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}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}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

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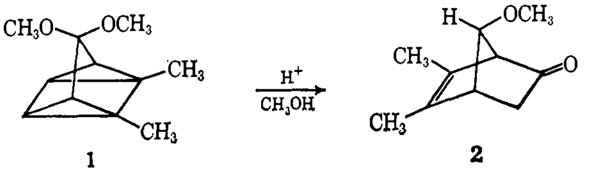
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received June 3, 1968*

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.

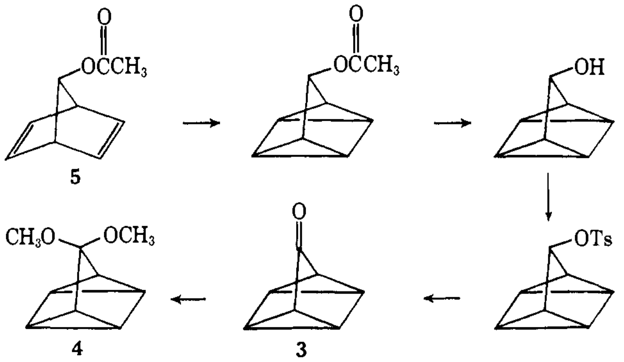
The extremely rapid, acid-catalyzed rearrangement of 3,3-dimethoxy-1,5-dimethyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**) to *anti*-7-methoxy-2,3-dimethylbicyclo[2.2.1]hept-2-en-5-one (**2**)[3] provided firm evidence for the unusually reactive character of the highly strained "quadricyclane" ring 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



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[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.

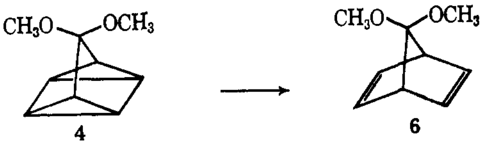
[5] Since our procedures produce yields superior to those recorded in the literature and since complete experimental conditions are not to be found in the literature for these synthetic steps, we have included detailed directions for these preparations in the Experimental Section.

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

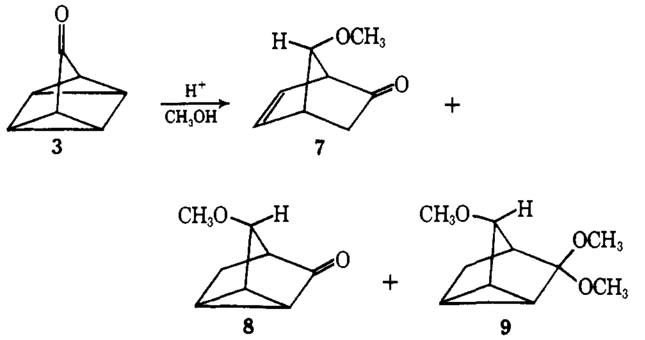
[7] P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964).

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

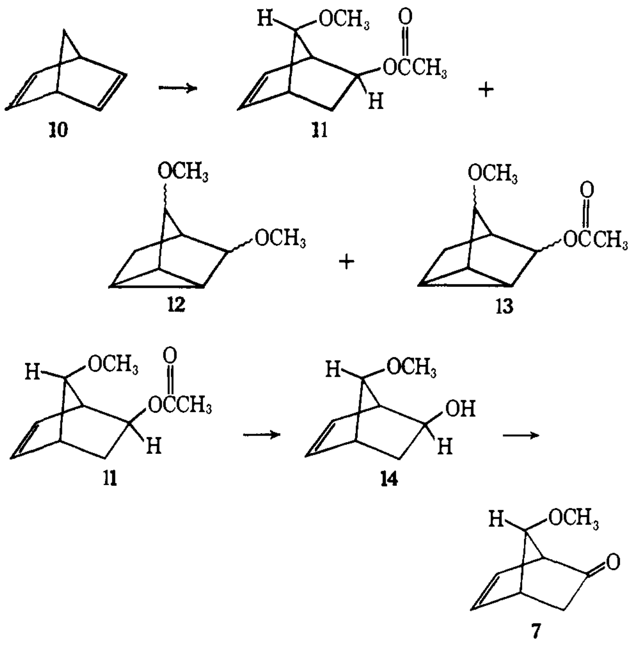
stability of **4** was quite dependent on the history of the sample. We have found that the critical historical aspect was whether or not the diene precursors of **4** had been exposed to metal surfaces at elevated temperatures. The role of metal complexes of norbornadiene in catalyzing the conversion of quadricyclanes to norbornadienes has recently been discussed.[9,10] Indeed, the stability of pure **4** was such that dichloro(bicyclo[2.2.1]heptadiene)palladium (II) was required as a catalyst in order to obtain **6**.



When **3** was exposed to methanolic sulfuric acid it underwent a slow reaction to yield a mixture of *anti*-7-methoxybicyclo[2.2.1]hept-2-en-5-one (**7**), *anti*-7-methoxytricyclo[2.2.1.$0^{2,6}$]heptan-3-one (**8**), and *anti*-7-methoxytricyclo[2.2.1.$0^{2,6}$]heptan-3-one dimethyl ketal (**9**). It should be noted at this point that **7** has its methoxyl group "*syn*" to the carbonyl function while **8** and **9** have their 7-methoxyl group "*anti*." This factor has a significant bearing on the mechanistic details of their formation. Under the reaction conditions **8** and **9** were equilibrated, and both components of the equilibrium mixture were stable to the reaction conditions. Unfortunately **7** was unstable under the reaction conditions, being slowly converted to high molecular weight, nonvolatile products. Thus the optimum yield of **7** is not known.[11] The same rearrangement products were obtained with **4** as the starting material.



The structure proof of compounds **7**, **8**, and **9** was based on both spectroscopic and chemical evidence. The origin of the chemical correlation of the reaction products with known compounds came from the investigations of Alder and coworkers,[12] who studied the lead tetraacetate oxidation of bicyclo[2.2.1]heptadiene (**10**) in methanol. This reaction was reported[12] to yield **11**, **12**, and **13**. Repeating Alder's procedure we obtained **12** as the major product, with the additional formation of small amounts of isomerically pure **11** and **13** (a mixture of three isomers). Lithium aluminum hydride reduction of **11** gave **14**. In addition to correct analytical data, **14** showed near-infrared absorptions at 1.657 μ (ϵ 0.520), characteristic of a norbornene olefinic C–H stretching overtone,[13] and at 1.442 μ (0.01 *M* in CCl_4), characteristic of a strong intramolecularly hydrogen-bonded hydroxyl absorption.[14] In agreement with Alder's postulated structure for **11**, the presence of the strong intramolecular hydrogen bond demonstrated the *syn–exo* nature of the substituents. Oxidation of **14** with Sarett reagent[15] gave a sample of **7** identical in all respects with that obtained from the rearrangement of **3**.



Spectroscopic evidence for the structure of **7** was in complete agreement with the chemical proof. The near-infrared spectrum of **7** had a maximum at 1.654 μ (ϵ 0.595) consistent with the presence of two norbornenyl vinyl hydrogens.[13] The ultraviolet spectrum, taken in cyclohexane, showed maxima at 296 mμ (ϵ 215), 306 (253), and 328 (144), consistent with the anomalous spectra expected of bicyclo[2.2.1]hept-2-en-5-one derivatives.[3,16] The important aspect of the nmr spectrum was the 2-cps coupling between the hydrogen at C-7 and the *endo* hydrogen at C-6. This W-form coupling places the hydrogen at C-7 *syn* to the double bond.[17] Hence the structure of **7** was firmly established.

The structure proof of **8** was considerably more complex than that used for **7**. As noted (*vide supra*) the lead tetraacetate oxidation of bicyclo[2.2.1]heptadiene in methanol gave a mixture of three isomeric tricyclic methoxy acetates. Since these components were not readily separated on a preparative scale, the mixture was reduced with lithium aluminum hydride to yield **15**, **16**, and **17**. The hydroxy ether **15**, being strongly intramolecularly hydrogen bonded, was readily separated from a mixture of **16** and **17**. Near-infrared

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(9) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967).

(10) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967).

(11) The instability of 7 is probably related to that of the very reactive 2-acetoxybicyclo[2.2.1]heptan-7-one which decomposes in the presence of acid, base, or heat to give aldehydic products which self-condense. For a leading reference, see P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966).

(12) K. Alder, F. H. Flock, and H. Wirtz, *Ber.*, **91**, 609 (1958).

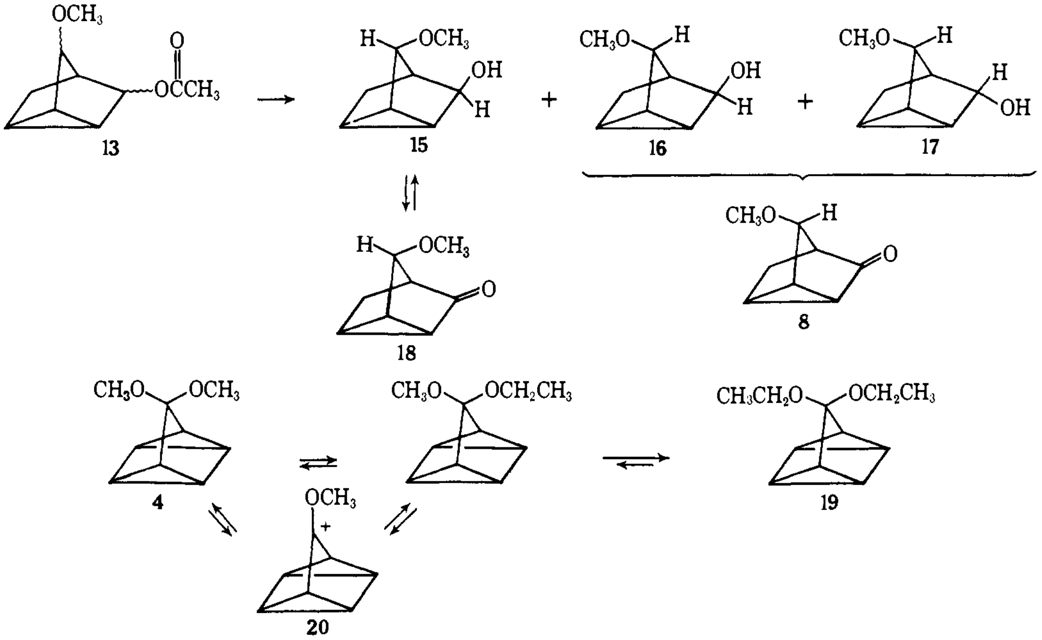
(13) P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965).

(14) For a comprehensive review of intramolecular hydrogen bonding, see M. Tichý, *Advan. Org. Chem.*, **5**, 115 (1965).

(15) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(16) A. Moscowitz, K. Mislow, M. A. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962).

(17) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964).



absorption at 1.660 μ (ε 1.278) showed that the basic skeleton was a tricyclo[2.2.1.0^{2,6}]heptane.[13] An absorption at 1.46 μ (0.011 *M* in CCl_4) showed that only intramolecularly hydrogen bonded hydroxyl was present, thus establishing that the methoxyl function was *syn* to the *exo*-hydroxyl group. Oxidation of **15** *via* the procedure of Meinwald and coworkers[18] gave **18**. Lithium aluminum hydride reduction of **18** gave back pure **15**.

Since **16** and **17** could not be separated by distillation or preparative vpc, the mixture was oxidized to yield **8**. This oxidation product was identical in all respects with the sample of **8** obtained from **3**. Near-infrared maxima at 1.651 μ (ε 0.980) and 1.657 (1.132) were consistent with its being a derivative of tricyclo[2.2.1.0^{2,6}]heptan-3-one.[13] The lack of intramolecular hydrogen bonding in the mixture of **16** and **17** proved that the methoxyl group at C-7 was *anti* to the hydroxyl function. Since reduction of **8** with lithium hydride regenerated a mixture of **16** and **17**, these alcohols must have been epimeric at C-3. Thus either **16** or **17** must have had an *exo*-hydroxyl function which would have been intramolecularly hydrogen bonded had the methoxyl group been *syn* to the carbonyl group in **8**.

Discussion of Results

In many respects the acid-catalyzed rearrangement of **4** bears close resemblance to the acid-catalyzed rearrangement of **1**. Both occur in dilute methanolic sulfuric acid and both yield derivatives of bicyclo[2.2.1]hept-2-en-5-one. However, the rearrangement of **1** to **2** in 0.01% methanolic sulfuric acid occurred *at least* 10^5 times faster than the rearrangement of **4** in 0.1% methanolic sulfuric acid. In addition to yielding a bicyclic product, **4** gave tricyclic products which were stereochemically and structurally unrelated to the bicyclic product. This indicated the presence of more than one mechanistic route for the acid-catalyzed rearrangement of **4**.

In order to establish the mechanism of these conversions we investigated several aspects of the reaction of **4** with dilute acid. We had previously postulated that **1** rearranged *via* initial protonation on oxygen. Although it seemed likely that protonation on oxygen and loss of methanol from **4** and from **1** would occur at comparable rates, we felt that it was essential to establish that **4** was being rapidly protonated on oxygen. The ketal, **4**, was stable in very pure ethanol. When a trace of acid was added to the ethanolic solution, **4** *was equilibrated with* **19** *in less than 90 sec at room temperature*. Hence, **4** did undergo rapid protonation followed by loss of methanol to yield the ion **20**. It appears that **20** readily reacted with solvent to eventually yield **19** in preference to rearranging. It could also be shown that **3** reacted rapidly with alcohols in the presence of acid. In pure ethanol **3** gave λ_{max} 295.5 mμ (ε 57). When a trace of acid was added, the n–π* absorption of **3** was completely gone in less than 100 sec.[19] Thus we had established that both **3** and **4** were rapidly protonated.

In order to ensure that **4** was not being converted to **6** under the reaction conditions with subsequent addition of methanol to **6** to give the observed product, we investigated the reaction of **6** with methanolic sulfuric acid. When **6** was exposed to the reaction conditions at room temperature it was completely converted to benzene. Thus **6** was not an intermediate in the reaction of **4** with acid.

Undoubtedly, in methanol containing catalytic amounts of acid, both **3** and **4** were converted to **20**. By analogy to the mechanism postulated for the rearrangement of **1**, **20** could slowly be converted to either **21** or **22**, which would eventually yield **7**.[20]

The mechanistic path from either **3** or **4** to **8** presents an interesting problem. Under the reaction conditions,

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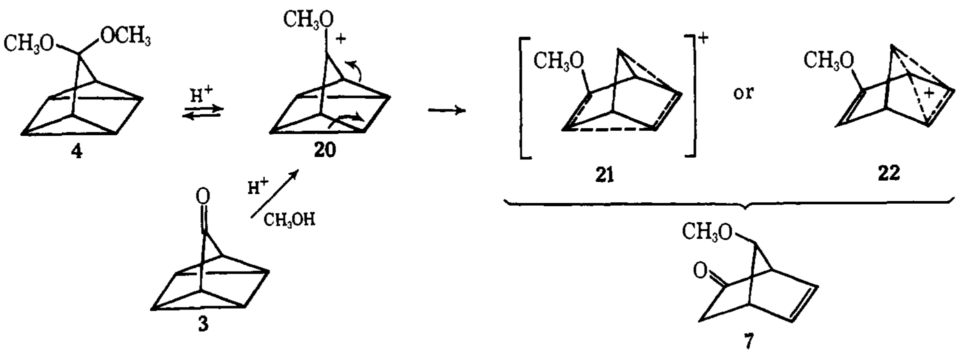
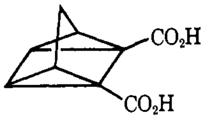
(18) J. Meinwald, J. Crandall, and W. Hymans, *Org. Syn.*, **45**, 77 (1965).

(19) Upon prolonged standing the ultraviolet spectrum indicated the presence of trace amounts of benzene. The presence of benzene was confirmed by vpc. It is felt that the benzene probably arises from small amounts of norbornadiene derivatives which are derived from 3.

(20) A less pleasing alternate explanation would involve protonation on the carbon adjacent to the ketal carbon. Since the methoxyls are electron withdrawing, electronegativity arguments would suggest that this protonation would be unlikely at this position. For a more detailed discussion of this argument see ref 3.





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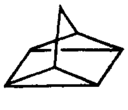

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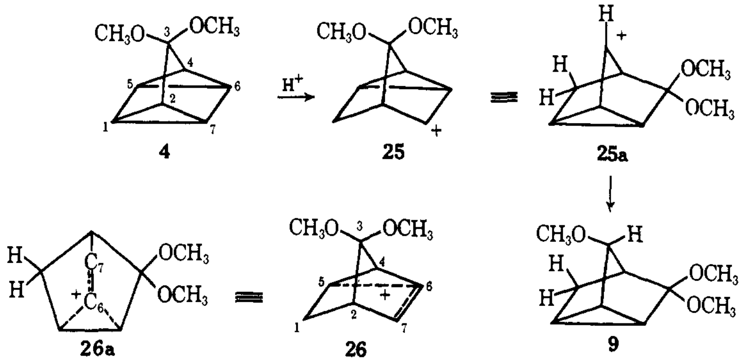
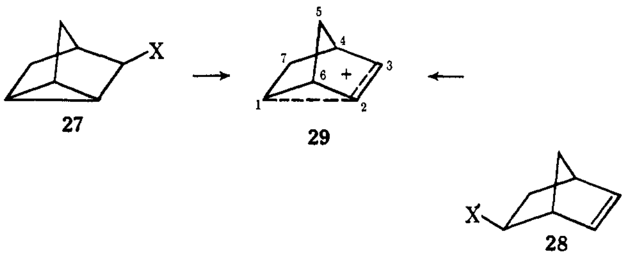


7 and 8 were not interconvertible. In addition, the mechanistic precursors postulated for 7 could not reasonably yield 8 since the stereochemistry of the C-7 methoxyl group in 7 was opposite of that found in 8. It seemed apparent that 8 must have arisen by some mechanism which did not involve initial formation of 20 *via* protonation on oxygen.

The conversion of 4 into an equilibrating mixture of 8 and 9 can occur *via* electrophilic attack on the quadricyclane molecule. Cristol and LaLonde have shown[21] that the quadricyclane derivative 23 yields only a tricyclo[2.2.1.0^{2,6}]heptane derivative on ionic addition of bromine. In contrast, Dauben and Cargill have stated[22] that the parent compound, 24, adds bromine to give dibromides of both tricyclo[2.2.1.0^{2,6}]heptane and bicyclo[2.2.1]heptene. On the basis of these two examples it seems that the nature of the products of electrophilic addition is quite dependent on the nature of the substituents.

In our case we feel that the initial step in the mechanistic path from 4 to 8 and 9 involved protonation at C-1 to yield the cation 25. In line with the well-known ability of a cyclopropyl group to stabilize a neighboring carbonium ion[23] it would be anticipated that there would be some delocalization of the positive charge into positions C-4 and C-5 as shown in 26.[24] We observed no products which would result from nucleophilic attack by solvent at either C-4 or C-5. This indicated to us that relatively little charge resides at either C-4 or C-5. Previous work on the cation derived from both nortricyclyl and 5-norbornenyl derivatives supports this postulate.[23,25,26] Both 27 and 28 yield the same product mixtures with the vast majority of the product resulting from attack at C-3 of 29. By analogy the majority of the attack on 25 (or 26) would be expected to occur at C-7.



The only remaining question involves the stereospecificity of the nucleophilic attack at C-7. In order to establish that the addition was stereospecific, the epimer of 8, 18, was submitted to the reaction conditions. It was recovered unchanged, showing that if any 18 had been formed in the reaction it would have been detected. Having established that solvent addition occurred stereospecifically from the side opposite of the ketal group, we explored the reason for this specificity.

Recent work on MeO-4 neighboring group participation has shown that electronic interaction of a neighboring methoxyl group results in the transfer of the methoxyl function.[27] This would give products

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[21] S. J. Cristol and R. T. LaLonde, *J. Am. Chem. Soc.*, **80**, 4355 (1958).

[22] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

[23] J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Am. Chem. Soc.*, 77, 3034 (1955).

[24] In view of the difference in the inductive effects felt by C-4 and C-5, less positive character should be associated with C-4 than with C-5.

[25] For a detailed discussion of these studies, see S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962), and references contained therein.

[26] Since our yield left considerable amounts of starting material unaccounted for, it is possible that some product was formed from attack at C-4 and C-5 of 26, but that these products were unstable under the reaction conditions.

[27] P. G. Gassman and J. L. Marshall, *Tetrahedron Letters*, 2429 (1968).

with stereochemistry opposite of that observed. This indicated that the ketal methoxyl group was not participating in the rearrangement of **4**. Since the ketal was not electronically involved *via* participation, it must have been sterically involved. As can be seen from either **25a** or **26a**, the cation would be relatively symmeterical were it not for the presence of the methoxyl groups at C-3. Since one side of C-7 was sterically shielded while the other side was relatively unhindered, it was reasonable that attack should occur to yield **9**, which requires that the attacking methanol and from the least hindered side.

On the basis of the findings discussed above, we feel that **4** was converted into the observed rearrangement products *via* two different mechanistic routes, one of which involved initial protonation on oxygen, and the other of which involved initial protonation on carbon.

Experimental Section[28]

7-Acetoxybicyclo[2.2.1]heptadiene (5). The diene **5** was prepared according to the method of Story.[29] A near-infrared absorption at 1.652 μ (ϵ 1.351) was observed for **5**.

3-Acetoxytetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (30). In an irradiation vessel equipped with a quartz probe was placed 13.77 g (0.0915 mol) of **5** and 2740 ml of pentane.[30] Prior to use, the quartz probe was cleaned by rinsing with 50% aqueous hydrofluoric acid and then thoroughly rinsing with water. The solution was irradiated for 2 hr with a Hanovia 450-W medium pressure arc. The probe was recleaned, as described above, and the irradiation was continued for an additional 2 hr. The irradiation mixture was then stirred vigorously with 50 ml of saturated aqueous silver nitrate to remove any unreacted **5**. The pentane solution was decanted from the aqueous solution and precipitated silver complex. The nondecanted material was washed twice with 100-ml portions of pentane and the pentane solutions were combined. The organic solution was dried over anhydrous magnesium sulfate, filtered, and the solvent distilled off. The residue was distilled *in vacuo* to yield 12.44 g (90%): bp 72° (6 mm); near-infrared 1.657 μ (ϵ 3.070). On cooling, this material crystallized to give a white solid, mp 33–35° (lit.[6] mp 33–35°).

3-Hydroxytetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (31). To a cold stirred slurry of 1.27 g of lithium aluminum hydride in 100 ml of anhydrous ether was added 9.06 g of **30** dissolved in 30 ml of anhydrous ether. The mixture was stirred at room temperature for 15 min and then cooled to 0°. Water (5.1 ml) was added dropwise with cooling. The precipitated inorganic salts were removed by filtration and the filtrate was concentrated by distillation. The residue was vacuum distilled to give 5.99 g (92%) of **31**: bp 78° (10 mm) (lit.[6] bp 52° (2 mm)); n^{29}D 1.5152; near-infrared 1.660 μ (ϵ 2.464).

3-Tosyloxytetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (32). To a cold stirred solution of 12.04 g of **31** dissolved in 100 ml of dry pyridine was added 31.8 g of *p*-toluenesulfonyl chloride over a 30-min period. The solution was let stand at −12° for 12 hr. The reaction mixture was poured into a slurry of 100 ml of concentrated hydrochloric acid and 500 g of ice. The precipitate was collected by filtration and then dissolved in methylene chloride. The resulting solution was dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator. The oily residue was crystallized from a pentane–methylene chloride mixture in a low-temperature recrystallization apparatus to give 21.06 g (72%) of white crystalline **32**, mp 65–67°.

Tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptan-3-one (3). Nitrogen was bubbled through a mixture of 5 g of sodium bicarbonate and 90 ml of dry dimethyl sulfoxide and the solution was heated to 100°. While maintaining the reaction mixture at 100°, 4.00 g of **32** dissolved in 10 ml of dry dimethyl sulfoxide was added rapidly. After 4.5 min the reaction mixture was poured onto 300 g of ice. Two additional 4.00-g runs were made and the resulting aqueous solutions were combined and continuously extracted with pentane for 64 hr. The pentane extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed by distillation. The residue was vacuum distilled to give 4.11 g (85%) of **3**: bp 46° (1 mm) (lit.[7,8] bp 50–55° (2 mm)); near-infrared, 1.653 μ (ϵ 3.090).

3,3-Dimethoxytetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane[8] (4). A solution of 3.00 g of **3**, 3.90 g of trimethyl orthoformate, and 0.032 g of *p*-toluenesulfonic acid in 5 ml of anhydrous methanol was stirred at room temperature for 9 hr. Sodium methoxide (11 mg) was added to the deep violet solution. The solution was concentrated by distillation under reduced pressure to give 3.73 g (87%) of **4**: bp 63° (2 mm); n^{23}D 1.4793; near-infrared absorption 1.659 μ (ϵ 3.010). This material was quite stable.[8]

Dichloro(bicyclo[2.2.1]heptadiene)palladium(II). Norbornadiene was allowed to react with dibenzonitrile dichloropalladium(II) according to published procedures.[31]

7,7-Dimethoxybicyclo[2.2.1]heptadiene[8] (6). A solution of 0.512 g of **4**, 0.016 g of dichloro(bicyclo[2.2.1]heptadiene)palladium(II) complex, and 3 ml of chloroform was stirred at room temperature for 8 hr. The solution was concentrated by distillation at atmospheric pressure and the residue was distilled *in vacuo* to give 0.340 g (66%) of **6**: bp 49–50° (7 mm); n^{28}D 1.4692; near-infrared absorption 1.653 μ (ϵ 1.237).

Reaction of Tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptan-3-one (3) with Methanolic Sulfuric Acid. In a 5-ml round-bottomed flask, equipped with provisions for magnetic stirring and a serum cap to exclude moisture, was placed 2.0 ml of methanolic sulfuric acid of the desired concentration which had been prepared by mixing sulfuric acid (Baker 97.5%) with the required amount of anhydrous methanol (Baker AR distilled from magnesium turnings). To this stirred solution was added 0.500 g of **3** at ice bath temperatures. The solution was stirred at ambient temperature for the specified time (Table I) and poured into 4.0 ml of water. After 15 min the solution was made basic with solid sodium bicarbonate and extracted with 5-ml portions of ether. The ethereal extracts were combined, washed with 5 ml of water, dried over anhydrous magnesium sulfate, filtered, and concentrated by distillation at atmospheric pressure. Distillation *in vacuo* of the residue gave a mixture of products, bp 40–46° (0.3 mm). The products were analyzed by analytical vpc on an Aerograph Model 600 with a Honeywell Brown recorder equipped with disk integrator using a Hewlett-Packard high efficiency packed column, $^1/_8$ in. × 6 ft stainless steel packed with 5% SE-30 on 80–100 Diatoport S. Corrections for the relative signal response were made using methyl *p*-bromobenzoate as an internal standard. Preparative vpc ($^3/_8$ in. × 5 ft copper column packed with 30% DEGS on 60–80 Chromosorb P) was used to obtain isolated yields. The isolated compounds were identified by comparison of spectral properties with authentic samples. It was found that **3** was isomerized to bicyclo[3.2.0]hepta-3,6-dien-2-one (**33**) during preparative vpc and yields of unrearranged **3** were based upon the amount of isomerized **33** collected or detected.

Table I. Acid-Catalyzed Rearrangement of **3**

Initial acid concn, wt %	Time, hr	Yield, %	Product composition, % 7	**8** + **9**	Method of analysis
11	1.5	32[a]	41[b]	59	Vpc
11	286	33	5[b]	95	Isolated
0.5	1678	33	18	82	Vpc
0.1	1776	33[a]	16	84	Vpc
0.1	1776	20[a]	16	84	Isolated

[a] In these reactions considerable starting material was detected (as **33**). Yields were based on unrecovered starting material. [b] Prolonged reaction times led to the decomposition of 7 decreasing both the ratio of 7 to **8** and **9** and the over-all yield.

Reaction of 3,3-Dimethoxytetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (4) with Methanolic Sulfuric Acid. In a 5-ml round-bottomed flask equipped with provisions for magnetic stirring and a serum cap to exclude moisture was placed 2.0 ml of methanolic sulfuric acid solution. The solution was cooled by means of an ice–water bath (omitted for 0.5 and 0.1% sulfuric acid reactions). The ketal **4** (0.500 g) was added over a period of 5 min. After 30 min, the

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(28) Melting points and boiling points are uncorrected.

(29) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(30) When solutions more concentrated than the above were irradiated, the yield was lowered and product purity was reduced.

(31) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

Table II

Initial acid concn, wt%	Time, hr	Total yield,[a] %	Product compn, %		Recovered starting material (as **33**)	Method of analysis
			7	**8** + **9**		
10	1.0	30	27	73	30	Vpc
11	1.5	24	38	62	14	Vpc
11	1.5	25	26	74	23	Vpc
11[b]	1.5	49	40	60	10	Vpc
11[b]	1.5	39	34	66	2	Isolation
10	28.0	32	11	89	0	Vpc
0.5	48.0	48	12	88	0	Vpc
0.5	48.0	43	11	89	4	Isolation
0.1	1776.0	47	6	94	0	Vpc
0.1	1776.0	43	7	93	0	Vpc

[a] Yields based on unrecovered starting material. [b] The reaction mixture was not initially cooled.

cooling bath was removed and the solution was stirred for the remaining time at room temperature. Water (6 ml) was added. After 15 min the solution was made basic with solid sodium bicarbonate and extracted with four 6-ml portions of ether. The ethereal extracts were combined, washed with 6 ml of water, dried over anhydrous magnesium sulfate, filtered, and concentrated by distillation at atmospheric pressure. Distillation *in vacuo* gave a product mixture, bp 46–56° (0.3 mm), which was analyzed according to the methods described for the reactions of **3** with methanolic sulfuric acid. The results are shown in Table II.

From the reaction of **4** with 0.1% methanolic sulfuric acid for 74 days was isolated (by preparative vpc) an analytical sample of **9**: bp 58° (0.6 mm); n^{27}D 1.4626; near-infrared absorption 1.660 μ (ϵ 1.260).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.38; H, 8.75.

A 2,4-dinitrophenylhydrazone was prepared in the usual manner, mp 161–163°. Comparison of this derivative with that derived from **8** showed them to be identical, mmp 161–163°.

Reaction of Norbornadiene (10) with Lead Tetraacetate. The reaction was carried out according to the procedure of Alder and coworkers[12] using 37.8 g of norbornadiene, 197.5 g of lead tetraacetate (G. Frederick Smith Chemical Co.), and 500 ml of methanol. The resulting product was fractionated on a Nester-Faust spinning-band column with a stainless steel band (28 theoretical plates), giving 36.8 g of 3,7-dimethoxytricyclo[2.2.1.$0^{2,6}$]heptane (**12**) (unknown stereochemistry), 5.1 g of a mixture of *exo*-5-acetoxy-*anti*-7-methoxybicyclo[2.2.1]hept-2-ene (**11**) and 3-acetoxy-7-methoxytricyclo-[2.2.1.$0^{2,6}$]heptane isomers (**13**), and 4.2 g of pure **13**.

Purification of *exo*-5-Acetoxy-*anti*-7-methoxybicyclo[2.2.1]hept-2-ene (11). Alumina (200 g of Baker Activity I) and 20 ml of saturated silver nitrate solution were combined and shaken until homogeneous. A chromatographic column was packed with this material using hexane as solvent. On this column was placed a distillation fraction (5.083 g) from the reaction of norbornadiene and lead tetraacetate which contained **11** (identified by infrared bands at 5.72 and 14.00 μ). The column was pressurized and eluted rapidly with three 500-ml portions of hexane which upon concentration afforded 3.903 g of **13**. Elution with two 500-ml portion of benzene–hexane (25:75%) and one 500-ml portion of benzene–hexane (50:50%), concentration of the combined fractions by distillation at atmospheric pressure, and distillation of the residue *in vacuo* gave 1.111 g of **11**, bp 87° (3 mm); n^{22}D 1.4700; near-infrared 1.657 μ (ϵ 0.656).

***exo*-5-Hydroxy-*anti*-7-methoxybicyclo[2.2.1]hept-2-ene (14).** Reduction of **11** by means of lithium aluminum hydride as described below for **13** gave **14** in 72% yield. An analytical sample was prepared by preparative vpc (3/8 in. × 5 ft copper column packed with 20% 4:1 Apiezon L-KOH on 60–80 Firebrick): bp 84° (15 mm); n^{26}D 1.4774; near-infrared 1.657 μ (ϵ 0.520), 1.442 (0.585, *c* 1.02 *M*), 1.412 (0.157, *c* 1.02 *M*), and 1.442 (very broad, *c* 0.01 *M*). No absorption around 1.41 μ was observed at a concentration of 0.01 *M*.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.47; H, 8.64.

***anti*-7-Methoxybicyclo[2.2.1]hept-2-en-7-one (7).** A solution of 0.764 g of **14** dissolved in 5 ml of pyridine was added to the complex formed from 1.64 g of chromium trioxide and 10 ml of pyridine. After being stirred for 6 hr the mixture was poured into 100 ml of water and continuously extracted with pentane for 60 hr. The extract was concentrated by distillation at atmospheric pressure and the pyridine was removed by neutralizing the residue with cold 50% hydrochloric acid and then rapidly extracted with four 20-ml portions of pentane. The pentane extracts were combined, washed with saturated sodium bicarbonate, dried over anhydrous magnesium sulfate, filtered, and concentrated by distillation at atmospheric pressure. Distillation of the residue *in vacuo* gave 0.263 g (35%) of **7**: n^{24}D 1.4807; λ_{max}^{EtOH} 298 mμ (ϵ 233); $\lambda_{max}^{cyclohexane}$ 286 mμ (shoulder ϵ 154), 296 (215), 306 (253), and 328 (144); near-infrared 1.654 μ (ϵ 0.595).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.51; H, 7.38.

This material was identical in all respects with the sample of 7 obtained from the rearrangement of **3** and **4**.

Reduction of 3-Acetoxy-7-methoxytricyclo[2.2.1.$0^{2,6}$]heptane (13). To a cold stirred slurry of 1.58 g (0.164 equiv) of lithium aluminum hydride and 100 ml of anhydrous ether was added a solution of 10.00 g of a mixture of **13**. The resulting mixture was stirred at room temperature for 1 hr, cooled in an ice–water bath, and hydrolyzed with 6.32 ml of water. The inorganic salts were removed by filtration and washed thoroughly with ether. The filtrate was concentrated by distillation at atmospheric pressure and the residue was distilled *in vacuo* to give 7.38 g (96%) of a mixture of **15**, **16**, and **17**, 30–60° (0.1 mm). The mixture was separated by preparative vpc (3/8 in. × 10 ft copper column packed with 25% XF-1150 cyanosilicone on 60–80 Chromosorb W at 150°).

An analytical sample of **15** (shorter retention time) was prepared by vpc and subsequent distillation: bp 35° (0.1 mm); n^{28}D 1.4742; near-infrared 1.660 μ (ϵ 1.278), 1.463 (broad, *c* 0.574 *M*), and 1.46 (broad, *c* 0.011 *M*). No absorption was observed at 1.41 μ at a concentration of 0.011 *M*.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.52; H, 8.53.

An analytical sample of **16** and **17** (unresolved mixture with longer retention time) was prepared by vpc and subsequent distillation: bp 60° (0.1 mm), n^{23}D 1.4942; near-infrared 1.662 μ (ϵ 1.203, *c* 0.831 *M*) and 1.412 (*c* 0.01 *M*). No absorption of bonded O–H was observed at a concentration of 0.01 *M*.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.29; H, 8.52.

Preparation of 8 and 18. Jones chromic acid oxidation of a mixture of **15**, **16**, and **17** according to the procedure used by Meinwald and coworkers[18] for the oxidation of nortricyclanol yielded a mixture of **8** and **18** in 62% yield, bp 62–64° (0.9 mm). The mixture was separated by preparative vpc (3/8 in. × 10 ft copper column packed with 19% Carbowax 20M on 60–80 Chromosorb W at 150°).

An analytical sample of **8** (shorter retention time) was prepared: n^{22}D 1.4827; λ_{max}^{MeOH} 278 mμ (ϵ 61); near-infrared 1.651 μ (ϵ 0.980) and 1.657 (1.132).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.33; H, 7.25.

A 2,4-dinitrophenylhydrazone was prepared in the usual manner, mp 161–163°.

Anal. Calcd for $C_{14}H_{14}N_4O_5$: C, 52.83; H, 4.43; N, 17.60. Found: C, 52.7; H, 4.41; N, 17.55.

An analytical sample of **18** (longer retention time) was prepared: n^{24}D 1.4845; near-infrared 1.648 μ (ϵ 0.795) and 1.659 (1.010).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.30; H, 7.25.

Reduction of *anti*-7-Methoxytricyclo[2.2.1.0^{2,6}]heptan-3-one (8). Lithium aluminum hydride reduction of pure **8** gave a mixture of **16** and **17** in 89% yield.

Reduction of *syn*-7-Methoxytricyclo[2.2.1.0^{2,6}]heptan-3-one (18). Lithium aluminum hydride reduction of pure **18** gave pure **15**. Identification was made by a comparison of infrared spectra and vpc retention times.

Reaction of 7,7-Dimethoxybicyclo[2.2.1]hepta-2,5-diene (6) with Methanolic Sulfuric Acid. The ketal **6** (194 mg) was treated with 10% methanolic sulfuric acid for 21 hr at room temperature. Hydrolytic work-up as described for reactions of **4** gave benzene and no residue after removal of ether and benzene by distillation at reduced pressure.

Equilibration of 3,3-Dimethoxytetracyclo[2.2.0.0^{2,7}.0^{4,6}]heptane (4) with Ethanol *via* Acid Catalysis. A sample of 177 mg of **4** was dissolved in 249 mg of dry ethanol (distilled from magnesium ethoxide). The nmr spectrum was recorded and showed the spectrum of **4** superimposed on the spectrum of ethanol. The triplet observed for ethanol's hydroxyl proton demonstrated that the sample was acid free.

A solution was prepared from 19 mg of sulfuric acid and 3.34 g of dry ethanol, and 86 mg of this solution was added to the nmr tube containing **4** and ethanol. The tube was shaken vigorously and the nmr spectrum was recorded (total elapsed time 100 sec).

In addition to showing the simplified ethanol spectrum (due to acid-catalyzed exchange of the hydroxyl proton), the spectrum showed a drastic decrease in the relative intensity of the absorption due to the dimethyl ketal and the presence of a new absorption due to methanol. This spectrum of equilibrated material did not undergo further change on rerunning.

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The Solvolysis of Triaryliodoethylenes. Structure and Selectivity of Vinyl Cations

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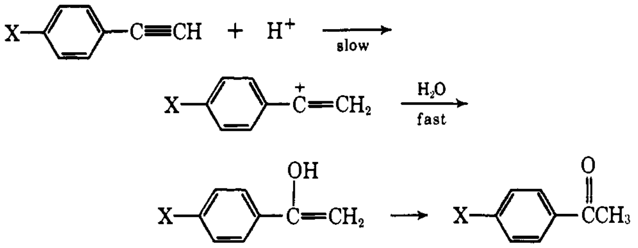
Abstract: Several triaryliodoethylenes have been synthesized from the triaryl olefins *via* bromination to the triarylbromoethylenes, followed by the formation of the vinyl Grignard reagent and reaction of this reagent with iodine. In aqueous dimethylformamide it is found that these vinyl iodides solvolyze to iodide ion and the substituted benzhydryl phenyl ketone by an SN1-type mechanism. The rate of appearance of iodide ion was (1) directly dependent on initial reactant concentration, (2) approximately first order in reactant, (3) not enhanced by added nucleophiles, (4) depressed in one case by the addition of a common ion iodide salt, (5) sensitive to substituents on the α-phenyl group. For the solvolysis of 2,2-diphenyl-1-anisyliodoethylene, $\Delta H^{\ddagger} = 23.5$ kcal/mol, $\Delta S^{\ddagger} = -16.3$ eu, and k_{-1}/k_2 (for rate depression by iodide at 130.5°) was approximately 40. A $\rho = -3.6$ was computed from the rates of solvolysis of 2,2-diphenyl-1-aryliodoethylenes at 189.5 and σ^+ constants. These data are consistent with formation of an intermediate vinyl cation with extensive delocalization of the positive charge into the α-phenyl ring. A comparison of the rates of 1,2,2-triphenyliodoethylene and 1,2-diphenyl-2-anisyliodoethylene shows little acceleration by the *p*-methoxy group. This and other data suggest that a structure of the type $R_2C^+\ddot{C}R$ is a relatively unimportant resonance contributor to the structure of the triphenylvinyl cation. Depression of the 2,2-diphenyl-1-anisyliodoethylene solvolysis rate by iodide ion is indicative of a relatively stable and selective intermediate cation. Reactant stabilization is, therefore, suggested as the major reason for the notoriously slow solvolysis of vinyl halides compared to alkyl halides.

Vinyl cations have been proposed as intermediates in a number of organic reactions. One reaction type for which these proposals have been substantiated is electrophilic addition to acetylenic or allenic bonds,[2-7] as in hydrations, brominations, and addition of hydrogen halides.

$$E^+ + RC{\equiv}CH \longrightarrow R\overset{+}{C}{=}CHE$$

$$E^+ + CH_2{=}C{=}CH_2 \longrightarrow ECH_2\overset{+}{C}{=}CH_2$$

Typical mechanistic results implicating vinyl cation intermediates were found, for example, in a thorough investigation of the sulfuric acid catalyzed hydration of phenylacetylene.[6] Noyce and coworkers measured secondary hydrogen isotope effects and the influence of substituents and the acidity of the medium on the rate of hydration. The data were consistent with a mechanism involving a rate-determining protonation of the terminal acetylenic carbon. The vinyl cation formed in this step is then rapidly trapped with water, leading to the enol of acetophenone and, hence, acetophenone itself.



The ρ value determined from a correlation of the re-

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[1] National Aeronautics and Space Administration Trainee, 1967–1969.

[2] D. S. Noyce, M. A. Matesich, and P. E. Peterson, *J. Amer. Chem. Soc.*, **89**, 6225 (1967), and early studies referenced there.

[3] P. E. Peterson and J. E. Duddey, *ibid.*, **88**, 4990 (1966), and the extensive list of papers cited there.

[4] R. C. Fahey and D. J. Lee, *ibid.*, **89**, 2780 (1967).

[5] P. E. Peterson and R. J. Bopp, *ibid.*, **89**, 1284 (1967).

[6] D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020, 1023 (1968).

[7] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Chem. Soc.*, 384 (1965).