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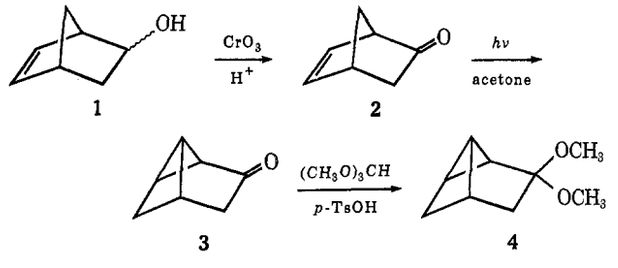
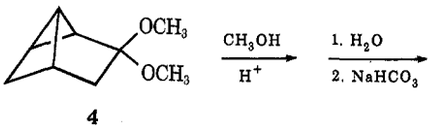
Although the chemistry of quadricyclyl cation has been well studied,[2–4] much less is known about the chemical reactions of the highly strained tricyclo[3.2.0.0^{2,7}]hept-3-yl cation. We attempted to elucidate the nature and ultimate fate of this carbenium ion. This note reports the preparation of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

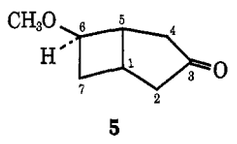
3,3-Dimethoxytricyclo[3.2.0.0^{2,7}]heptane (**4**) was prepared by the sequence of reactions shown below. The initial reaction involved the conversion of 5-norbornen-2-ol (**1**) to 5-norbornen-2-one (**2**) *via* oxidation with



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).

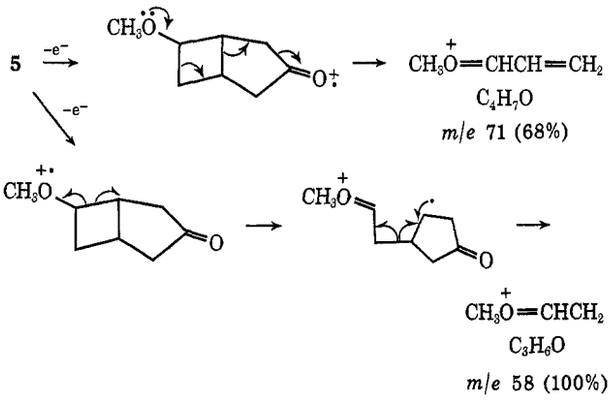
The ketone **3** and its dimethyl ketal **4** were quite stable under aqueous acid conditions at room temperature. In 10% sulfuric acid, **4** was ultimately hydrolyzed to **3** but no rearrangement products were found. When **4** was exposed to methanolic sulfuric acid solution (10% sulfuric acid by 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-

(1) Xerox Corporation, Rochester Research Center, Webster, N. Y. 14580.

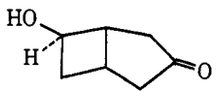
(2) H. G. Richey, Jr., and N. C. Buckley, *J. Amer. Chem. Soc.*, **85**, 3057 (1963).

(3) P. R. Story and S. R. Fahrenholtz, *ibid.*, **88**, 374 (1966).

(4) P. G. Gassman and D. S. Patton, *ibid.*, **90**, 7276 (1968).

(5) J. Ipaktschi, *Tetrahedron Lett.*, 2153 (1969).

(6) F. Scheimann, "An Introduction to Spectroscopic Methods for the Identification of Organic Compounds," Vol. 1, Pergamon Press, New York, N. Y., 1970, pp 179, 187.



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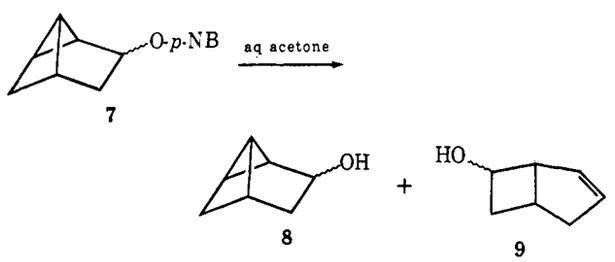
centrated solution, at 3625 (free OH) and 3440 cm^{-1} (broad and intense band, hydrogen-bonded OH). The latter band was absent in the more dilute solution and is attributed to intermolecular hydrogen bonding.[7] The carbonyl frequency of **6** was 1745 cm^{-1}, indicating the absence of intramolecular hydrogen bonding.[7] The nmr spectra of **6** in carbon tetrachloride appropriately paralleled that of **5** except for the signal of the hydroxyl proton, which showed a concentration-dependent chemical shift, thus indicating the absence of intramolecular hydrogen bonding. From the spectral data, it is evident that both the hydroxyl group in **6** and methoxyl group in **5** should be at the exo position.

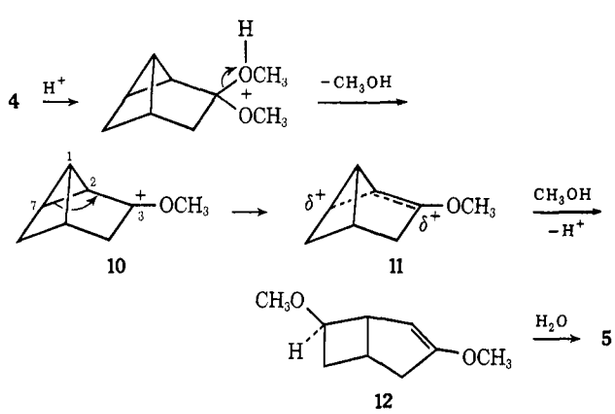
While this work was in progress a paper by Lustgarten[8] appeared in which was reported that solvolysis products from both epimers of tricyclo[3.2.0.$0^{2,7}$]hept-3-yl *p*-nitrobenzoate (**7**) consisted mainly of unrearranged tricyclic alcohols (**8**) and homoallylic bicyclo[3.2.0]heptanols (**9**). The exo to endo ratio of **9** was



7 8 9

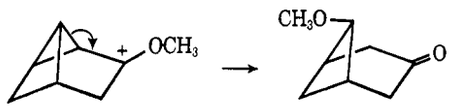
reported to be 10:1. His results further supported our structure **5** and moreover revealed a common cationic intermediate from both epimers.

In the acid-catalyzed rearrangement of **4**, the initial step in the mechanistic path may involve the protonation of the oxygen function followed by loss of methanol to yield carbenium ion **10**. The manner in which **10** cleaves determines the topology of final rearrangement product. Cleavage of the C_2–C_7 bond in **10**



10 11 12

will lead to the formation of the observed rearrangement product **5**, while the breaking of the C_1–C_2 bond would give **13**. Examination of a stereomodel of **10**



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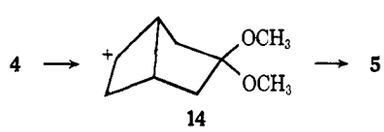
reveals that the orientation of the p orbital of the carbenium ion at the C_3 position is almost parallel to the adjacent cyclopropane bent δ bond C_2–C_7. The C_1–C_2 bond possesses much less overlap with the developing p orbital of the adjacent carbenium ion. Therefore, it is most favorable to cleave the C_2–C_7 bond in **10** to produce a delocalized or equilibrating ion **11**, which should be a particularly stable ion having one end of the homoallylic cation relatively strainless and the other end stabilized by a methoxyl group. The nucleophilic attack by solvent (methanol) at **11** would yield **12**, which, under the aqueous conditions of the work-up, would hydrolyze the enol ether function to yield the rearrangement product **5**. The isolation of only exo methoxyl product is also consistent with preferred approach of solvent from the less hindered side or of the nonclassical nature of the homoallylic ion.[9]

A less pleasing alternate rationale for the formation of **5** would involve initial protonation on the carbon adjacent to the ketal carbon to yield the bicyclic carbenium ion **14**. Although this would be consistent



14

with the formation of **5**, it requires initial protonation on the carbon adjacent to the carbon bearing the methoxyl groups. Since the methoxyls are electron withdrawing, electronegativity arguments might predict that this carbon should be the least likely to be protonated. However, further study is required to determine the possible role of this reaction.

Experimental Section

Proton magnetic resonance spectra were obtained with a JEOL Model JNM-C-60HL high-resolution nmr instrument. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer. Infrared spectra were measured on a Perkin-Elmer Model 137, Model 421, or Model 457 infrared spectrophotometer. Glpc analyses were carried out with a Hewlett-Packard F & M Model 700 with a Model 7127A strip chart recorder equipped with integrator or a Varian Aerograph Model 90-P gas chromatograph. Microanalytical analyses were performed by Micro-Tech, Skokie, Ill.

Tricyclo[3.2.0.$0^{2,7}$]heptan-3-one (3).—This tricyclic ketone was prepared by irradiation of 5-norbornen-2-one[10] in acetone.[5] A solution of 3.00 g (27.8 mmol) of 5-norbornen-2-one in 900 ml of acetone was placed in an ice–water-cooled quartz immersion apparatus equipped with a reflux condenser and a magnetic stirring bar. A stream of nitrogen was passed through the solution for about 10 min to remove dissolved oxygen. The solution was then kept under nitrogen and was irradiated with a 450-W Hanovia medium-pressure mercury lamp. The progress of the reaction was monitored by glpc analysis. The reaction was completed after 2 hr of irradiation. Acetone was removed on a rotary evaporator. The concentrated mixture was combined with four other runs (in each run 3.00 g of 5-norbornen-2-one was used) and distilled under reduced pressure through an 18-in. spinning band column to give 9.75 g (65%) of tricyclo[3.2.0.$0^{2,7}$]-heptan-3-one: bp 83–84° (21 mm); ir (neat) 5.85 μ (C=O);

(7) J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 99–106.

(8) R. K. Lustgarten, *J. Amer. Chem. Soc.*, **93**, 1275 (1971).

(9) P. R. Brook, *Chem. Commun.*, 565 (1968).

(10) S. J. Cristol and P. K. Freeman, *J. Amer. Chem. Soc.*, **83**, 4427 (1961).

nmr ($CDCl_3$) δ 1.1–1.4 (m, 2 H), 1.9–2.3 (m, 4 H), and 2.5–3.0 (m, 2 H); mass spectrum parent *m/e* 108.

Anal. Calcd for C_7H_8O: C, 77.78; H, 7.41. Found: C, 77.68; H, 7.39.

3,3-Dimethoxytricyclo[3.2.0.0^{2,7}]heptane (4).—*p*-Toluenesulfonic acid (0.028 g) was added to a solution of 2.71 g (25 mmol) of tricyclo[3.2.0.0^{2,7}]heptan-3-one and 3.68 g of trimethyl orthoformate in 5 ml of anhydrous methanol. The reaction mixture was stirred at room temperature for 8 hr. Sodium methoxide (10 mg) was added to the reaction mixture. The resulting solution was put on a rotary evaporator to remove methanol and distilled under reduced pressure to give 3.27 g (85%) of 3,3-dimethoxytricyclo[3.2.0.0^{2,7}]heptane: bp 38–39° (4 mm); nmr ($CDCl_3$) δ 1.3–1.8 (m, 6 H), 2.35 (m, 2 H), 3.12 (s, 3 H), and 3.28 (s, 3 H); mass spectrum parent peak *m/e* 154; ir (CCl_4) 2815 (symmetric CH stretching for methoxyl group), 1150–1050 cm^{-1} (C–O–C asymmetric stretching) and no carbonyl absorption.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 69.96; H, 9.12.

Reaction of 3,3-Dimethoxytricyclo[3.2.0.0^{2,7}]heptane (4) with Anhydrous Methanolic Sulfuric Acid.—Methanol was purified and dried by distilling Mallinkrodt AR methanol from magnesium turnings. In a 10-ml, round-bottomed flask equipped with magnetic stirring bar and drying tube was placed 3 ml of methanolic sulfuric acid solution (10% concentrated H_2SO_4 by weight). The dimethyl ketal (0.500 g) was added to this stirred solution at ice–water-bath temperature. The solution was stirred at room temperature for 2 hr. Water (6 ml) was added. After stirring for 15 min the solution was made basic with solid sodium bicarbonate and extracted with five 6-ml portions of ether. The ethereal extracts were combined, washed with two 5-ml portions of water, and dried over anhydrous magnesium sulfate. After filtration, the ether was removed by distillation at atmospheric pressure to give yellow liquid residue. The residue was distilled *in vacuo* [bulb to bulb distillation at 50–56° (5 mm)] to give 0.324 g of colorless liquid. This colorless liquid was analyzed by analytical glpc on a Hewlett-Packard high-efficiency packed column, 0.125 in. × 6 ft stainless steel packed with 10% UCON-98 on 80–100 Chromosorb W, indicating that only one compound was present. Thin layer chromatography of this colorless liquid also showed it to be one compound.

The analytical sample of **5** was obtained by preparative glpc (0.25 in. × 6 ft 17% SE-30 on 30–60 mesh Chromosorb P at 150°). The colorless liquid **5** has the following spectral properties: ir (CCl_4) 1745 (five-membered cyclic carbonyl stretching frequency), 1050–1150 (C–O–C stretching), and 2810 cm^{-1} (symmetric CH stretching for methoxyl group); nmr ($CDCl_3$) δ 2.00–2.60 (m, 6 H), 2.80–3.00 (m, 2 H, fused ring junction protons), 3.26 (s, 3 H, methoxyl hydrogens), and 3.65 (m, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 140 (5), 71 (68), 58 (100), 41 (23) (see text for interpretation of spectra).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.57; H, 8.57. Found: C, 68.30; H, 8.65.

Registry No.—**2**, 694-98-4; **3**, 37939-83-6; **4**, 39008-47-4; **5**, 39003-10-6.

Acknowledgment.—Partial support of this work by the U. S. Public Health Service (Grant CA 11326) is gratefully acknowledgen.

The Preparation of α,β-Unsaturated Aldehydes from Acid Chlorides

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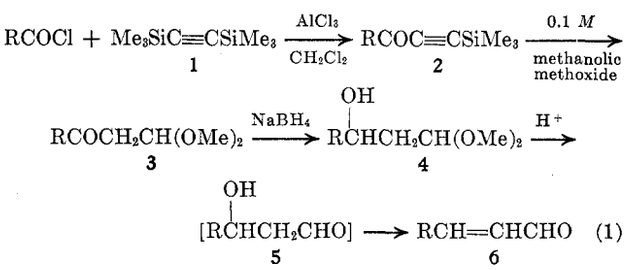
Received February 1, 1973

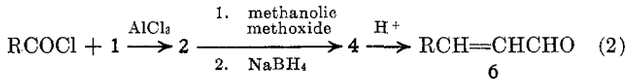
We describe here a simple procedure for the preparation of α,β-unsaturated aldehydes which involves a facile 2-carbon homologation of an acid chloride. The method, which, we belatedly became aware, is related to that previously reported by Wakayama, *et al.*,[11] represents a useful alternative to those already available[1a–m] since acid chlorides are usually easily prepared.

The method is summarized in the following generalized equation and is illustrated with *p*-biphenylcarbonyl chloride, benzoyl chloride, and cyclohexylcarbonyl chloride. It involves Friedel–Crafts alkynylation of an acid chloride with bistrimethylsilyl acetylene (**1**) as first reported by Birkofer, *et al.*,[2] then by Walton and Waugh,[3] followed by further sequential rapid transformation of the acyl trimethylsilylacetylene **2** to the β-keto acetal **3**, the β-hydroxy acetal **4**, the β-hydroxyaldehyde **5** and the α,β-unsaturated aldehyde **6**. Since the



alkynylation reaction appears to have appreciable scope,[2–4] the outlined sequence would appear to be reasonably general.

The intermediates indicated in eq 1 were actually isolated and characterized in the case of R = *p*-biphenylyl.[5] For the other acid chlorides the sequence was telescoped as indicated in eq 2. The various



intermediates indicated in eq 1 are presumably also involved in these cases.

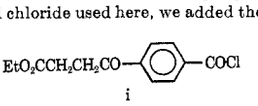
The fact that the foregoing method also provides a simple preparation of β-hydroxyaldehydes should not be overlooked. As indicated in the Experimental Section, mild acid hydrolysis of the hydroxy acetal **4** (R = *p*-biphenyl)[5] gave the corresponding hydroxyaldehyde **5** (obtained in this case as the hydrate.)

(1) (a) M. Jacobson, *J. Amer. Chem. Soc.*, **75**, 2584 (1953); (b) R. I. Hoaglin and D. Hirsh, U. S. Patent 2,628,257 (1953); *Chem. Abstr.*, **48**, 1423 (1954); (c) L. Crombie, *J. Chem. Soc.* 1007 (1955); (d) C. Jutz, *Chem. Ber.*, **91**, 1867 (1958); (e) G. Wittig and H. D. Frommeld, *ibid.*, **97**, 3548 (1964); (f) J. P. Ward and D. A. van Dorp, *Recl. Trav. Chim. Pays-Bas*, **86**, 545 (1967); (g) S. Satsumabayashi, K. Nakajo, R. Soneda, and S. Motoki, *Bull. Chem. Soc. Jap.*, **43**, 1586 (1970); (h) A. I. Meyers, *et al.*, *J. Amer. Chem. Soc.*, **91**, 764 (1969); (i) E. J. Corey, B. W. Erickson, and R. Noyori, *ibid.*, **93**, 1724 (1971); (j) E. J. Corey and S. Terashima, *Tetrahedron Lett.* 1815 (1972); (k) E. Hunt and B. Lythgoe, *Chem. Commun.*, 757 (1972); (l) S. Wakayama, S. Itoh, S. Yui, and H. Mackawa, *J. Chem. Soc. Jap.*, **78**, 1525 (1957); (m) see review by J. Carnduff, *Quart. Rev., Chem. Soc.*, **20**, 169 (1966).

(2) L. Birkofer, A. Ritter and H. Uhlenbrauck, *Chem. Ber.*, **96**, 3280 (1963).

(3) D. R. M. Walton and F. Waugh, *J. Organometal. Chem.*, **37**, 45 (1972).

(4) To the examples cited in ref 2 and 3 and *p*-biphenylcarbonyl chloride and cyclohexylcarbonyl chloride used here, we added the acid chloride i which



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we found reacted in the anticipated manner with **1** at room temperature (2.25 hr) in CH_2Cl_2 in the presence of 3 molar equiv of aluminum chloride. (Very little if any reaction occurred with 1 molar equiv.)

(5) The detailed work was done in this series because of our interest in the products as chemical intermediates.