3 ml were collected, and the elution was monitored by tlc (silica gel, ethyl acetate–acetone–dimethylformamide 5:5:1, R_f 0.62). Fractions containing only II were combined, concentrated, and crystallized from ethanol to give 77 mg of yellow needles, which showed a single spot upon chromatography in several systems. Fractions containing mixtures of II and elymoclavine *O*-acetate were combined and chromatographed in the same way a second and a third time to give 52 and 48 mg of product, bringing the total yield to 177 mg (0.6 mmol, 15.6%). II has a melting point of 178–180° dec, gives a green color with Ehrlich's spray reagent, and shows a strong blue fluorescence under uv; ir (KBr) 1750, 1368, 1210, and 1049 cm^{-1}; uv (MeOH) λ_{max} 248 nm (log ϵ 4.19) and 339 (4.11); major mass spectral peaks *m/e* (rel intensity) 294.13551 (M^+) (calcd 294.13682) (100), 252 (22), 251 (45.6), 249 (13.4), 235 (24.2), 223 (32.9), 222 (14.4), 221 (32.2), 192 (16.2), 154 (15.4). The 220-MHz nmr spectrum ($CDCl_3$) shows signals at δ 2.18 (singlet, 3 H) for the acetyl methyl group, 2.60 (singlet, 3 H) for the *N*-methyl, 2.73 (dd, J = 10, 14 Hz, 1 H, 4α proton), 3.07 (d, J = 14 Hz, 1 H, 7β proton), 3.32 (dd, J = 6, 10 Hz, 1 H, C-5 proton), 3.52 (dd, J = 6, 14 Hz, 1 H, 4β proton), 3.94 (d, J = 14 Hz, 1 H, 7α proton), 6.84 (broad singlet, 1 H, for the vinyl proton at C-9), 6.89 (broad singlet, 1 H, indole 2 H), 7.22 (multiplet, 3 H, aromatic protons), 7.35 (broad singlet, 1 H, vinyl proton at C-17) and 8.03 (broad singlet, indole NH).

Registry No.—I, 548-43-6; I acetate, 5080-45-5; II, 39717-29-8; III (R = H), 39717-30-1; III (R = OH), 82-58-6; dimethyl sulfoxide, 67-68-5; acetic anhydride, 108-24-7.

Acknowledgments.—We thank the Purdue University Mass Spectrometry Center for the mass spectra, C. J. Chang, E. W. Hagaman, and Dr. E. Wenkert, Indiana University, for the 220-MHz nmr spectra, and Drs. A. Hofmann and H. Kobel, Sandoz AG, Basle, for samples of elymoclavine used in the early phases of this work. Financial support by the U. S. Public Health Service (Research Grants AM 13555 and AM 11662 and Research Career Development Award GM 42382) is gratefully acknowledged.

Rearrangement in the Indan-1,3-dione System

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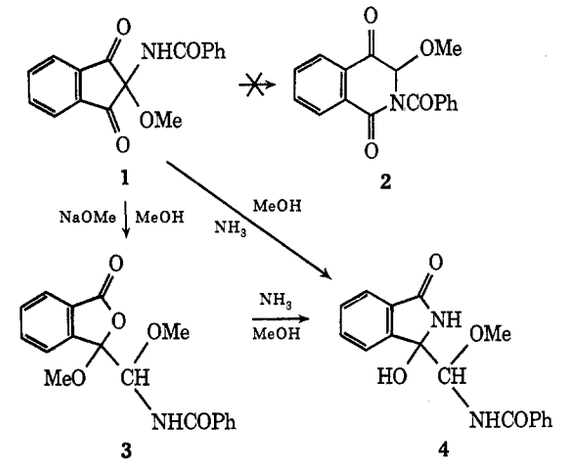
Received December 1, 1972

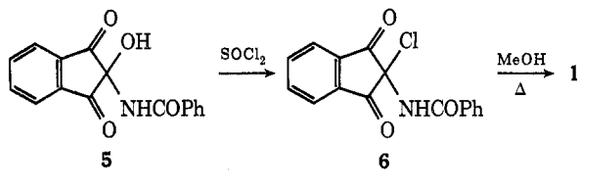
In an attempt to synthesize azanaphthaquinone[1] we tried to prepare the precursor 2-benzoyl-3-methoxytetrahydroisoquinoline-1,4-dione (**2**) by a base-catalyzed internal displacement ring enlargement[2] of 2-benzamido-2-methoxyindan-1,3-dione (**1**).

Instead of the expected ring enlargement product **2**, we obtained the rearranged phthalide derivative **3**, which was further converted to the isoindolone **4** on treatment with methanolic ammonia solution. The same isoindolone derivative **4** was also obtained from the starting material **1** on treatment with methanolic ammonia solution. Attempts to induce an acid-catalyzed ring enlargement on the isoindolone derivative were also unsuccessful.

The starting material 2-benzamido-2-methoxyindan-1,3-dione (**1**) was prepared in high yield from ninhydrine hydrate and benzamide. The addition product **5** was converted to the methoxybenzamidoindandione (**1**) by treatment with thionyl chloride followed by refluxing a methanolic solution of the chloroamide **6**, for 1 hr.



1 **2** **3** **4**



5 **6**

Experimental Section

Melting points are corrected; infrared spectra were measured in chloroform solutions and nmr in deuteriochloroform (unless otherwise indicated).

2-Benzamido-2-hydroxyindan-1,3-dione (5).—A mixture of ninhydrin hydrate (10.0 g, 0.05 mol) and benzamide (6.8 g, 0.05 mol) in benzene (100 ml) was refluxed for 1 hr. The water, formed in the reaction, was removed by azeotropic distillation. The mixture was cooled and the solid formed was filtered to give 15.1 g (86%) of product: mp 143–144°; ir 1760, 1720, and 1650 (CO), 3500 (OH), and 3300 cm^{-1} (NH). The hydroxyamide was used in the following procedure without further purification.

2-Benzamido-2-chloroindan-1,3-dione (6).—A mixture of the hydroxyamide **5** (2.0 g) and thionyl chloride (1.2 ml, 2 equiv) in methylene chloride (40 ml) was refluxed for 2 hr. The solvent was evaporated and the residue was triturated with benzene, filtered, and crystallized from benzene to give 1.97 g (93)% of product which melted at 173–174°: ir 1775, 1735, and 1660 (CO) and 3430 cm^{-1} (NH); *m/e* 399.

Anal. Calcd for $C_{16}H_{10}NO_3Cl$: C, 64.10; H, 3.34; N, 4.68; Cl, 10.80. Found: C, 64.17; H, 3.44; N, 4.32; Cl, 10.49.

2-Benzamido-2-methoxyindan-1,3-dione (1).—A solution of the chloroamide **6** in absolute methanol (25 ml) was refluxed for 1 hr. The solvent was evaporated and the residue was triturated with ether–hexane and filtered. It was crystallized from benzene–hexene: mp 166–167°; yield 66%; ir 1725, 1760, 1660 (CO), and 3420 cm^{-1} (NH); nmr δ 8.2–7.3 (m, 10 H) and 3.57 (s, 3 H).

Anal. Calcd for $C_{17}H_{13}NO_4$: C, 69.14; H, 4.44; N, 4.74. Found: C, 68.87; H, 4.52; N, 5.06.

3-Methoxy-3-(α-methoxy-α-benzamidomethyl)phthalide (3).—A solution of 2-benzamido-2-methoxyindan-1,3-dione (**1**, 1.0 g) and sodium methylate (20 mg) in absolute methanol (20 ml) was left at room temperature for 48 hr. The solvent was evaporated and the residue was dissolved in ethyl acetate (50 ml) and washed with water. The organic layer was dried over magnesium sulfate and evaporated. The residue was triturated with ether, filtered, and crystallized from ethyl acetate–hexane: mp 178°; yield 60%; ir 1780, 1670 (CO), and 3430 cm^{-1} (NH); nmr δ 8.2–7.3 (m, 9 H), 6.85 (d, 1 H, J = 10 cps), 5.80 (d, 1 H, J = 10 cps), 3.32 (s, 3 H), and 3.10 (s, 3 H).

Anal. Calcd for $C_{18}H_{17}NO_5$: C, 66.05; H, 5.28; N, 4.28. Found: C, 65.92; H, 5.27; N, 4.04.

3-Hydroxy-3-(α-methoxy-α-benzamidomethyl)isoindolone (4).—A mixture of the lactone **3** (1.0 g) in methanolic ammonia

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solution (10 ml of a 10% solution) was stirred at room temperature for 1 hr. The solid was filtered off to give a product which melted at 224–226°. The solution was evaporated and the residue was triturated with ethyl acetate to give an additional crop of the same product: yield 77%; ir (KBr) 1700, 1650 (CO), and 3200 cm^{-1} (OH and NH, broad); nmr (DMSO-d_6) δ 8.32 (d, 1 H, J = 10 cps), 8.2–7.4 (m, 9 H), 6.58 (s, 1 H), 5.40 (d, 1 H, J = 10 cps), 3.32 (s, 3 H).

The compound was identical with the product obtained by treating the starting material **1** with methanolic ammonia for 24 hr at room temperature.

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.68; H, 5.31; N, 9.02.

Registry No.—**1**, 39253-47-9; **3**, 39253-48-0; **4**, 39253-49-1; **5**, 39253-50-4; **6**, 39253-51-5.

Preparation and Acid-Catalyzed Rearrangement of 3,3-Dimethoxytricyclo[3.2.0.0^{2,7}]heptane

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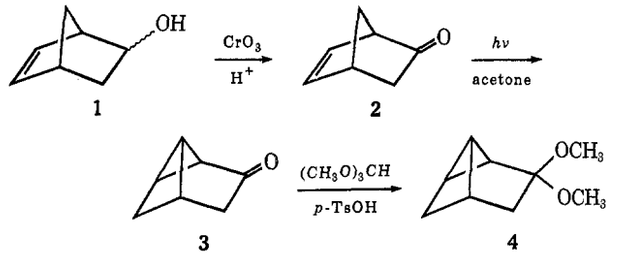
Received December 22, 1972

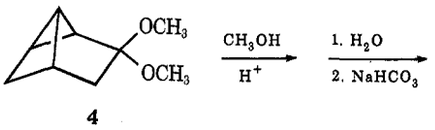
Although the chemistry of quadricyclyl cation has been well studied,[2–4] much less is known about the chemical reactions of the highly strained tricyclo[3.2.0.0^{2,7}]hept-3-yl cation. We attempted to elucidate the nature and ultimate fate of this carbenium ion. This note reports the preparation of 3,3-dimethoxytricyclo[3.2.0.0^{2,7}]heptane (**4**) and the subsequent acid-catalyzed rearrangement of this disubstituted tricyclane.

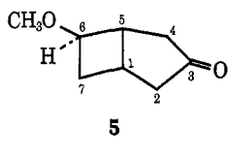
3,3-Dimethoxytricyclo[3.2.0.0^{2,7}]heptane (**4**) was prepared by the sequence of reactions shown below. The initial reaction involved the conversion of 5-norbornen-2-ol (**1**) to 5-norbornen-2-one (**2**) *via* oxidation with



Jones reagent. Tricyclo[3.2.0.0^{2,7}]heptan-3-one (**3**) was prepared by irradiation of **2** in acetone.[5] Reaction of **3** with trimethyl orthoformate using small amounts of *p*-toluenesulfonic acid as catalyst gave an 85% yield of **4**, bp 38–39° (4 mm).

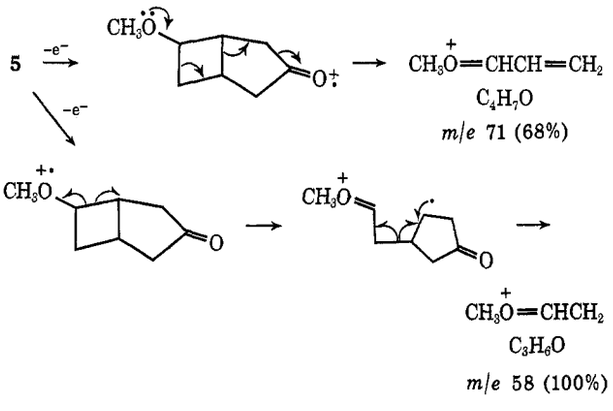
The ketone **3** and its dimethyl ketal **4** were quite stable under aqueous acid conditions at room temperature. In 10% sulfuric acid, **4** was ultimately hydrolyzed to **3** but no rearrangement products were found. When **4** was exposed to methanolic sulfuric acid solution (10% sulfuric acid by weight) at room temperature for 2 hr and followed by the aqueous conditions of the work-up, it underwent an acid-catalyzed rearrangement reaction to yield 6-methoxybicyclo[3.2.0]-heptan-3-one (**5**) in 71% yield as the only monomeric





product. The same rearrangement product was obtained with **3** as the starting material but the rate of the rearrangement reaction was slower.

The structure of **5** was assigned on the basis of spectral data. The ir spectrum showed absorption at 2810 (symmetric C–H stretching for methoxyl group), 1150–1050 (C–O–C stretching), and 1745 cm^{-1} (five-membered cyclic carbonyl stretching frequency), indicative of a methoxy and cyclopentanone structure.[6] The mass spectrum revealed a molecular ion peak of empirical formula $C_8H_{12}O_2$ and two major fragments of empirical formulas C_4H_7O and C_3H_6O. These observed fragmentations are consistent with structure



5, which would be expected to undergo cleavage to produce C_4H_7O and C_3H_6O ions. The nmr spectrum of **5** was likewise consistent with this structure. Signals due to C_1 and C_5 methine hydrogens appeared as complex multiplets at δ 2.80–3.00. The C_6 hydrogen signal occurred as a multiplet at δ 3.56 and that of the methoxyl hydrogens as a singlet at δ 3.26. Signals displayed at δ 2.00–2.60 are assigned to the rest of the hydrogens.

The stereochemistry of the methoxyl group in **5** was deduced from the observed ir and nmr spectra of the corresponding alcohol. When **3** was treated with 20% sulfuric acid in aqueous THF solution at 60° for 4 hr it underwent a very slow reaction to give predominantly unrearranged starting material along with about 5% of 6-hydroxybicyclo[3.2.0]heptan-3-one (**6**). To distinguish between the exo and endo configuration of OH we examined the effect of concentration on the ir and nmr of the OH proton. The ir spectrum of **6** showed two bands in the more con-

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