tion state. In the above-mentioned solvolysis of 2-

$$S + H^+ (Hg^{2+}) \overset{\text{fast}}{\rightleftarrows} SH^+ (SHg^{2+})$$

$$SH^+ (SHg^{2+}) + H_2O \xrightarrow{\text{slow}} \text{products}$$

phenyl-4,4,5,5-tetramethyldioxolane (A2), Fife[8] observed general acid catalysis of hydrolysis by formic acid. This finding coupled with the magnitude of ρ, k_D/k_H, and $\Delta S^{\ddagger}$ for that study suggests the possibility of a concerted protonation and nucleophilic attack by water on the substrate. In the present study no evidence of catalysis by chloroacetic acid or acetic acid was detected. Thus proton transfer to oxathiolanes is virtually complete prior to the rate-determining step.

Acknowledgment. This investigation was supported by a training grant (5-Tl-GM-555-06) from the Division of Medical Sciences, U. S. Public Health Services, Bethesda, Md.

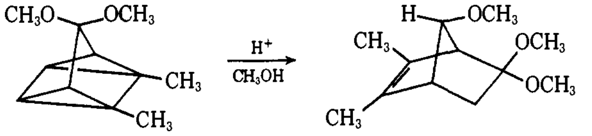
The Synthesis and Acid-Catalyzed Rearrangement of 3,3-Dimethoxy-1,5-dimethyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane[1]

Paul G. Gassman,[2] Donald H. Aue,[3] and David S. Patton[4]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received June 3, 1968*

Abstract: 7,7-Dimethoxy-2,3-dimethylbicyclo[2.2.1]heptadiene was prepared and photochemically converted into 3,3-dimethoxy-1,5-dimethyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane by both photosensitized and direct irradiation. The photoproduct was extremely sensitive to mildy acidic conditions, yielding a dehydronorcamphor derivative virtually instantly on exposure to 0.01% methanolic sulfuric acid. The mechanistic implications of this unusual rearrangement are discussed.

Although "quadricyclane" derivatives[5] have become relatively well-known compounds (as illustrated by some 25 publications in the area), a dearth of information exists concerning the reactions of this highly strained ring system. In relation to our long-standing interest in carbonium ion chemistry we were particularly concerned about the nature and ultimate fate of carbonium ions generated on the quadricyclane skeleton. This paper presents our findings on the reactions of 3,3-dimethoxy-1,5-dimethyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (1), a quadricyclane derivative which rapidly rearranges to 5,5-dimethoxy-*anti*-7-methoxy-2,3-dimethylbicyclo[2.2.1]hept-2-ene (2) in weakly acidic methanol.



1 2

The known triene, 3, prepared by a modification of the procedure of Hoch[6] served as the origin of our synthetic work. Dechlorination of 3 with sodium tetrahydrofuran–*t*-butyl alcohol gave a mixture of 4 and 5 in 38 and 24% yields, respectively. 7,7-Dimethoxy-2,3-dimethylbicyclo[2.2.1]heptadiene, 4, which arose *via* a novel 1,4 reduction of the conjugated diene system was of prime importance to our synthetic approach. Hence, the structure of 4 was substantiated in several ways. Catalytic reduction of 4 over palladium on carbon resulted in the rapid uptake of 1 mol of hydrogen followed by the relatively slow addition of 1 additional mol of hydrogen indicating the presence of two double bonds. The ultraviolet spectrum of 4 showed weak end absorption,[7] while the near-infrared spectrum showed a maximum at 1.655 μ (ϵ 0.676) characteristic of norbornadiene derivatives.[8] Additional definitive evidence for the assigned structure was provided by the nmr spectrum of 4 which showed the six allylic methyl hydrogens as a singlet at τ 8.30, two methoxyl methyls as singlets at τ 7.02 and 6.92,

---

[1] For a preliminary report on part of this work, see P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Am. Chem. Soc.*, **86**, 4211 (1964).

[2] Alfred P. Sloan Research Fellow, 1967–1969.

[3] The Ohio State University Undergraduate Research Scholar, 1962–1963.

[4] The Ohio State University Undergraduate Research Scholar, 1963–1964; National Science Foundation Undergraduate Research Participant, summer 1963, 1964; Goodyear Fellow, 1966–1967.

[5] The term "quadricyclane" is the commonly accepted name for the tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane ring system. For the systematic nomenclature and numbering details, see J. Meinwald and J. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

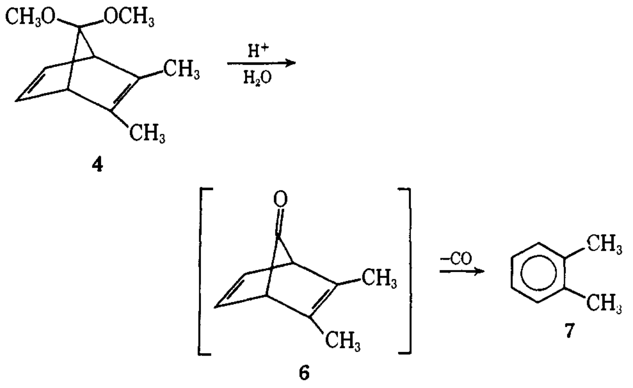
[6] P. E. Hoch, *J. Org. Chem.*, **26**, 2066 (1961).

[7] The ultraviolet spectrum of 4 showed end absorption in 95% ethanol at 210 mμ (ϵ 2000) and 214 (1350). This to be compared with norbornadiene which shows end absorption at 214 mμ (ϵ 1480).

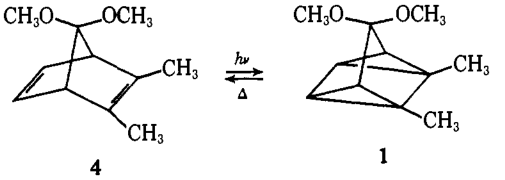
[8] P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965).

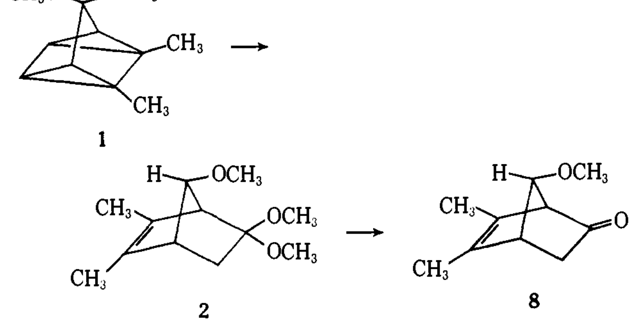
two bridgehead hydrogens as a triplet at τ 6.81, and the two olefinic hydrogens as a triplet at τ 3.42.

The norbornadiene derivative, **4**, was extremely unstable to acidic conditions. Reaction with dilute acid at −20° gave violent gas evolution with *o*-xylene (**7**) being formed in high yield. The conversion of **4** into **7** probably occurred *via* the intermediacy of the norbornadienone, **6**. It is interesting to note that the orbital symmetry of **6** is such that a concerted loss of carbon monoxide is permitted. Hence the facile formation of *o*-xylene was to be expected. The diene **4** was also converted to **7** on pyrolysis.[9]



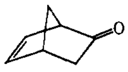
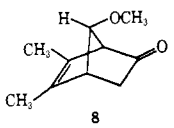
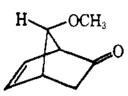
The conversion of **4** into **1** was achieved by both photosensitized and direct irradiation. Irradiation of a pentane solution of **4** in a quartz vessel using a 450-W Hanovia medium pressure lamp gave an 82% yield of **1**, bp 37° (0.05 mm). The stability of **1** was very dependent on the purity and history of **4**. In general **4** was purified by fractional distillation through a spinning-band column. When a stainless steel spinning-band column was used, the quadricyclane derivative **1** was unstable and rapidly reverted to **4**, even at −12°. When **4** was purified by distillation through a Teflon spinning-band column and then converted to **1**, the resulting quadricyclane showed no detectable change after 4 months at −12°.[10] Low-temperature recrystallization from pentane gave very pure material, mp 18–19°. Both the thermal reversal of **1** to **4** and the low boiling point of **1** (indicative of its monomeric character) were consistent with the assigned structure. In addition, spectral evidence was obtained which could only be reconciled with the designated quadricyclic arrangement of **1**. The nmr spectrum of **1** showed six methyl protons as a singlet at τ 8.78, three methoxy protons as a singlet at τ 6.70, three methoxy protons at τ 6.67 (singlet), and two doublets at τ 8.82 and 8.51 (two protons each). The doublet at τ 8.51 was assigned to the hydrogens α to the ketal function, while the doublet at τ 8.82 was attributed to the other two cyclopropyl hydrogens. The ultraviolet spectrum of **1** showed only end absorption at 210 mμ (ϵ 380) and the near-infrared spectrum gave $\lambda_{max}^{CCl_4}$ 1.668 μ (ϵ 1.625). Thus all of the spectroscopic data unequivocally demonstrated the authenticity of the assigned structure.





The quadricyclane **1** was extremely sensitive to acidic conditions. When **1** was dissolved in 0.01% sulfuric acid in methanol a mild exotherm resulted with the immediate formation of **2** in 83% yield. Under somewhat more acidic conditions (0.3% sulfuric acid in methanol) **1** was converted directly into **8** in 84% yield. The structure of **8** was established in several ways. The appearance of a carbonyl stretching vibration at 5.72 μ coupled with the facile formation of a 2,4-dinitrophenylhydrazone established the presence of a carbonyl group. The ultraviolet spectrum of **8** showed the position of the ketone function relative to the skeletal structure. As shown in Table I, **8** showed an anomalous n→π* absorption which was only consistent with the presence of the dehydronorcamphor (**9**) skeleton.[11] The absence of vinylic hydrogen

Table I. Ultraviolet Spectra of Dehydronorcamphor Derivatives

Compound	Solvent	λ_{max}, mμ	ϵ
 9	Isooctane	287.5	162
		296.5	242
		307.5	277
		319.5	177
	Ethanol[a]	300.5	292
 8	Cyclohexane	286.5	386
		294	436
		304	413
		316	242
	Ethanol	299	487
 10[b]	Cyclohexane	286	154
		296	215
		306	253
		328	144
	Ethanol	298	233

[a] P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956). [b] For the preparation of **10**, see P. G. Gassman and D. S. Patton, *ibid.*, **90**, 7276 (1968).

---

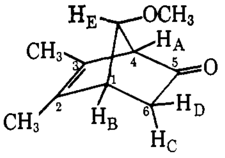
(9) This conversion probably results from the expulsion of dimethoxycarbene. For similar examples, see J. Diekmann, *J. Org. Chem.*, **28**, 2880 (1963); R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197 (1964); D. M. Lemal, E. P. Gosselink, and A. Ault, *ibid.*, 579 (1964).

(10) It is interesting to speculate on the cause of this facile isomerization of **1** to **4**. It has recently been noted that noble metal complexes of norbornadiene catalyze the thermal conversion of quadricyclane to norbornadiene [H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967)]. The noble metal complex catalyzes the process by changing the transformation from a symmetry-forbidden conversion into a symmetry-allowed concerted process [F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967)]. It appears likely that trace amounts of catalytic material may have been incorporated into the starting diene, **4**, during its distillation through the metal spinning-band column.

(11) A. Moscowitz, K. Mislow, M. A. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962); H. Labhart and G. Wagniere, *Helv. Chim. Acta*, 42, 2219 (1959).

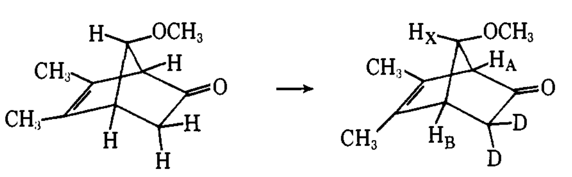
absorptions in both the nmr and near-infrared spectra indicated that the double bond was tetrasubstituted. It is interesting to note that the presence of the methyl groups on the double bond significantly increase the extinction coefficient of the anomalous $n \rightarrow \pi^*$ absorption while having relatively little effect on the position of the maxima.

The 100-Mc nmr spectrum of **8** was quite solvent dependent. In carbon tetrachloride, the methyl hydrogens appeared at τ 8.34 and 8.29. The 6-*endo* proton, H_C, appeared at τ 8.42 as a quartet due to W-form coupling with the C-7 proton H_E (J_{CE} = 1.8 cps)[12] and geminal coupling with the *exo* proton H_D (J_{CD} = 16 cps) in accordance with expectations.[13] Half of the quartet was buried under the methyl absorptions. By changing to deuteriochloroform as the solvent, the H_C absorption could be shifted downfield, making the other half of the multiplet visible. The C-7 proton, H_E, appeared as a six-peak multiplet at τ 6.26. As has been shown[14] this multiplicity requires that H_E be coupled to H_A, H_B, and H_C. The 6-*exo* proton, H_D, appeared as a quartet centered at τ 7.95 (J_{CD} = 16 cps; J_{BD} = 1.5 cps). The bridgehead protons, H_A and H_B, appeared as a complex multiplet centered at τ 7.30. The C-7 methoxyl group gave a sharp singlet at τ 6.74. Spin decoupling *via* irradiation of the H_E absorption caused H_C to appear as a doublet with only geminal coupling, while irradiation of the bridgehead protons collapsed the H_D signal to a doublet with only geminal coupling. Hence the nmr spectrum was completely consistent with the assigned structure.



8

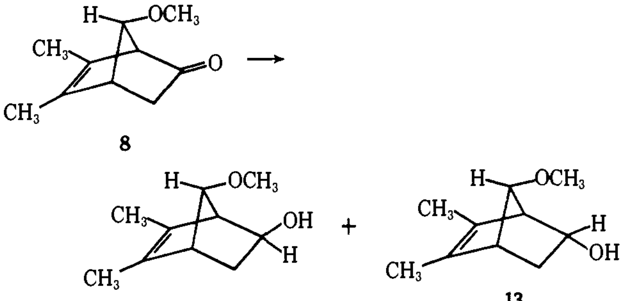
Chemical evidence for the presence of two enolizable hydrogens adjacent to the carbonyl function was obtained from the base-catalyzed exchange of **8**. Using deuterium oxide–methanol-O-*d* as solvent, base catalysis[15] gave **11** with the incorporation of two deuteriums.



8 **11**

In addition to proving the presence of an unsubstituted methylene adjacent to the carbonyl function, the deuterium exchange provided material whose nmr spectrum confirmed the assignments made in the unlabeled case. The C-7 proton of **11** now appeared as a quartet centered at τ 6.22 in an ABX pattern with J_{AX} = 2.3 cps and J_{BX} = 1.3 cps. The bridgehead hydrogens appeared as a six-peak multiplet and the absorptions previously assigned to the *exo* and *endo* hydrogens at C-6 were absent in agreement with expectations.

Reduction of **8** with lithium aluminum hydride gave a mixture of **12** and **13** which were readily separated by preparative glpc. Hydrogen-bonding studies showed that **12** had a strong intramolecular hydrogen bond while **13** possessed a weak intramolecular hydrogen bond. Since strong intramolecular hydrogen bonding is known to occur between *exo*-hydroxyls and *syn*-methoxyls,[16] additional evidence was provided for the position of the methoxyl function being *syn* to the carbonyl (*anti* to the double bond). The weak hydrogen bonding exhibited by **13** was consistent with that expected for an *endo*-hydroxyl intramolecularly hydrogen bonded to the norbornenyl double bond.[17]

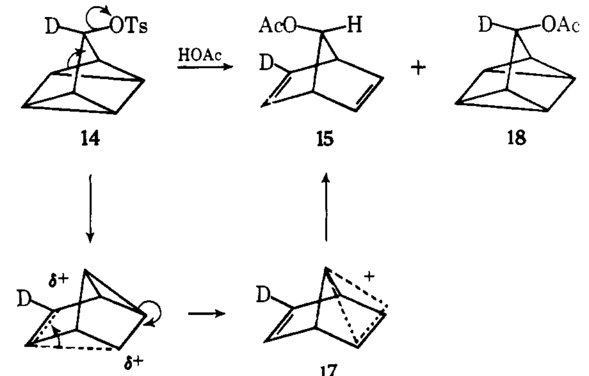


8

12 **13**

Discussion

Having unequivocally established the structure of **8**, we turned our attention to the mechanism of its formation. The rapid conversion of **1** into **8** undoubtedly occurs *via* a carbonium ion mechanism. In principle this rearrangement could have proceeded along the same mechanistic path as that suggested by Richey and Buckley[18] and by Story and Fahrenholtz[19,20] for the solvolytic conversion of quadricyclyl arenesulfonates (**14**) into norbornadienyl acetate (**15**). The use of deuterium labeling indicated that the carbon which initially bore the tosylate function became the C-2 carbon in the solvolysis product.[20] Since **15** represented 50% of the isolated product (the other 50% was **18**), and adequate mechanistic pathway would be represented by initial formation of the delocalized ion



14 **15** **18**

16 **17**

---

[12] For a discussion of W-form coupling, see J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **86**, 4074 (1964).

[13] D. H. Williams and N. S. Bhacca, *ibid.*, **85**, 2861 (1963).

[14] P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964); E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

[15] J. M. Jerkunica, S. Borčič, and D. E. Sunko, *Tetrahedron Letters*, 4465 (1965).

[16] P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **88**, 2822 (1966), and references contained therein.

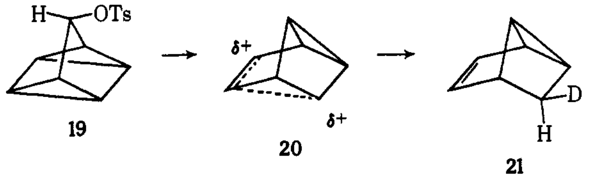
[17] For a comprehensive review of intramolecular hydrogen bonding, see M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).

[18] H. G. Richey, Jr., and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963).

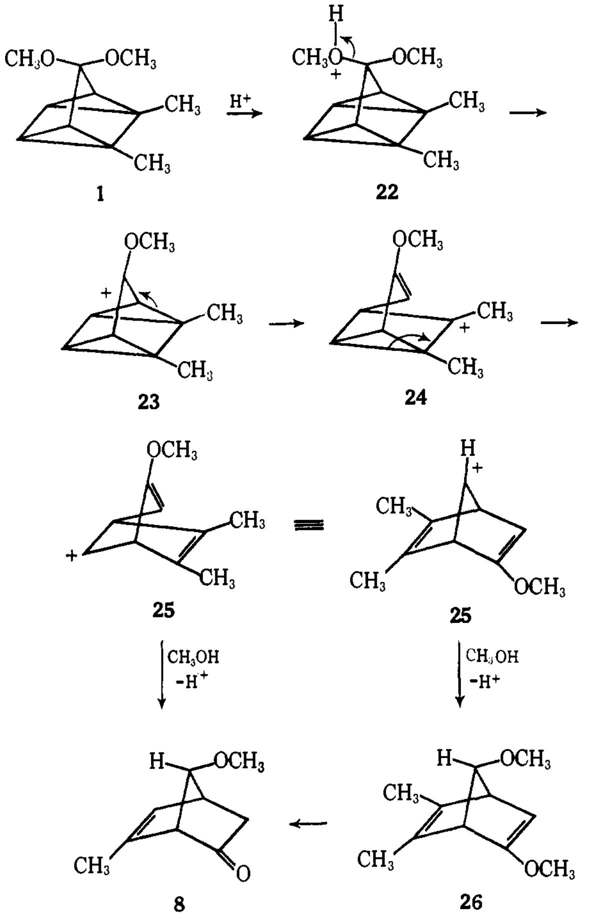
[19] P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964).

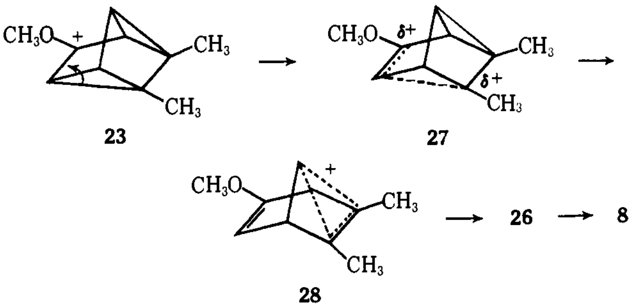
[20] P. R. Story and S. R. Fahrenholtz, *ibid.*, **88**, 374 (1966).

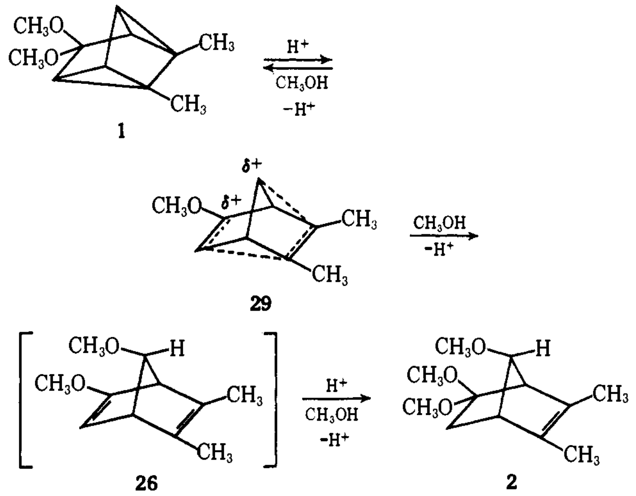
16 followed by stepwise conversion to **17**. Two discrete ions (**16** and **17**) were proposed[20] in order to explain the formation of two products and the stereospecific relationship between the deuterium and the acetate function in **17**. Borodeuteride trapping experiments gave about a 1.5% yield of **21**, also indicating the intermediacy of an ion such as **20**.[20]



In the acid-catalyzed rearrangement of **1**, we picture the initial step as protonation of the oxygen function followed by loss of methanol to yield **23**. In terms of the classical ions **24** and **25**, it is apparent that one could obtain **26**, which under the aqueous conditions of the work-up would hydrolyze the enol–ether function to yield **8**. Unfortunately these classical ions offer no satisfactory explanation of the observed stereospecific incorporation of the methoxyl function. Utilizing delocalized intermediates, the mechanistic route can be evisaged as conversion of **23** into **27**, which should be a particularly stable ion having one end of the homoallylic cation tertiary in nature and the other end stabilized by a methoxyl group. Leakage of **27** into **28** would give an ion which would add solvent to yield **26** with the requisite stereospecificity.[20,21] An alternative possibility involves direct formation of the highly delocalized ion **29**. Although orbital overlap would not be maximized in **29**, we feel that this type of ion represents a reasonable intermediate. Thus we prefer either **28** or **29** as the probable mechanistic precursor which eventually produced **8**.[22]







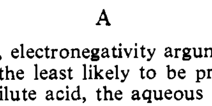
Attempts to isolate **26** were unsuccessful. However, when extremely dilute acid was used one could isolate **2**, which probably arose *via* acid-catalyzed addition of methanol to **26**.[22,23] It would be anticipated that acid-catalyzed addition of methanol to a strained vinyl ether such as is present in **26** should be extremely facile.

The exothermic rearrangement of **1** to **2** at 0° in the presence of 0.01% sulfuric acid in methanol indicates the extremely labile nature of **1**. This instability was very dependent on the presence of the two methyl groups as demonstrated by the comparative stability of quadricyclanone and quadricyclanone ketal under similar reaction conditions.[24]

---

(21) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959); S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, 77, 4183 (1955).

(22) An alternate rationale would involve initial protonation on carbon to yield the ion A. Although this would be consistent with the isolation of **2**, it requires initial protonation on the carbon adjacent to the carbon bearing the methoxyl groups. Since the methoxyl function



A

is electron withdrawing, electronegativity arguments would predict that this carbon should be the least likely to be protonated.

(23) With the very dilute acid, the aqueous work-up could be completed before significant hydrolysis of **2** had occurred.

(24) For a detailed discussion of the acid-catalyzed rearrangement of quadricyclanone and quadricyclanone ketal, see P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, **90**, 7276 (1968).

Experimental Section[25]

Materials. Hexachlorocyclopentadiene was purchased from Matheson Coleman and Bell and was used without purification. The methanol used in the rearrangement studies was Baker Analyzed Reagent which was dried according to the procedure of Fieser.[26] Sulfuric acid, 97.5% Baker Analyzed Reagent, was used as obtained.

7,7-Dimethoxy-1,2,3,4-tetrachloro-5,6-bis(methylene)bicyclo-[2.2.1]hept-2-ene (3). Hexachlorocyclopentadiene was converted into **3** *via* a three-step process involving formation of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (**30**). Diels–Alder addition of **30** with *trans*-1,4-dichlorobutene-2 to yield 7,7-dimethoxy-1,2,3,4-tetrachloro-5,6-*trans*-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (**31**), and dehydrohalogenation of **31** according to the procedure of Hoch were performed.[6]

7,7-Dimethoxy-2,3-dimethylbicyclo[2.2.1]heptadiene (4). To a stirred mixture of 37.0 g (1.61 g-atoms) of finely chopped sodium metal in 450 ml of tetrahydrofuran and 75 ml of *t*-butyl alcohol at reflux was added dropwise over a 1-hr period 16.88 g (0.0552 mol) of **3** dissolved in 100 ml of tetrahydrofuran. The reaction mixture was refluxed for 12 hr and cooled and the liquid decanted from the remaining sodium and the precipitated sodium salts. This residue was washed with petroleum ether (bp 30–60°) and the washings were added to the organic solution. Water (500 ml) was *cautiously* added to the solution. The solution was then extracted with three 200-ml portions of petroleum ether (bp 30–60°). The combined ether extracts were washed with two 250-ml portions of water and one 250-ml portion of saturated sodium chloride solution, followed by drying over anhydrous magnesium sulfate, and removal of the drying agent by filtration. After removal of the solvent by distillation, the residue was vacuum distilled to give 6.76 g (68%) of dechlorinated product, bp 84–89° (15 mm). Vapor phase chromatography showed a mixture of products consisting of 58% of **4**, 35% of **5**, and 7% of minor impurities.

Separation of the mixture was accomplished by preparative glpc on a $^3/_8$ in. × 15 ft aluminum column packed with 30% SE-30 on 60–80 Chromosorb P. An analytical sample of **3** was obtained in this manner: $n^{26}\text{D}$ 1.4731; ultraviolet end absorption, λ^{EtOH} 214 mμ (ε 1350), 210 (2000); near-infrared maximum 1.655 μ (ε 0.676).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.22; H, 8.99.

The glpc separation also gave a pure sample of **5**, $n^{25}\text{D}$ 1.4818; near-infrared absorptions at 1.637 μ ($>C{=}CH_2$) and 1.656 μ (norbornene vinylic C–H stretching overtone).[8]

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.14; H, 8.98.

Distillation of the mixture of dechlorinated products through a Nester–Faust Annular spinning-band column with a high-speed Teflon band gave **4**, bp 87.5–88.0° (16 mm), and **5**, bp 94–95° (16 mm). Material purified in this way was satisfactory for subsequent steps.

Hydrolysis of 7,7-Dimethoxy-2,3-dimethylbicyclo[2.2.1]heptadiene. To a solution of 0.115 g of **4** in 5 ml of ether was added 0.075 g of sulfuric acid in 1 ml of wet ether. After the vigorous evolution of gas had subsided the solution was washed with three 3-ml portions of water and one 3-ml portion of a saturated sodium chloride solution. The ether was removed by distillation. An infrared absorption spectrum of the residue was identical with that of an authentic sample of *o*-xylene.

Pyrolysis of 7,7-Dimethoxy-2,3-dimethylbicyclo[2.2.1]heptadiene. In a 0.25-cc Pyrex tube was placed 0.035 g of **4**. The tube was sealed under a nitrogen atmosphere and heated at 310° for 2 hr. The opening of the tube, after cooling to −78°, was accompanied by the release of considerable pressure. Analysis of the contents of the tube by glpc showed 90% *o*-xylene and 10% starting material. These products accounted for a 98% material balance.

3,3-Dimethoxy-1,5-dimethyltetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (1). In a quartz irradiation vessel was placed 3.00 g of **4**, which had been purified by distillation through a spinning-band column with a Teflon band as described above, dissolved in 1 l. of pentane. The solution was irradiated with a Hanovia 450-W medium pressure internal lamp for 1 hr with external cooling. Removal of the solvent by distillation through a helices-packed column, followed by distillation of the residue, gave 2.46 g (82%) of **1**: bp 37° (0.05 mm); $n^{30}\text{D}$ 1.4583; $\lambda_{\text{max}}^{\text{EtOH}}$ 210 mμ (ε 330); near-infrared maximum 1.668 μ (ε 1.625).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.37; H, 9.04.

Use of **4** purified by glpc or by distillation through a spinning-band column with a stainless steel band gave **1** in 38–46% yields utilizing either direct irradiation in quartz apparatus or photosensitized excitation in Pyrex apparatus with 2,4-dimethylbenzophenone as photosensitizer. Samples of **1** prepared in this manner readily isomerized back to **4** upon standing or upon distillation. Purification by low-temperature recrystallization from pentane gave white crystals, mp 18.5–19.0°.

Rearrangement of 3,3-Dimethoxy-1,5-dimethyltetracyclo[3.2.0.-$0^{2,7}$.$0^{4,6}$]heptane in 0.01% Methanolic Sulfuric Acid. To 0.508 g of **1** was added 2 ml of 0.01% methanolic sulfuric acid with stirring at room temperature. The exothermic reaction which occurred under these conditions was controlled by means of an ice–water bath. After 5 min infrared spectroscopy indicated the absence of any starting material and the presence of **2**. After 15 min water (4 ml) was added and the reaction mixture was stirred for 30 min. The solution was made basic with solid sodium bicarbonate and extracted with four 5-ml portions of ether. The combined ethereal extracts were washed with 5 ml of water and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was removed by fractional distillation. Distillation of the residue *in vacuo* gave 0.494 g (83%) of **2**, bp 57° (0.2 mm). An analytical sample was prepared by preparative glpc on a $^3/_8$ in. × 5 ft column packed with 20% 4:1 Apiezon L-KOH on 60–80 Firebrick; $n^{23}\text{D}$ 1.4708; no near-infrared absorbance due to vinyl–hydrogen stretch.

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.79; H, 9.52.

A 2,4-dinitrophenylhydrazone was prepared in the usual manner, mp 180–181°. Comparison of this derivative with the 2,4-dinitrophenylhydrazone derived from **8** (*vide post*) showed these materials to be identical, mmp 180–181°.

Reaction of 3,3-Dimethoxy-1,5-dimethyltetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]-heptane in 0.3% Methanolic Sulfuric Acid. In a 5-ml round-bottomed flask equipped with a serum cap and provision for magnetic stirring was placed 0.0081 g of concentrated sulfuric acid. The flask was cooled in an ice–water bath and 2.86 g of anhydrous methanol was added to yield 0.3% methanolic sulfuric acid (by weight). To this cold, stirred solution was added 0.547 g of **1** over a 5-min period. After 15 min infrared spectroscopy showed the complete absence of **1** and the presence of **9** as the only detectable product. After 1 hr the solution was poured into 10 ml of cold water and the resulting solution was stirred for 5 min. The reaction mixture was made basic with solid sodium bicarbonate and extracted with four 6-ml portions of ether. The ethereal extracts were combined, washed with 5 ml of water, dried over anhydrous magnesium sulfate, filtered, and concentrated by fractional distillation of the ether at atmospheric pressure. Vacuum distillation of the residue gave 0.426 g (84%) of **8**. Redistillation gave an analytical sample: bp 57–58° (0.35 mm); $n^{28}\text{D}$ 1.4781; $\lambda_{\text{max}}^{\text{EtOH}}$ 299 *m*μ (ε 487); $\lambda_{\text{max}}^{\text{cyclohexane}}$ 286 mμ (ε 386, shoulder), 294 (436), 304 (413), 316 (242).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.98; H, 8.41.

A 2,4-dinitrophenylhydrazone was prepared in the usual manner, mp 180–181°.

Anal. Calcd for $C_{16}H_{18}N_4O_5$: C, 55.48; H, 5.24; N, 16.18. Found: C, 55.58; H, 5.37; N, 16.23.

Base-Catalyzed Deuterium Exchange of *anti*-7-Methoxy-2,3-dimethylbicyclo[2.2.1]hept-2-en-5-one (8). In a stainless steel bomb was placed 0.584 g of **8** and a 6-ml portion of a solution prepared from 2.98 g of sodium methoxide, 2.8 ml of methanol-O-*d*, and 12 ml of deuterium oxide. The mixture was heated for 9 hr at 100°. After being cooled to room temperature, the reaction mixture was extracted with three 10-ml portions of ether. The extracts were combined, washed with two 5-ml portions of deuterium oxide, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the filtrate was concentrated. An analytical sample of the deuterated material was obtained *via* preparative glpc of the concentrated solution on a $^3/_8$ in. × 5 ft column packed with 20% Apiezon L-KOH on 60–80 Firebrick.

Anal. Calcd for $C_{10}H_{12}D_2O$: % excess D, 14.28. Found: % excess D, 13.65.

Lithium Aluminum Hydride Reduction of *anti*-7-Methoxy-2,3-dimethylbicyclo[2.2.1]hept-2-en-5-one (8). To a stirred slurry of 0.11 g of lithium aluminum hydride in 5 ml of anhydrous ether was added 0.265 g of **8**. After stirring for 15 min the reaction mixture

---

(25) Melting points and boiling points are uncorrected.

(26) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 289.

was hydrolyzed by dropwise addition of 0.44 ml of water. The precipitated inorganic salts were removed by filtration and the filtrate was concentrated and vacuum distilled to give 0.217 g (81%) of a mixture of the epimeric alcohols, **12** and **13**. This epimeric mixture was separated by preparative glpc on a $^3/_8$ in. × 10 ft column packed with 25% XF-1150 on 60–80 Chromosorb W.

Vacuum distillation of the sample of **12** (isolated from preparative glpc) gave an analytical sample: bp 87–88° (6 mm); $n^{22}\text{D}$ 1.4774. Near-infrared spectroscopy showed **12** to have a strong intramolecularly hydrogen-bonded hydroxyl absorption at 1.441 μ at a concentration of 0.01 *M* in carbon tetrachloride.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.18; H, 9.72.

Vacuum distillation of the sample of **13** (isolated from preparative glpc) gave an analytical sample: bp 94–96° (6 mm); $n^{22}\text{D}$ 1.4905. A 0.01 *M* solution of **13** in carbon tetrachloride showed weak intramolecular hydrogen-bonding absorption at 1.423 μ and free hydroxyl absorption at 1.410 μ.

Acknowledgment. The authors are indebted to the Petroleum Research Fund administered by the American Chemical Society for a grant which supported this research.

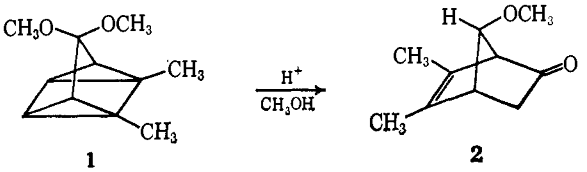
The Acid-Catalyzed Rearrangement of Quadricyclanone and Quadricyclanone Dimethyl Ketal. Product Dependency on Carbon Protonation *vs.* Oxygen Protonation

Paul G. Gassman[1] and David S. Patton[2]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received June 3, 1968*

Abstract: Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-one (quadricyclanone) and 3,3-dimethoxytetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (quadricyclanone dimethyl ketal) were prepared *via* modified literature procedures. Under acidic contions, where ketal exchange was extremely rapid, rearrangement of the quadricyclanes proceeded relatively slowly to yield *anti*-7-methoxybicyclo[2.2.1]hept-2-en-5-one, *anti*-7-methoxytricyclo[2.2.1.0^{2,6}]heptan-3-one, and *anti*-7-methoxytricyclo[2.2.1.0^{2,6}]heptan-3-one dimethyl ketal. The nature of the products obtained suggested that two different rate-determining steps were occurring, one which produced the bicyclic product, and one which yielded the tricyclic products. Since each pathway requires initial protonation, it is suggested that the products arise partially from initial protonation on oxygen and partially from initial protonation on carbon.

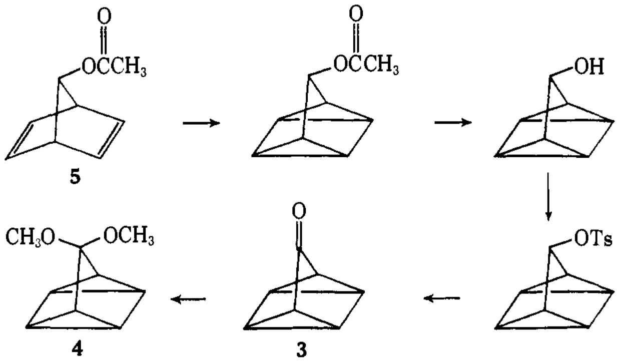
The extremely rapid, acid-catalyzed rearrangement of 3,3-dimethoxy-1,5-dimethyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**) to *anti*-7-methoxy-2,3-dimethylbicyclo[2.2.1]hept-2-en-5-one (**2**)[3] provided firm evidence for the unusually reactive character of the highly strained "quadricyclane" ring system. In addition, this reaction posed several questions concerning the related reactions of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-one (**3**)[4] and 3,3-dimethoxytetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**4**).[4] Of particular concern was the role of the methyl groups in determining both the rate and products of this rearrangement. This paper presents the details of our investigation of the acid-catalyzed reactions of **3** and **4**.



1 **2**

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-one (**3**) and its dimethyl ketal, **4**, were prepared from 7-acetoxybicyclo[2.2.1]heptadiene (**5**) by modifications[5] of procedures developed by the research groups of Richey,[6] Story,[7] and Lemal.[8] The over-all yield of **3** from **5** was 51% *via* the path outlined in Scheme I. Reaction of **3** with trimethyl orthoformate gave **4** in 87% yield. In contrast to reports in the literature[8] concerning the rapid valence tautomerization of **4** to 7,7-dimethoxybicyclo[2.2.1]heptadiene (**6**), we have found that **4** was quite stable under a broad range of conditions. In fact, numerous attempts to convert thermally **4** into **6** were unsuccessful. As reported by Lemal,[8] the

Scheme I



---

(1) Alfred P. Sloan Research Fellow, 1967–1969.

(2) Goodyear Fellow, 1966–1967.

(3) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Am. Chem. Soc.*, **90**, 7271 (1968).

(4) Compound **3** is generally referred to as "quadricyclanone" and compound **4** would be "quadricyclanone dimethyl ketal" by the same nomenclature.

(5) Since our procedures produce yields superior to those recorded in the literature and since complete experimental conditions are not to be found in the literature for these synthetic steps, we have included detailed directions for these preparations in the Experimental Section.

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

(7) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964).

(8) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965).