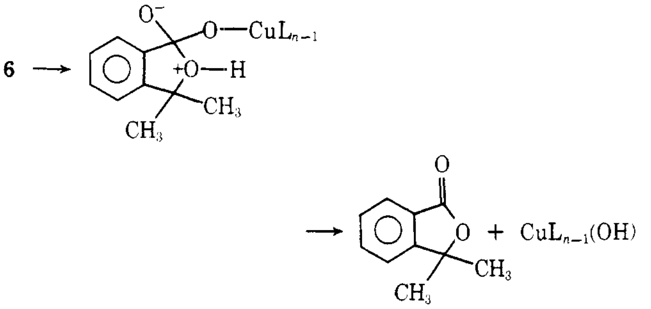
$$CuL_n + RCO_2^- \rightleftharpoons CuL_{n-1}(O_2CR) + L$$

6



However, rates are slower than in unbuffered solutions of comparable copper concentration even though the buffer components are known to catalyze cyclization of the hydroxy acid. Additionally, the pH of the unbuffered solutions (5.8–6.3) is greater than that of the buffered solutions (4.74) and hence cannot account for the increased reactivity in unbuffered media. The rate suppression in buffered media follows from the increased amount of free uncomplexed hydroxy acid and hydroxy acid salt in the buffered medium. In the absence of buffer, more substrate is complexed with copper and hence faster rates are observed.

In contrast, lactonization rates of **4** are faster in buffered media (Figure 2) and rate plots give nonlinear behavior as a function of copper concentration. This is attributed to the presence of significant buffer catalysis in the buffered medium. Such buffer catalysis apparently contributes less to the overall lactonization rate of **3** than for **4**. In general, the effect of carrying out studies in buffered media is to partially obscure the metal ion promoted reaction. Studies show less spectacular catalysis in lactonization of **2** and **5** which are less well aligned for cyclization.

The mechanism suggested is similar to the microscopic reverse of the process proposed by Buckingham for the recently observed metal-catalyzed hydrolysis of propionic anhydride.[5] Our results suggest that copper and zinc ions can promote analogous esterifications when aqueous equilibria strongly favor the synthesis side of the reaction.

Experimental Section

Preparation of Hydroxy Acid Salts. General Procedure. A given amount of the appropriate lactone was saponified by refluxing with 1.05 equiv of potassium hydroxide in methanol. The solvent was removed in vacuo and the dry salt was used for rate measurements.

Preparation of Lactones. The lactones employed were all prepared using literature procedures. Phthalide was prepared by zinc reduction of phthalimide.[6] 3-Methylphthalide was prepared by sodium borohydride reduction of *o*-acetylbenzoic acid. 3,3-Dimethylphthalide was prepared by reaction of methylmagnesium iodide with diethyl phthalate.[7] 1,8-Naphthalide was prepared by cleavage of acenaphthenequinone with potassium hydroxide followed by reduction of the 1,8-naphthaldehydic acid with formaldehyde.[8] 4,4-Dimethylhydrocoumarin was prepared by acid-catalyzed reaction of phenol and methyl 3-methyl-2-butenoate.[9]

Kinetic Procedure. A solution of appropriate concentration of a given hydroxy acid salt in methanol was prepared. Injection of a 0.01-mL aliquot of this solution into a temperature equilibrated cuvette in a constant temperature compartment of a Cary 15 or Gilford 240 spectrophotometer initiated the kinetic run. Changes in absorbances at a given wavelength were monitored as a function of time. Substrate concentrations were typically 10^{-4}–10^{-5} M. Rate constants were calculated by the usual least-squares procedure. For the copper-promoted reactions, rates were monitored at 280–285 nm. At higher copper concentrations, this region becomes obscured by absorbance due to copper. At the copper concentrations employed, rates could be conveniently monitored at these wavelengths. For compounds **4** and **5**, decreases in absorbances were observed as a function of time (disappearance of the copper complex) while **2** and **3** led to absorbance increases. Upon completion of a kinetic run, the spectrum was identical with that of corresponding lactone solutions prepared independently.

Other copper(II) salts also promoted lactonization. However, precipitation of copper(II) hydroxides interferes with spectral measurements and rate determinations. In cupric acetate media or copper(II) sulfate in acetate buffered media, precipitation of copper(II) hydroxides did not present a problem. The following wavelengths were used for monitoring lactonization rates for copper-promoted reactions: **2**, 280 nm; **3**, 283 nm; **4**, 285 nm; **5**, 282 nm. Zinc sulfate promoted reactions of **4** were monitored at 240 nm.

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Registry No.—**3**, 61490-94-6; **4**, 61490-95-7.

References and Notes

(1) (a) D. R. Storm and D. E. Koshland, *J. Am. Chem. Soc.*, **94**, 5805, 5815 (1972); (b) S. Milstein and L. A. Cohen, *ibid.*, **94**, 9158 (1972); (c) K. N. G. Chrong, S. D. Lewis, and J. A. Shafer, *ibid.*, **97**, 418 (1975); (d) J. F. Bunnett and C. F. Hauser, *ibid.*, **87**, 2214 (1965); (e) R. T. Borchardt and L. A. Cohen, *ibid.*, **94**, 9175 (1972); (f) C. Danforth, A. W. Nicholson, J. C. James, and G. M. Loudon, *ibid.*, **98**, 4275 (1976); (g) R. E. Winans and C. F. Wilcox, Jr., *ibid.*, **98**, 4281 (1976).

(2) (a) D. P. Weeks and X. Creary, *J. Am. Chem. Soc.*, **92**, 3418 (1970); (b) N. Tomoto, W. J. Boyle, Jr., and J. F. Bunnett, *J. Org. Chem.*, **37**, 4315 (1972).

(3) (a) H. Kroll, *J. Am. Chem. Soc.*, **74**, 2036 (1952); (b) M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957); (c) J. I. Hoppe and J. E. Prue, *J. Chem. Soc.*, 1775 (1957); (d) M. D. Alexander and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 1130 (1966).

(4) The structure of the complex represented by **7** may be analogous to polymeric copper benzoate in which carboxylate is coordinated to two copper atoms. See M. Inove, M. Kishita, and M. Kubo, *Inorg. Chem.*, **4**, 626 (1965).

(5) D. A. Buckingham and L. M. Engelhardt, *J. Am. Chem. Soc.*, **97**, 5915 (1975).

(6) "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 526.

(7) B. B. Elsner, H. E. Strauss, and E. J. Forbes, *J. Chem. Soc.*, in press.

(8) R. C. Fuson and G. Munn, *J. Am. Chem. Soc.*, **71**, 1870 (1949).

(9) M. Julia, M. M. Baillargé and G. Tchernoff, *Bull. Soc. Chim. Fr.*, 776 (1956).

Interconversions in Pentamethylbicyclo[3.2.0]- and Bicyclo[2.2.1]heptadienyl Cations

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Recently several communications have dealt with the properties and rearrangements of polymethylbicyclo[3.2.1]octadienyl[1] and -[2.1.1]hexenyl[2] cations. In view of the intriguing interconversions within these ions we were interested to learn about the behavior of carbonium ions, which are intermediate between these types as far as the number of skeleton carbon atoms is concerned—seven instead of eight and six, respectively—viz., the polymethylbicyclo[3.2.0]- and -[2.2.1]heptadienyl cations. In the present publication the results of a study of the pentamethyl derivatives are reported.

Reduction of ketone **1**[3] with LiAlH$_4$ gave in good yield (77%) the crystalline secondary alcohol **2**. Upon ionization of **2** in

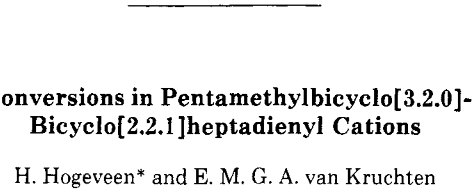
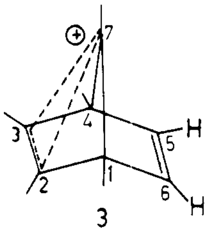
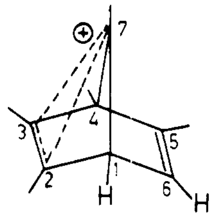
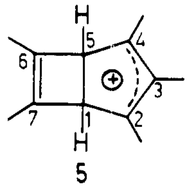
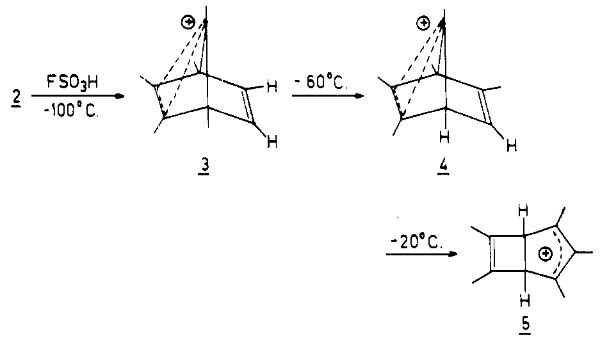


Table I. ^{1}H NMR[a] and ^{13}C NMR[b] Chemical Shifts[4]

		C-1,4	C-2,3	C-5,6	C-7
 3	^{1}H NMR	1.70	2.17	5.92	1.33
	^{13}C NMR, CH_3	9.9	10.9		1.6
	^{13}C NMR, ring C	68.8	133.0	129.8	75.4
 4	^{1}H NMR	4.34 (H), 1.64 (CH_3)	2.17/2.26	5.70 (H), 1.87 (CH_3)	1.44
	^{13}C NMR, CH_3	8.6	11.2/12.3	14.6	4.7
	^{13}C NMR, ring C	75.0/71.1	140.5/135.0	130.8/118.7	63.2
		C-1,5	C-2,4	C-6,7	C-3
 5	^{1}H NMR	4.65	2.90	1.90	2.15
	^{13}C NMR, CH_3		11.8	23.6	10.4
	^{13}C NMR, ring C	68.5	234.5	139.5	155.8

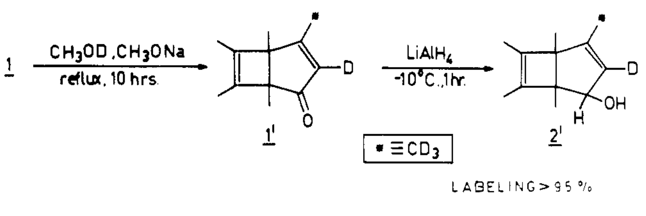
[a] Measured relative to internal CH_2Cl_2 (δ 5.30). [b] Measured relative to internal CD_2Cl_2 (δ 53.16).

FSO_3H/SO_2ClF at −100 °C, a carbonium ion was generated to which we assign structure **3**. Warming up this solution to −60 °C caused an irreversible rearrangement of ion **3** into ion **4**, which has an additional stabilization because of a higher alkyl-substituted double bond. The thermodynamically most stable ion **5**, in which the double bond is completely alkyl substituted, was finally formed when the solution of **4** was warmed to −20 °C.



The assignments of structures **3, 4,** and **5** are based on NMR spectroscopic evidence, as summarized in Table I.

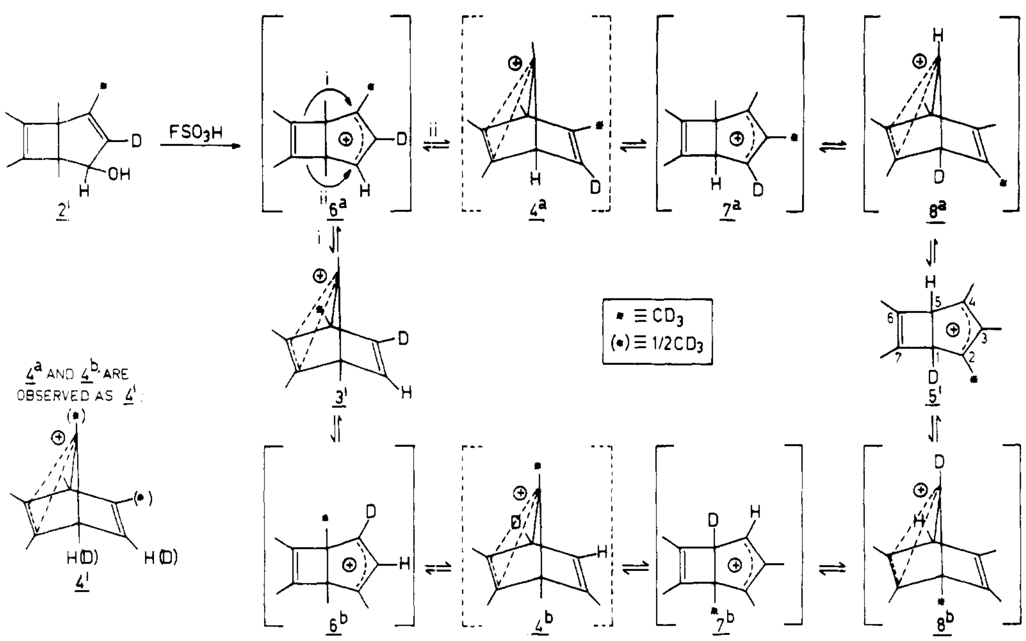
The two hydrogen atoms appeared to be good labels to test the mechanism for the interconversions of these carbonium ions. Additional affirmation was obtained by the use of the labeled alcohol **2′**, which was prepared from compound **1** by the sequence **1** → **1′** → **2′**. The interconversions are in accord with a mechanism involving a stepwise circumambulatory motion of five carbon atoms (C-1,4,5,6,7 in **3**) with respect to the remaining two carbon atoms (C-2,3 in **3**) analogues to the one Winstein observed in 7-norbornadienyl cations.[5] The ions **3′, 4′,** and **5′**[6] showed the correct areas for the ^{1}H NMR signals, which confirms the proposed mechanistic sequence. Remarkably, none of the intermediate carbonium ions which have a hydrogen at a positively charged carbon atom is observed (**6, 7, 8,** and their deuterated analogues). An explanation for the kinetic formation of ion **3** in preference to ion **4** is the stabilizing effect of three methyl groups on the positive charge in the transition state A, that belongs to the conversion **6** → **3** (path i) as compared to that of two methyl groups in the transition state B for the conversion **6** → **4** (path ii). The effect of the number of methyl groups on the stability of protonated cyclopropane rings has recently been summarized by Brouwer and Hogeveen.[7] The difference in thermodynamic stability between ions **3** and **4** is due to the different number of alkyl substituents at the C=C bond whereas the difference between ions **4** and **5** not only resides in that factor, but also in the different geometry and, as a consequence, the different strain of the [2.2.1] vs. the [3.2.0] carbon skeleton.[8] The results are finally drawn schematically in the free-enthalpy diagram.

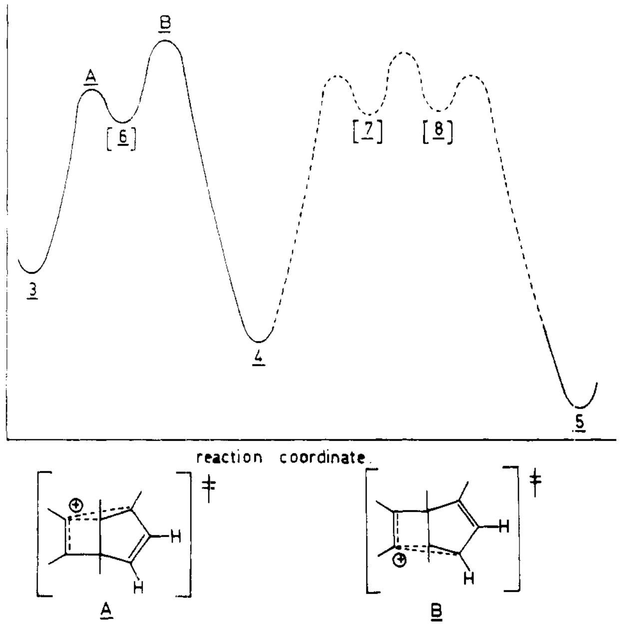


Experimental Section

General. The IR spectra were taken on a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained on a AEI MS-902 by Mr. A. Kiewiet. Proton magnetic resonance spectra were recorded using Varian A-60D or JEOL C-60HL spectrometers equipped with variable temperature probes and tetramethylsilane (δ 0.00) as internal standard (unless otherwise stated). Natural abundance carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were obtained with a Varian XL-100 spectrometer operating at 25.2 MHz. Spectra were recorded with the use of Fourier transform and were proton-noise decoupled. We thank Drs. W. Mellink for assistance in recording the ^{13}C spectra.

Generation of Carbonium Ions in Strong Acid Media. No attempt will be made to detail all the procedures used. One of the most satisfactory techniques is described below.





In a typical experiment 80 mg of FSO_3H was brought into a dry, clean ^1H NMR tube at −115 °C followed by condensation of SO_2ClF (about 0.35 mL). With the aid of a cooled glass rod 30 mg of precursor was introduced and the obtained mixture homogenized. Appropriately larger amounts were used for the ^{13}C NMR than for the ^1H NMR spectra.

1,2,5,6,7-Pentamethylbicyclo[3.2.0]hepta-2,6-dien-4-ol (2). To a stirred solution of 500 mg of ketone 1 in 25 mL of ether (freshly distilled from $LiAlH_4$), cooled to −10 °C, was slowly added 45 mg of $LiAlH_4$. This mixture was stirred for 1 h at −10 °C. After warming up to 0 °C a 20% NaOH solution and a 20% NH_4Cl solution were simultaneously added dropwise. After filtration the ether layer was washed with water untill neutral and dried ($CaCl_2$). The solvent was removed in vacuo using a rotary evaporator. The resulting white crystals were recrystallized from pentane (−30 °C) to give 381 mg (77%; one major stereoisomer) of **2**: IR 3320 cm^{-1} (broad); ^1H NMR (CCl_4) δ 5.00 (1 H, C-3, broad m), 4.07 (1 H, C-4, broad m), 1.65 (3 H, C-2 methyl, d, $J = 1.5$ Hz), 1.54 (6 H, C-6 and C-7 methyls), 1.08 and 0.93 (3 H each, C-1 and C-5 methyls), 1.01 (1 H, OH); mass spectrum parent peak *m/e* 178; correct elemental analysis.

1,5,6,7-Tetramethyl-2-trideuteriomethyl-3-deuteriobicyclo[3.2.0]hepta-2,6-dien-4-ol (2'). A solution containing 1 g of ketone 1 and 50 mg of CH_3ONa in 10 mL of CH_3OD was refluxed overnight. The methanol was evaporated under reduced pressure and the solid residue was treated with water and extracted with CH_2Cl_2. The organic layer was washed with water until neutral and dried over $MgSO_4$ and the solvent was removed in vacuo using a rotatory evaporator, giving a nearly quantitative yield of **1'**. Compound **1'** was treated with $LiAlH_4$ as described for ketone **1**, affording alcohol **2'**, whose ^1H NMR spectrum differed from that of **2** by lacking the hydrogen signal at δ 5.00 (due to hydrogen at C-3) and the allylic methyl signal at δ 1.65 (due to the C-2 methyl). Mass spectrum parent peak *m/e* 182.

Registry No.—**1**, 15971-77-4; **1'**, 61463-56-7; **2**, 61463-57-8; **2'**, 61463-58-9; **3**, 61505-78-0; **4**, 61505-77-9; **5**, 61463-63-6; CH_3OD, 1455-13-6.

References and Notes

(1) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **98**, 1551 (1976), and references cited therein.

(2) H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975), and references cited therein.

(3) H-N. Junker, W. Schäfer, and H. Niedenbrück, *Chem. Ber.*, **100**, 2508 (1967).

(4) For comparison with similar carbonium ions see N. C. Deno in "Carbonium Ions", Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., , 1970, p 796; D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, **91**, 261 (1972); R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2347 (1972); G. A. Olah and L. A. Paquette, *J. Org. Chem.*, **40**, 700 (1975).

(5) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2347 (1972).

(6) In ion **5** the CH_3 signal at δ 2.90 is observed as a doublet ($J = 1.4$ Hz). This is due to a coupling between the bridgehead hydrogen at C-1 (or C-5) and the CH_3 group at C-4 (or C-2), and not to a coupling between the hydrogen at C-1 (or C-5) and the CH_3 group at C-2 (or C-4). It is substantiated by the fact that in ion **5'** there is no such coupling.

(7) D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **91**, 179 (1972).

(8) H. Hogeveen, C. F. Roobeek, and H. C. Volger, *Tetrahedron Lett.*, 221 (1972).

A Proposed Experimental Model for Molecular Orbital Calculations on Aryl Cations

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A proposal, made 15 years ago, that the phenyl cation may exist as the σ,π triplet diradical 1 in its ground state[1,2] has now been examined by several molecular orbital methods. Extended Hückel,[3] INDO (with and without geometry optimization),[4,5] CNDO/S–CI,[6] and ab initio[7,8,9] calculations all