was eluted to give 30 mg of **5**: mp 143–148°; ν_{max} 3290 and 1770 cm^{-1}; nmr 47.5 (18-methyl), 83.5 cps (doublet, J = 6.0 cps, C-3-methyl).

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 72.98; H, 9.34.

B.—Acetyl acid **1a** (110 mg) was dissolved in methanol (7 ml) and titrated with 1 N sodium hydroxide until a phenolphthalein end point was reached. After the addition of sodium borohydride (150 mg) the mixture was stored overnight. The solvent was removed, the solution was acidified, and the steroids were recovered with ethyl acetate. Removal of the solvent gave 110 mg of crude product, which was separated on a silica tlc plate. Elution of the mobile zone gave 60 mg of lactone **5** identical with the sample obtained in part A.

17β-Acetoxy-3ξ-methoxy-3ξ-methyl-2-oxa-1-oxo-A-norestr-5(10)-ene (4d).—The mother liquors (150 mg) from the methylation and acetylation of lactol **4c** (525 mg) were chromatographed on tlc silica plates. The lactol ether **4d** (80 mg) was eluted and recrystallized from methanol to give colorless crystals: mp 145–147°; ν_{max} 1735 and 1670 cm^{-1}; λ_{max} 218 mμ (ε 7000); nmr 50.5 (18-methyl), 93 (doublet, *ca.* J = 1.0 cps, C-3-methyl), 121.5 (17-acetate), 186 and 189 (total equivalent to three protons, C-3-methoxyl), 279 cps (triplet, J = 7.5 cps, 17α-hydrogen).

Anal. Calcd for $C_{20}H_{28}O_5$: C, 68.94; H, 8.10. Found: C, 69.24; H, 8.40.

3ξ,17β-Diacetoxy-3ξ-methyl-2-oxa-1-oxo-A-norestr-5(10)-ene (4e).—The lactol **4c** was acetylated[10] as usual to yield the diacetate **4e**. Repeated recrystallizations from ethyl acetate gave an analytical sample: mp 131–134°; ν_{max} 1760, 1730, 1670 cm^{-1}; λ_{max} 225 mμ (ε 7400); nmr 50.5 (18-methyl), 100 and 102 (total equivalent three protons, C-3-methyl), 121.5 cps (3- and 17-acetates).

Anal. Calcd for $C_{21}H_{28}O_6$: C, 67.00; H, 7.50. Found: C, 66.70; H, 7.46.

Methyl 17β-Hydroxy-4-methyl-4-oxo-1,4-seco-2,3-bisnor-5α-estran-1-oate (1b).—The acetoxy lactol **4a** (60 mg) was dissolved in methanol (5 ml) and 1 N sodium hydroxide (1 ml) and the mixture was refluxed for 2 hr under nitrogen. Upon a conventional work-up, 45 mg of acid **1a** was obtained, which was treated with diazomethane to yield the ester **1b** identical with the previously described sample.[5]

(10) We wish to thank Dr. P. K. Grover for this experiment.

The Schmidt Reaction with Camphorquinone

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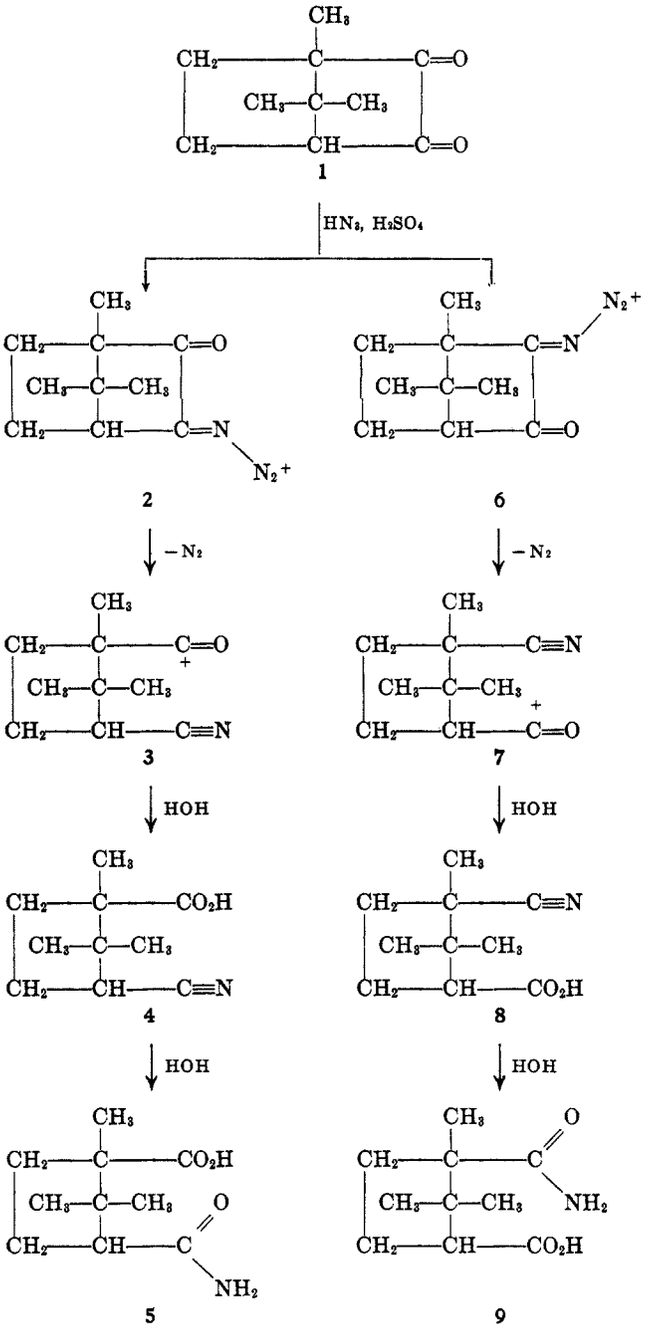
The similarity of the Beckmann rearrangement of the camphorquinone-3-oximes and the rearrangement of the camphorquinone-3-hydrazones[1] and -semicarbazones[2] led to the present study. A common product was α-camphoramic acid, having been produced by cleavage instead of the normal carbon to nitrogen rearrangement.

When subjected to Schmidt reaction conditions (sulfuric acid added to a chloroform solution of the ketone and hydrogen azide) as described in the Experimental Section, camphorquinone (**1**, Scheme I) produced α-camphoramic acid (**5**), β-camphoramic acid (**9**), and a small amount of α-camphornitrilic acid (**4**). It is considered that **4** and **5** arose from attack on the 3 position, whereas attack at the 2 position produced **9**. That the majority of the reaction product is **5** is in accord with the well-known fact that the 3 position in **1** is much more reactive than the 2 position.

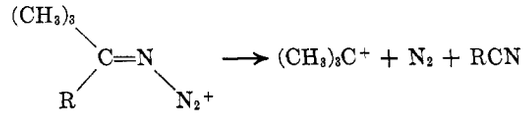
SCHEME I



Smith[3] has recently reviewed the cleavage-type Schmidt reaction. He also suggests[4] that the hydrazone rearrangement and Schmidt reaction have a common iminodiazonium ion intermediate. Zook and Paviak[5] applied the Schmidt reaction to a series of *t*-butyl alkyl ketones and found that the bulkier *t*-butyl group migrated in the normal manner as expected but in very poor yields, the main reaction being cleavage to the *t*-butyl carbonium ion (which alkylated the solvent if benzene or toluene were used) and a nitrile or hydrolysis product of a nitrile. Intermediates **2**, **3**, **4**, **6**, **7**, and **8** are consistent with their mechanism

(1) K. N. Carter, *J. Org. Chem.*, **23**, 1409 (1958).
(2) K. N. Carter and G. S. Blakely, unpublished results.
(3) P. A. S. Smith in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 517.
(4) Reference 3, p 527.
(5) H. D. Zook and S. C. Paviak, *J. Am. Chem. Soc.*, **77**, 2501 (1955).

SCHEME II



shown in Scheme II. Actual isolation of **4** helps to confirm the postulated reaction path. This compound was not isolated in the production of α-camphoramic acid from the camphorquinone-3-hydrazones,[1] but it was isolated by Nagata and Takeda[6] from the Beckmann cleavage of *anti*-camphorquinone-3-oxime and proved by them to be a precursor of α-camphoramic acid, which was also isolated.

It is interesting to note that Spielman and Austin,[7] when they applied the Schmidt reaction to the α-diketone benzil, obtained benzoylphenylurea and oxanilide, interpreted as arising from normal Schmidt reactions instead of the cleavage type.

Experimental Section[8]

Several runs were made differing only in method of work-up of product. The method of product treatment given here was chosen for efficiency of analysis. A chloroform solution of hydrazoic acid was prepared by the standard method[9] using an aqueous paste of sodium azide, chloroform, and sulfuric acid. To 11.6 g (0.070 mole) of camphorquinone (**1**), mp 203.5–204.5° (prepared[10] from D-camphor), was added 49.0 ml (0.077 mole) of the hydrazoic acid solution. The resulting solution was cooled to 1°, and 23.8 ml of concentrated sulfuric acid was added, with stirring, over a period of 2 hr, the temperature being maintained between 1 and 7° by means of a cooling bath. Stirring was continued for 1 additional hr. The reaction mixture was in two layers. Subsequent distillation of the chloroform layer showed it to be devoid of product. The acid layer was carefully poured into ice–water, giving 2.3 g of white solid. The filtrate was made alkaline with sodium hydroxide and extracted with three 50-ml portions of ether. The aqueous layer was then acidified with sulfuric acid and subjected to continuous ether extraction for 8 hr. The 2.3 g of solid was then dissolved in sodium hydroxide solution, and the solution was extracted with three 50-ml portions of ether. The ether extracts from the alkaline solutions were combined, and the ether was removed by distillation, leaving 0.1 g of unidentified oil. The sodium hydroxide solution was acidified with sulfuric acid and added to the other acid solution being extracted. Ether extraction was then continued for 17 hr. A white solid was present in the flask with the ether, 7.6 g, mp 163–170°. Infrared analysis indicated this to be approximately 85% **5** and 15% **9**. Pure **5** has a specific rotation[11] of +25° in ethanol while the specific rotation of **9** is +74°. A solution of 1.50 g of the 7.6-g crop in 25.0 ml of ethanol had an observed rotation (at 25–26°) of +3.75° in a 2-dm tube. This is indicative of 88% **5** and 12% **9**. The ether was subjected to distillation until about 75 ml remained. A white solid crystallized, 2.1 g, mp 152–163°. Infrared analysis indicated this to be a 50:50 mixture of **5** and **9**. A solution of 1.50 g of the material in 25.0 ml of ethanol had an observed rotation of +5.60° in a 2-dm tube. This indicates 55% **5** and 45% **9**.

Complete removal of the ether from the remaining solution gave 1.4 g of an oil which had a strong infrared absorption at 4.4 μ. Attempts to induce the oil to crystallize were unsuccessful. The oil was then dissolved in 20 ml of ether, and the solution was first extracted with 10 ml of saturated sodium bicarbonate solution and then with 20 ml of 0.5 *M* sodium hydroxide solution. The sodium hydroxide solution was acidified with hydrochloric acid. The resulting solution was extracted with three 10-ml portions of ether giving 0.3 g of oily solid upon removal of the ether by distillation. The product when recrystallized from water gave as the second crop 0.1 g of pure α-camphornitrilic acid (**4**), mp 159.5–160°. The identity of **4** was established by infrared spectra comparison and mixture melting point with an authentic sample.[12] Acidification of the sodium bicarbonate extract gave a viscous oil which was extracted with 10 ml of petroleum ether (bp 65–110°). Evaporation of the solvent gave 0.1 g of additional **4**. While no more pure **4** was isolated, various crystallization fractions contained small amounts as indicated by infrared spectra. At no time was there any indication of the presence of β-camphornitrilic acid (**8**).

Thus, the major products were α-camphoramic acid (57%) and β-camphoramic acid (14%). They could be separated from one another by fractional crystallization from ethyl acetate giving **5**, mp 177–178.5°, and **9**, mp 178–179.5°. The identity of each was confirmed by comparison of its infrared spectrum with an authentic sample[11] and by mixture melting point determination.

Acknowledgment.—The author wishes to express appreciation to Research Corporation for a Frederick G. Cottrell Grant.

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(7) M. A. Spielman and F. L. Austin, *J. Am. Chem. Soc.*, **59**, 2658 (1937).

(8) Melting points are corrected. Optical rotation measurements were made with a Rudolph Routine polarimeter. Infrared spectra were determined on a Perkin-Elmer 137B spectrophotometer. The quantitative spectra were run using the KBr pellet method. The Beer's law plots using absorbance at 8.06 μ for **5** and 7.88 μ for **9** were excellent, but there was some slight overlapping with mixtures of the two. The polarimetric analysis was considered more accurate, and those are the figures used in the final yield calculations.

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The Catalytic Isomerization of 4-Vinylcyclohexene to Bicyclo[3.2.1]oct-2-ene

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Previously reported syntheses of bicyclo[3.2.1]oct-2-ene include a four-step synthesis from cyclopentadiene,[1] phosphoric acid dehydration of 2-hydroxymethylbicyclo[2.2.1]heptane,[2] ferric chloride catalyzed isomerization of bicyclo[2.2.2]oct-2-ene,[3] and isomerization of 4-vinylcyclohexene with massive quantities of alkylaluminum compounds.[4] We wish to report a new and convenient method for catalytic isomerization of 4-vinylcyclohexene to bicyclo[3.2.1]oct-2-ene.

Catalysts prepared from lithium aluminum hydride and anhydrous cerous chloride, magnesium chloride, or strontium chloride in benzene diluent were found to effect cyclization of 4-vinylcyclohexene at temperatures of 200–250°. In a typical preparation, 20 mmoles each of lithium aluminum hydride and anhydrous cerous chloride were magnetically stirred overnight in 200 ml of benzene at room temperature under nitrogen; the resulting suspension was then heated with 250 g of 4-vinylcyclohexene in a stirred autoclave at 230°. Work-up and distillation gave recovery of 64% of the materials as C_8 compounds, along with considerable high-boiling residue. Gas chromatographic analysis of the C_8 mixture showed that there were four com-

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