the crude chloro ketone **11b** (λ_{max}^{film} 5.89 μ), which yielded 294 mg of a mixture of unsaturated ketones **8g** and (presumably) **9b** upon treatment with methanolic potassium hydroxide.[17a]

The remainder of the reaction mixture was poured onto ice after 13 hr and the product was isolated with ether,[17b] affording 343 mg of unsaturated ketones **8b** and **9b**, bp 90° (bath temperature) at 0.25 mm. This mixture was purified by preparative gas chromatography, affording material which was identical with that secured *via* cyclization of the acid **5b**. The 2,4-dinitrophenylhydrazone derivative, mp 147–160°, showed no melting point depression upon admixture with the sample prepared in that experiment.

Fragmentation of Oxime 12a.—A mixture of 27.8 g of oxime **12a** (mp 128–130°), 70 g of *p*-TsCl, and 700 ml of pyridine was heated at reflux for 2.5 hr.[17a] The mixture was cooled and diluted with aqueous NaOH, and the product was isolated with hexane[17b] and distilled affording 16.8 g (66%) of nitrile **15a**, bp 96–98° (1.2 mm): $n^{23}D$ 1.4795; λ_{max}^{film} 3.24 (vinyl CH), 4.45 (CN), 6.08 (C=C), 7.25, and 11.23 μ. A center cut was redistilled for analysis, $n^{27}D$ 1.4767.

Anal. Calcd for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.0; H, 11.1; N, 7.7.

A small amount (*ca.* 2%) of another isomer, presumably **14a**, could be detected by gas chromatography.

When the fragmentation of oxime **12a** was carried out as above, but at room temperature for 18 hr, nitrile **15a** was secured in 16% yield and lactam **13a**, mp 139–140°, was obtained in 36% yield.

Fragmentation of Oxime 12b.—The procedure outlined above was applied to 5.33 g of oxime **12b** (mp 185–187°), affording 3.62 g (74%) of nitrile **15b**, bp 90° (0.2 mm): λ_{max}^{film} 3.26 (vinyl CH), 4.46 (CN), 6.08 (C=C), 7.25, and 11.22 μ.

Anal. Calcd for $C_{13}H_{21}N$: C, 81.61; H, 11.06; N, 7.32. Found: C, 81.8; H, 11.05; N, 7.6.

When the fragmentation of oxime **12b** was carried out as above, but at room temperature for 28 hr, the nitrile **15b** was secured in 36% yield and the lactam **13b**, mp 175–180°, was obtained in 54% yield. The analytical sample had mp 178–180° after recrystallization from methanol: λ_{max}^{KBr} 3.12, 3.24 (NH), 6.03 (CO), 8.03, 8.37, 8.89, 9.07, 12.2, 12.5, 12.8, 13.2, and 14.1 μ; $\delta_{TMS}^{CHCl_3}$ 1.32, 1.25 (CH_3's), and 0.99 ppm (CH_3, d, J = 7 Hz).

Anal. Calcd for $C_{13}H_{23}NO$: C, 74.59; H, 11.07; N, 6.69. Found: C, 74.4; H, 11.05; N, 7.0.

Fragmentation of Lactam 13b.—The above described procedure was employed on 2.0 g of lactam **13b**, affording 1.12 g (61%) of nitrile **15b** containing about 1% of the presumed isopropylidene isomer **14** according to the gas chromatogram.

Conversion of Nitrile 15a to the Bicyclic Alcohols 17a and 18a.—A 265-mg sample of nitrile **15a** was added at −30° to a mixture derived from 77 mg of lithium aluminum hydride, 0.23 ml of ethyl acetate, and 6 ml of ether. After 25 min at −30° and 15 min at 0°, 1.9 ml of 5 *N* aqueous sulfuric acid was added and the product was isolated with ether,[17b] affording the crude aldehyde **16a**.

This mixture was dissolved in 30 ml of anhydrous benzene and treated with 50 μl of stannic chloride.[17a] After 10 min at room temperature, the product was isolated by extraction[17b] and distilled affording 98 mg (47%) of alcohols **17a** and **18a**: λ_{max}^{film} 2.93 (OH), 3.26 (vinyl H's, J = 2 Hz, $\Delta\nu$ = 8 Hz), 3.89 (H-4 m), and 2.38 ppm (H-3's; J_{gem} = −13 Hz, J_{vic} = 3.6 and 6.8 Hz, $\Delta\nu$ = 20.7 Hz).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.7; H, 11.3.

The gas chromatogram indicated three components: aldehyde **16a** (11.5%), alcohol **17a** (82.7%), and alcohol **18a** (5.8%), Aldehyde **16a** must arise *via* thermal rearrangement during the course of this analysis since the infrared spectrum showed no carbonyl bands in the initial alcohol mixture.

A sample of alcohol **17a** underwent *ca.* 10% conversion to aldehyde **16a** upon heating at 260° in a sealed ampoule for 4 min.

Reduction of Nitrile 15b.—A solution of 2.32 g of nitrile **15b** in 120 ml of hexane was cooled to −70° and 24.6 ml of 1 *M* diisobutylaluminum hydride in hexane was added. The mixture was stirred at −70° for 30 min and at ambient temperature for 5 hr, whereupon 2 ml of ethyl formate was added and stirring was continued for 1 hr. The mixture was poured into saturated ammonium chloride solution and, after 20 min, aqueous sulfuric acid was added and the product was isolated with ether,[17b] affording 2.31 g (96%) of aldehyde **16b**: λ_{max}^{film} 3.26 (vinyl CH), 3.68 (aldehyde CH), 5.79 (CO), 6.08 (C=C), 7.25, and 11.23 μ.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.2; H, 11.2.

Cyclization of Aldehyde 16b.—A solution of 141 mg of **16b** in 45 ml of benzene was stirred at room temperature for 10 min with 25 μl of stannic chloride.[17a] Aqueous ammonium chloride was added and the product was isolated with benzene,[17b] affording 135 mg (96%) of alcohols **17b** and **18b**, bp 75° (0.05 mm): λ_{max}^{film} 2.96 (OH), 3.26 (vinyl CH), 6.08 (C=C), 8.45, 8.82, 9.20, 9.68, 9.84, 11.2–11.3, and 11.71 μ; $\delta_{TMS}^{CCl_4}$ 4.89 (vinyl H's, complex), 3.89 (carbinyl H, $J_{4,3}$ = 5.0 and 7.0 Hz, $J_{4,5} + J_{4,5'}$ = 10.4), 2.97 (OH), 2.39 (allylic H's J_{gem} = −13.0; J_{vic} = 5.0 and 7.0; $\Delta\nu$ = 28.7 Hz), and 0.89 ppm (CH_3 doublet, J = 6 Hz).[18]

The gas chromatogram indicated the presence of about 3% of the presumed epimeric alcohol **18b** and a variable amount of the aldehyde **16b** resulting from thermal rearrangement in the injection port.

Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.3; H, 11.1.

The *p*-bromophenylurethane crystallized as needles, mp 130–131°, from hexane.

Anal. Calcd for $C_{20}H_{26}NO_2Br$: C, 61.20; H, 6.69; N, 3.57. Found: C, 61.3; H, 6.7; N, 3.7.

Conversion of Alcohols 17a and 18a to Ketones 8a and 9a.—A solution of 61 mg of alcohols **17a** and **18a** (over 90% **17a**) in 3 ml of acetone was oxidized with 0.016 ml of Jones Reagent[14] affording 56 mg (93%) of ketone **19a**: λ_{max}^{film} 3.25 (vinyl CH), 5.86 (CO), 6.08 (C=C), 8.25, 8.48, 10.48, 11.01, 11.14, 11.29, 11.71, and 13.34 μ; $\delta_{TMS}^{CCl_4}$ 5.03 (vinyl H's, m) and 3.11 ppm (H-3's, J_{gem} = 15.4 Hz, $\Delta\nu$ = 4.6 Hz).

Treatment of the above ketone with 10% methanolic KOH at room temperature for 2 hr afforded a 4:1 mixture of ketones **8a** and **9a**, and a small amount of enone **7a**, identified by spectral comparison with material prepared as outlined above.

Conversion of Alcohols 17b and 18b to Ketones 8b and 9b.—The above procedure was employed on 18 mg of alcohols **17b** and **18b** (over 90% **17b**) affording the ketone **19b**: λ_{max}^{film} 3.25 (vinyl CH), 5.85 (CO), 6.08 (C=C), 8.26, 8.5–8.6, 8.77, 9.51, and 11.2–11.3 μ.

Basic equilibration then gave the enones **8b** and **9b**, identified by spectral comparison with the material prepared as outlined above.

Registry No.—**2a**, 22950-92-1; **2b**, 22950-93-2; **3**, 22950-94-3; **5a**, 22950-95-4; **5a** cyclohexylammonium salt, 22950-96-5; **5b**, 22950-97-6; **8a**, 22950-98-7; **8a** semicarbazone, 22950-99-8; **8b**, 22951-00-4; **8b**, 2,4-DNP, 22951-01-5; **9a**, 22951-02-6; **9a** semicarbazone, 22946-53-8; **9b**, 22951-03-7; **9b**-2,4-DNP, 22951-04-8; **13a**, 22951-05-9; **13b**, 22951-06-0; **15a**, 22951-07-1; **15b**, 22951-08-2; **16b**, 15564-47-3; **17a**, 22951-10-6; **17b**, 22951-11-7; **17b**-*p*-bromophenylurethan, 22951-12-8; **18a**, 22951-13-9; **18b**, 22951-14-0; **18b**-*p*-bromophenylurethan, 22951-15-1; **19a**, 22951-16-2; **19b**, 22951-17-3.

Acknowledgments.—We gratefully acknowledge support from the National Science Foundation and the National Institutes of Health.

(18) The allylic H pattern was reproduced *via* a computer simulated spectrum using the indicated J and $\Delta\nu$ values. We are indebted to Professor J. B. Lambert for his assistance in this analysis.