and the error by

$$\sum_{1}^{n} \frac{(kn - ka)}{n}$$

Product Analysis. This was performed by nmr using a CAT, triggering from internal tetramethylsilane. The purity of each acetate (**16**- and **17**-OAc) was determined by scanning the methyl resonances (τ 7.78 and 8.07, respectively) 100 times. The amount of **17**-OAc in the sample of **16**-OAc used was shown to be less than 0.25% by cutting and weighing the appropriate peaks. Likewise **17**-OAc contained less than 0.25% **16**-OAc and less than 0.5% of either **16**-OH or **17**-OH. The latter was determined by scanning the *H*-COR resonances. These same signals were used to estimate the ratio of **16**-OH and **17**-OH present upon solvolysis of the acetates in aqueous acetone. The OMe resonances of the methoxy ethers obtained upon methanolysis of the acetates were used in the same manner. The error in the analyses is ±0.25%. Results are given in Table III.

Solvolysis of 16-OAc in 80% Acetone. The cis acetate (**16**-OAc) (23 mg) dissolved in acetone (4 ml) treated with saturated sodium bicarbonate solution (1 ml) was heated at 75° in an ampoule for 21 hr. The solution was poured into water (25 ml) and extracted with ether (two 15-ml portions), the combined extracts being washed with water (20 ml). Removal of the ether gave 20.5 mg of residue which was dissolved in CS_2 for nmr analysis with the CAT–TMS trigger.

Methanolysis of 16-OAc. The cis acetate (**16**-OAc) (22 mg) was dissolved in methanol[46] (5 ml), with sodium bicarbonate (100 mg) added, heated at 100° for 10 hr in an ampoule, and worked up in a similar manner to that described above to give 16 mg of recovered material, which was dissolved in CS_2 for assay.

(46) E. C. Evans and A. G. Knox, *J. Amer. Chem. Soc.*, **73**, 1739 (1951).

Solvolysis of 17-OAc in Aqueous Acetone. The trans acetate (**17**-OAc) (21 mg) in 6 ml of 80% acetone–20% water with sodium bicarbonate (100 mg) was heated at 100° for 9 days in an ampoule and worked up as previously described giving 16.5 mg (93.5%) of alcohols, **16**- and **17**-OH.

Methanolysis of 17-OAc. The trans acetate (**17**-OAc) (26 mg), sodium bicarbonate (100 mg), and anhydrous methanol[46] (8 ml) were heated at 100° for 18 days and worked up as before giving 20 mg (86%).

Product Analysis of 7-Acetoxy-1,2;5,6-dibenzocycloheptа-1,3,5-triene. The acetate **20**-OAc (51 mg) was heated in 12 ml of 80% acetone–20% water and sodium bicarbonate (13 mg) at 50° for 12 hr and worked up as described before; 40 mg of **20**-OH was obtained with nmr and ir spectra identical with an authentic sample.

Product Analysis of 7-Acetoxy-1,2;5,6-dibenzocycloheptа-1,5-diene. The acetate (**21**-OAc) (50 mg) in 10 ml of 80% acetone–20% water with sodium bicarbonate (130 mg) was heated at 100° for 18 hr and worked up as described above to recover 42 mg of **21**-OH with nmr and ir spectra identical with authentic material, melting point, and mixture melting point, 88–89°.

The Formation and Quench of the Dibenzohomotropylium Ion. Cis alcohol (**16**-OH) (25 mg) was dissolved in the minimum amount of methylene chloride added to concentrated sulfuric acid (0.5 ml) at room temperature. The mixture was stirred and the two layers allowed to separate and the organic layer was removed. The nmr spectrum indicated essentially complete formation of the homotropylium ion. The sulfuric acid solution was slowly added to a rapidly stirred suspension of sodium bicarbonate (4 g) in methanol (30 ml) at −78°. After warming to room temperature the methanol was poured into water (100 ml) and the products were extracted into ether (20 ml). The ether layer was washed with water (two 50-ml portions) and dried over potassium carbonate. Evaporation gave 21 mg of an oil which was assayed by nmr as before.

Acknowledgment. We are grateful to Dr. Richard Leute and Dr. George Levy for assistance in some phases of the above research.

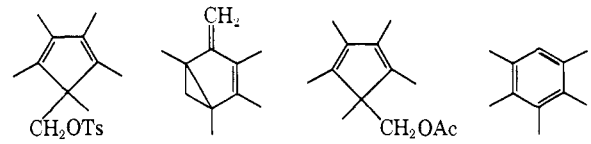
1-Isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene. Synthesis and Reactions

R. H. Chung,[1] Grace J. Lin,[1] J. M. Nicholson, Anna Tseng,[1] O. Tucker,[1] and J. W. Wheeler*[2]

Contribution from the Department of Chemistry, Howard University, Washington, D. C. 20001. *Received October 16, 1970*

Abstract: Dehydration of the isomeric umbellulols **5** and **6** gives 1-isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**). Acetolysis of diene **7** produces the bicyclic acetates **9** and **10** as well as the cyclopentadienylmethyl acetate (**11**) under more drastic conditions. Under acidic conditions, diene **7** gives a mixture of *p*- and *m*-cymene. This system is contrasted to the analogous pentamethylcyclopentadienylmethyl system studied by Winstein and Battiste.

Winstein and Battiste[3] have reported the acetolysis of pentamethylcyclopentadienylmethyl *p*-toluenesulfonate (**1**) gives predominantly olefin **2** and only a small amount of acetate **3**. On standing, **2** adds acetic acid, **3** becoming the major component of the mixture. Pentamethylbenzene (**4**) was not observed except under more vigorous acidic conditions, when it then became the major product.



1 2 3 4

Treatment of the bicyclic umbellulols **5** (and/or **6**)[4] with dimethyl sulfoxide at elevated temperatures gives 1-isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**) as well as ketone **8**[5] if oxygen is not excluded from the

(1) Abstracted from the M.S. Theses of R. H. Chung, 1968, Grace J. Lin, 1969, Anna Tseng, 1970, and Otis Tucker, 1971.

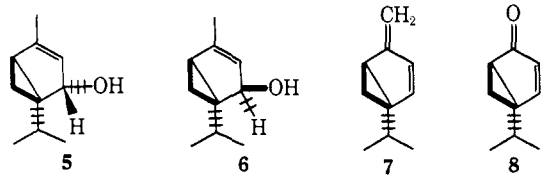
(2) Author to whom correspondence should be addressed.

(3) S. Winstein and M. Battiste, *J. Amer. Chem. Soc.*, 82, 5244 (1960); L. de Vries, *ibid.*, **82**, 5242 (1960); R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968).

(4) J. W. Wheeler and R. H. Chung, *J. Org. Chem.*, **34**, 1149 (1969).

(5) The structure of the α,β-unsaturated ketone 8 was confirmed by converting it to diene 7 by a Wittig reaction. Ketone 8 is an air-oxidation product of diene 7 and may be prepared in that manner.

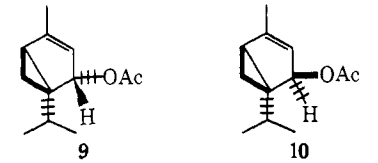
reaction. The products of acetolysis of diene **7** provide a striking contrast to the analogous reaction of **2**.



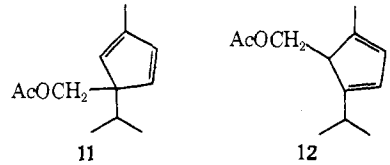
5 **6** **7** **8**

Acetolysis of diene **7** in acetic acid containing sodium acetate at room temperature gave three products (**9**, **10**, and **11**) in the ratio 2.2:3.4:1 in addition to starting diene. At 10° only two acetates (**9** and **10**) were formed in a ratio of 1:1.75.

The structures of **9** and **10** were established by synthesis from the corresponding alcohols **5** and **6**. Treatment of either alcohol with sodium acetate in acetic anhydride at 50° gave stereospecifically the corresponding acetate **9** or **10** plus unreacted alcohol. At 90° a mixture of acetates was formed from either pure alcohol, **10** predominating in both cases. At 125°, only diene **7** and a third acetate **11** were found in the reaction mixture.



9 **10**



11 **12**

The structure of **11** is based upon its infrared and pmr spectra and analytical data for $C_{12}H_{18}O_2$. None of **12** was found in any reaction mixture.[6] Acetate **11** exhibits absorption at 12.48 μ in its infrared spectrum indicative of a cis disubstituted double bond as well as two nonequivalent saturated methyl groups, a singlet for the methylene group adjacent to the oxygen, and three vinyl protons in its pmr spectrum. The nonequivalence of the isopropyl methyl groups indicates that an asymmetric carbon atom is proximate in accord with structure **11**.

The preference for bicyclic acetates **9** and **10** over cyclopentadienylmethyl acetate (**11**) is in striking contrast to the results of Winstein.[3] Addition of acetic acid to diene **2** would produce a tertiary allylic acetate which might not survive under these conditions. Although diene **2** is converted to acetate **3** easily even at room temperature (20 hr), acetate **11** is a minor product in our system at room temperature and at 10° it is not found.

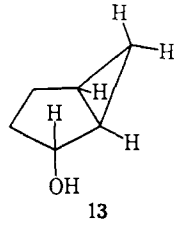
Equilibrium studies of the individual components of our system indicate that acetates **9** and **10** rapidly form a kinetic equilibrium mixture with diene **7**. In this mixture **10** predominates over **9** in a ratio of 3:2 and this ratio remains constant as **11** is formed. Ultimately (24 days) **11** becomes the major product.[6]

(6) Dimers of **12** (and/or **11**) may be present but were not isolated. Longer reaction times resulted in the diminution of **11** and formation of higher molecular weight materials. Chromatography of **11** gave similar materials.

Thus, although **11** is the thermodynamic product of the reaction, the formation of acetates **9** and **10** provides an alternate pathway in our system which is not important for **2**. Since the ratio of **10**:**9** remains constant as **11** is formed, it appears that **11** is produced from a common intermediate (*i.e.*, the allylic cation) rather than from **9** and/or **10** themselves. Although **11** might be derived from diene **7** directly, the equilibrium studies do not support this assumption.

The slight preference for acetate **10** over acetate **9** is understood on the same basis that **5** is preferred over **6** in reduction[4] of umbellulone. The stereochemistry of these two alcohols was assigned originally on the basis of Dreiding models which indicate slightly more steric hindrance by the cyclopropyl group than by the isopropyl group. The preference of **10** over **9** is in accord with the results of that reduction. The major alcohol from the reduction becomes the minor acetate in the acetolysis of diene **7** while the minor alcohol becomes the major acetate in that acetolysis. The major alcohol elutes faster from the column and is converted to diene **7** faster. We have assigned structure **5** to major alcohol and **6** to minor[4] on the basis of additional pmr and chemical evidence.

The highest absorption for the major umbellulol is at δ −0.15, apparent t, J = 3.5 Hz, with additional cyclopropyl absorption at 0.85. The highest absorption in the minor umbellulol occurs at 0.55. Dauben and Wipke[7] have studied a series of bicyclic cyclopropyl compounds containing hydroxyl groups. Their results indicate that those compounds which have the cyclopropyl and hydroxyl groups cis have absorptions for the 6-exo and 6-endo protons at lower fields than those where the cyclopropyl and hydroxyl are trans. In such systems the 6-endo proton normally absorbs at higher fields than the 6-exo. Berson and Hasty[8] assign the absorption at −0.15 to the 6-endo proton and the absorption at 0.92 to the 6-exo proton for **13**. Our coupling constant is only consistent with the trans arrangement[7] of bridgehead and 6-endo proton. The appearance of the 6-endo proton as an apparent triplet appears inconsistent with the reported[7] negative coupling constant for geminal protons on a cyclopropane ring. However, diene **7** as well as acetate **9** also exhibit an apparent triplet in this region at 0.50, J = 3.5 Hz, and a coupling of ~2 Hz is reported for the 6-endo and 6-exo protons in **13**.

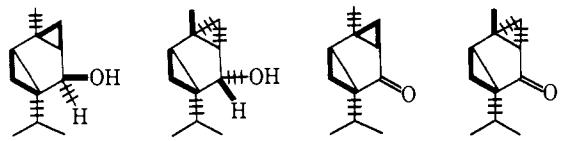


13

A chemical confirmation of this assignment of isomers was obtained by converting the two umbellulols **6** and **5** to the tricyclic alcohols **14** and **15** using a Simmons–Smith reaction. Oxidation of **14** and **15** gave two different tricyclic ketones, **16** and **17**, one of which, **17**, was identical with the tricyclic ketone obtained by Eastman[9] from a Michael addition to umbellulone.

(7) W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967).
(8) J. A. Berson and N. M. Hasty, Jr., *J. Amer. Chem. Soc.*, **93**, 1549 (1971).

Since Dauben[10] has shown that the Simmons–Smith reaction stereospecifically introduces a cyclopropyl ring on the same side as the hydroxyl group and neither **16** nor **17** was contaminated by the other ketone, a chemical confirmation of the pmr assignment results.

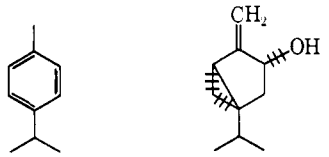


14 15 16 17

Although the endo bicyclic alcohol predominates in hydride reduction of the unsubstituted bicyclic ketone,[8] the bridgehead isopropyl group in umbellulone provides enough steric hindrance so that the exo umbellulol is the major product.

Action of Dimethyl Sulfoxide on Umbellulols (5 and 6) and Diene 7. The dehydration of *sec*- and *tert*-benzylic alcohols and *tert*-aliphatic alcohols in dimethyl sulfoxide has been studied by Traynelis, *et al.*[11] Dehydration normally is effected at 160–185° over a period of 9–16 hr. The dehydration of umbellulols **5** (and **6**) to diene **7** occurs cleanly[12] at 110° in 5 hr. Raising the temperature gives a mixture of **7** and cymene (**18**) as well as ketone **8** when oxygen is present. Dehydration of sabinol[13] (**19**) to the enantiomer of **7** did not occur when DMSO was used without acid. When acidic conditions that gave exclusively **7** from **5** (and/or **6**) were used for **19**, a mixture of enantiomeric **7** and cymene was obtained.

This difference in the reactivity of umbellulol (**5** or **6**) and sabinol (**19**) must be related to direct extension of the conjugated system in **5** and **6** (*i.e.*, removal of an allylic hydrogen *vs.* a methylene hydrogen in **19**).



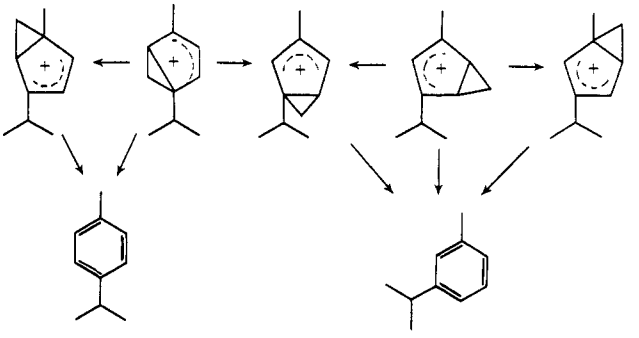
18 19

Umbellulols **5** (or **6**) are converted to diene **7** in dimethyl sulfoxide containing *p*-toluenesulfonic acid at 25°. This reaction is first order in alcohol **5** (or **6**) and first order in acid. Although both alcohols give diene **7**, umbellulol **5** ($K_{av} = 5.5 \times 10^{-3}\ F^{-1}\ min^{-1}$) reacts 19 times as fast as umbellulol **6** ($K_{av} = 0.3 \times 10^{-3}\ F^{-1}\ min^{-1}$).[14]

Conversion of diene **7** to cymene (**18**) is also acid catalyzed in dimethyl sulfoxide at 80°. The rate of rearrangement of diene to cymene is first order in diene and first order in acid. Upon careful examination of the cymene mixture under conditions which separated meta from para, 25% of the cymene was shown to be meta.

The thermal rearrangement of diene **7** to cymene is much less facile, a temperature of 150° being required to convert it at a rate comparable to the acid-catalyzed reaction. The mechanism of the thermal rearrangement of **7** to cymene is not clear and is currently under investigation.

Both the acetolysis and acidic dimethyl sulfoxide reactions of diene **7** involve a bicyclo[3.1.0]hexenyl cation intermediate in its progress to cymene. The appearance of *m*-cymene in the product is consistent with a series of [1,4]sigmatropic migrations[15] established by Childs and Winstein[15d] and Vogel, Saunders, Hasty, and Berson[15e] for similar systems.



Experimental Section

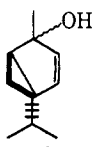
All melting points and boiling points are recorded in degrees Celsius, and are uncorrected. Melting points were taken on a Thomas-Hoover melting point apparatus in open capillaries. Infrared spectra were taken on a Perkin-Elmer Model 137B infracord with sodium chloride optics using polystyrene as a calibration. Proton magnetic resonance spectra were taken on a Varian A-60 spectrometer in carbon tetrachloride with tetramethylsilane as an internal reference. The gas chromatography was done on an Aerograph Model 661 flame ionization instrument using 5 ft × 1/8 in. stainless steel columns. Thin-layer chromatography was done on 250-μ silica gel GF plates obtained from Analtech, Inc., Wilmington, Del. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Preparation of Umbellulols (5 and 6). The umbellulols were prepared according to the method of Wheeler and Chung.[4] One absorption was noted at δ 0.15 (apparent t, 1, J = 3.5 Hz) in addition to those reported for **5**.

Treatment of Umbellulols (5 and 6) with Dimethyl Sulfoxide. Umbellulol (**5** or **6**), 1.52 g (0.01 mol) in 20 ml of undistilled dimethyl sulfoxide,[16] was heated at 150° for 1.5 hr. Water was added and the whole extracted with pentane; the pentane extracts were combined, washed and dried. Upon removal of pentane on a rotary evaporator, 1.20 g of residue was obtained: ir (neat) 2.90, 3.28, 5.85, 6.10, 6.20, 6.37, 6.45, 6.58, 7.25. and 7.35 μ.

Analysis by gas chromatography (15% Apiezon L column, 134°) showed three distinct peaks with retention times of 6, 10.2, and 16 min, respectively. Preparative gas chromatography gave three fractions. The first two fractions with retention times of 6 and 10.2 min were gas chromatographically homogeneous. The compound relative to peak one showed: ir (neat) 5.74, 5.87, 6.15,

(9) R. H. Eastman, *J. Amer. Chem. Soc.*, **76**, 4115 (1954).
(10) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).
(11) V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964); V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *ibid.*, **27**, 2377 (1962); V. J. Traynelis and W. L. Hergenrother, *ibid.*, **29**, 221 (1964).
(12) Preparative gas chromatography of a partially dehydrated sample of **6** gave an intermediate whose spectra were consistent with i.



i

(13) Obtained from sabinyl acetate from oil of savin (Fritzsche) by the procedure of A. G. Short and J. Reed, *J. Chem. Soc.*, 1415 (1939).
(14) The rate constants are an average of three determinations, and were followed under pseudo-first-order conditions with [substrate] = 0.05 F and [*p*-toluenesulfonic acid] = 0.10 F.
(15) (a) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); (b) T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968); (c) H. E. Zimmerman and D. S. Crumvine, *ibid.*, **90**, 5612 (1968); (d) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); (e) P. Vogel, M. Saunders, N. M. Hasty, and J. A. Berson, *ibid.*, **93**, 1551 (1971).
(16) Use of dried dimethyl sulfoxide (molecular sieves) did not alter the results.

6.45, and 11.61 μ; pmr (CCl_4) δ 0.50 (apparent t, 1, J = 3.5 Hz), 0.94 (d, 3, J = 6.8 Hz), 0.98 (d, 3, J = 6.8 Hz), 0.86–1.15 (m, 1), 1.60 (m, 1), 1.87 (m, 1), 4.80 (d, 2, J = 7.0 Hz), 5.65 (d, 1, J = 5.5 Hz), and 6.10 (d, 1, J = 5.5 Hz). On the basis of these spectral data, the structure assigned is 1-isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**).

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.36; H, 10.52.

The compound corresponding to peak two showed: ir (neat) 6.64, 12.27, and 13.90 μ; pmr (CCl_4) δ 1.19 (d, 6, J = 7.0 Hz), 2.23 (s, 3), 2.77 (septet, 1, J = 7.0 Hz), and 7.00 (s, 4). This compound had identical pmr and ir spectra and the same gas chromatographic retention times as an authentic sample of cymene (**18**) (see Acknowledgment).

The third fraction, corresponding to peak three, exhibited a broad peak in its pmr spectrum for the isopropyl methyl absorptions. On this basis it appeared that this fraction was a mixture of at least two compounds which had the same retention time under these conditions. Distillation of the mixture at reduced pressure gave a mixture of **7** and **18**, and a residue which was chromatographed on neutral alumina.

The fraction eluted with petroleum ether–ether (7:3) showed: ir (neat) 5.70 (sh), 5.85, 5.98 (sh) and 6.37 μ; pmr (CCl_4) δ 0.98 (d, 3, J = 6.5 Hz), 1.08 (d, 3, J = 6.5 Hz), 1.23 (d, 1, J = 1.5 Hz), 1.33 (singlet with two small shoulders on either side, 1), 1.50–2.10 (m, 2), 5.47 (d, 1, J = 6.0 Hz), and 7.45 (d, 1, J = 6.0 Hz). On the basis of these spectral data, the structure assigned is 5-isopropylbicyclo[3.1.0]hex-3-en-2-one (**8**).

The other fraction eluted with ether–methanol (9:1) showed: ir (neat) 3.05, 9.61, and 9.90 μ; pmr (CCl_4) δ 0.2 (m, 1), 0.65 (m, 2), 0.88–0.98 (overlapping doublets, 9, J = 7.0 Hz), 1.15–1.84 (m, 2), 1.84–2.50 (m, 2), 2.07 (s, 1), and 4.20 (broad m, 1). The structure assigned is 1-isopropyl-4-methylbicyclo[3.1.0]hexan-2-ol (I). This saturated alcohol was shown to be a minor contaminant in the original lithium aluminum hydride reduction of umbellulone.

At 150° under nitrogen the crude material obtained exhibited no carbonyl group in its infrared spectrum and showed three peaks on gas chromatography. The three peaks were found to correspond to **7**, **18**, and I. 1-Isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**) predominated. At 110° under nitrogen the crude residue obtained showed two peaks in its gas chromatogram with retention times of 6 and 16 min, corresponding to **7** and I, respectively. The two compounds could be separated by distillation or chromatography on neutral alumina with petroleum ether–ether–methanol mixtures. With *p*-toluenesulfonic acid (20 mg) in pentane (16 ml) at 37° under nitrogen the crude residue showed three peaks by gas chromatography corresponding to **7**, **18**, and I. 1-Isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**) predominated.

Synthesis of 7 from Umbellulol. Umbellulol (1.008 g, 0.007 mol) in 70 ml of 0.1 *M p*-toluenesulfonic acid in dimethyl sulfoxide was stirred at room temperature overnight under nitrogen and transferred to a separatory funnel. A work-up similar to that described previously gave 0.87 g of residue. The purified **7** was distilled at 28–29° (4 mm). The spectra were consistent with those obtained previously.

Treatment of 19 with *p*-Toluenesulfonic Acid in DMSO. *d*-Sabinol[13] (0.300 g, 0.001 mol) and 25 ml of 0.1 *M p*-toluenesulfonic acid in dimethyl sulfoxide were heated at 100° for 5 hr under nitrogen and transferred to a separatory funnel, and a work-up similar to those described above gave 0.205 g of residue. Analysis by gas chromatography (15% Carbowax 20 M column, 105°) showed one peak with a retention time of 10 min. This compound had identical pmr and infrared spectra and the same gas chromatographic retention time as an authentic sample of cymene (**18**).

Synthesis of Sabinyl Stearate. Sabinol[13] (1.52 g, 0.01 mol) and stearoyl chloride (2.94 g, 0.01 mol) in 45 ml of pyridine–benzene (1:3) were magnetically stirred at room temperature for 20 hr. The mixture was cooled with a Dry Ice–acetone bath and the precipitate filtered. The solvent was evaporated from the filtrate leaving 1.23 g of crude sabinyl stearate which was chromatographed on an alumina column. Sabinyl stearate (0.93 g), mp 33–34°, was eluted with 8:2 petroleum ether–ether mixture: ir (neat) 5.75, 6.02, and 9.90 μ; pmr (CCl_4) δ 0.91 (m, 11), 1.24 (broad s, 30), 1.43–2.18 (m, 6), 4.98 (s, 2), and 5.39 (d, 1).

Anal. Calcd for $C_{28}H_{50}O_2$: C, 80.32; H, 12.04. Found: C, 80.41; H, 12.34.

Pyrolysis of Sabinyl Stearate. Sabinyl stearate (1.206 g, 0.003 mol) in a 5-ml flask was heated with Wood's metal whereupon a few drops of light yellow distillate were collected. The residue left in the flask after distillation showed distinct bands at 3.30–4.00 and 5.88 μ indicating it to be the stearic acid produced during pyrolysis.

Analysis of the distillate by gas chromatography (15% Apiezon L column, 134°) showed six peaks with retention times of 6, 7.3, 10.2, 15, 22, and 27 min. Two of these compounds with retention times of 6 and 10.2 min were found to be **7** and **18**, the latter predominating. The other compounds were small and no attempt was made to identify them.

Treatment of Sabinene with *N*-Bromosuccinimide. Sabinene[17] (2.04 g, 0.015 mol), *N*-bromosuccinimide (2.65 g, 0.015 mol) and 25 ml of dry, redistilled carbon tetrachloride were refluxed for 19 hr. The succinimide was filtered and the solvent removed, leaving 3.2 g of crude residue.

Analysis by gas chromatography (15% Apiezon L column, 130°) showed four peaks with retention times of 8.3, 12.7, 15.3, and 18.0 min. Two of these compounds, retention times 8.3 and 12.7 min, were found to be **7** and **18**, the latter predominating.

Oxidation of 7. A gentle flow of oxygen (or air) was maintained through a flask containing 0.400 g (0.003 mol) of **7** for 19 days. The crude residue, ir (neat) 5.70 (sh), 5.85, and 5.98 μ (sh), was chromatographed on neutral alumina. Elution with petroleum ether–ether (7:3) gave **8** (0.051 g). This compound had identical pmr and infrared spectra, and the same gas chromatographic retention time as those of the compound obtained previously.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.42; H, 8.99.

Synthesis of 7 from 8. To an ethereal solution of *n*-butyllithium (3 ml, 0.004 mol/ml) in 7 ml of anhydrous ether was added 0.305 g (0.008 mol) of triphenylmethylphosphonium bromide cautiously over a period of 5 min. The solution was stirred for 2.5 hr at room temperature. Then 0.116 g (0.0008 mol) of **8** in 3 ml of anhydrous ether was added dropwise. The contents were heated under reflux for 20 hr, and transferred to a separatory funnel. A work-up similar to that described above gave 0.120 g of residue corresponding to **7** with a small amount of unreacted **8**.

Treatment of 7 with *p*-Toluenesulfonic Acid. In a 10-ml one-necked flask was placed 7 ml of 0.10 *M p*-toluenesulfonic acid in dimethyl sulfoxide solution. After the contents had been swept with dry, oxygen-free nitrogen, 50 μl of **7** was added directly into the reaction flask in a stream of nitrogen. The reaction mixture was fitted with a rubber stopper and an aliquot of the solution (0.5 ml) was taken out with a syringe and extracted with pentane and water. The contents were shaken, the pentane layer separated, and was reextracted twice with water, and the solution injected into a gas chromatograph (15% Apiezon L column, 135°). Only one peak was observed corresponding to **7**. The sample in the stoppered flask was heated at 81° and the reaction mixture was tested after similar treatment at intervals. The results are recorded in Table I.

Table I

T, min	% of **7**	% of **18**
0	100.0	0.0
30	86.6	13.4
90	65.6	34.4
150	49.7	50.3
210	39.0	61.0

Synthesis of *cis*-1-Isopropyl-4-methylbicyclo[3.1.0]hex-3-en-2-yl Acetate (10). *cis*-Umbellulol (**6**) (0.152 g, 0.001 mol), 0.120 g (0.001 mol) of acetic anhydride and 0.083 g (0.001 mol) of sodium acetate were heated at 50° overnight and transferred to a separatory funnel. A work-up similar to those above gave a crude product which was separated by chromatography on alumina. The title compound was eluted with pentane–ether (9:1), while unreacted **6** was eluted with pentane–ether (1:9–0:10). Purified **10** (0.116 g, 60%) was distilled at 62–64° (6 mm); ir (neat) 5.79, 6.10, and 8.08 μ; pmr (CCl_4) δ 0.55–0.75 (m, 2), 0.85 (d, 3, J = 6.5 Hz), 0.95 (d, 3, J = 6.5 Hz), 1.23–1.60 (m, 2), 1.75 (t, 3), 1.92 (s, 3), 4.91 (broad abs, 1), and 5.8 (broad abs, 1).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.18; H, 9.47.

Synthesis of *trans*-1-Isopropyl-4-methylbicyclo[3.1.0]hex-3-en-2-yl Acetate (9). The standard method described above was used with

(17) Obtained from oil of savin (Fritzsche) by distillation.

the same quantities of materials. The crude product was separated by column chromatography on alumina. The purified **9** (0.106 g, 55%) was distilled at 62–64° (6 mm); ir (neat) 5.79, 6.10, 8.08, and 8.20 μ; pmr (CCl_4) δ 0.01 (apparent t, 1), 0.73 (d, 3, J = 7.0 Hz), 1.02 (d, 3, J = 7.0 Hz), 0.82 (m, 1), 1.40 (m, 1), 1.81 (t, 3), 1.96 (s, 3), 2.27 (m, 1), 5.02 (broad abs, 1), and 5.40 (broad abs, 1).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.91; H, 9.44.

Preparation of 2-Methyl-5-isopropyl-5-acetoxymethyl-1,3-cyclopentadiene (11). Umbellulol (**5** or **6**) (0.775 g, 0.005 mol), 0.720 g (0.006 mol) of acetic anhydride, and 0.410 g (0.005 mol) of sodium acetate were heated at 125° for 2 days under nitrogen. After a similar work-up as in the preceding experiment, 0.737 g of residue was obtained. Analysis by gas chromatography (15% Carbowax 20 M column, 105°) showed two peaks with retention times of 5 and 18 min corresponding to **7** and **11**, respectively.

Chromatography of the mixture on neutral alumina gave two fractions. The fraction corresponding to peak two had bp 62–64° (6 mm); ir (neat) 5.76, 6.16, 8.08, and 12.48 μ; pmr (CCl_4) δ 0.8 (d, 3, J = 7.0 Hz), 0.9 (d, 3, J = 7.0 Hz), 1.92 (d, 3, J = 2.0 Hz), 1.96 (s, 3), 2.25 (m, 1), 3.92 (broad abs, 2), 5.8 (broad abs, 1), and 6.16 (d, 2, J = 2.0 Hz). On the basis of these spectral data, the structure assigned is 2-methyl-5-isopropyl-5-acetoxymethyl-1,3-cyclopentadiene (**11**).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.04; H, 9.43.

Treatment of 7 with Sodium Acetate in Acetic Acid at Room Temperature. 1-Isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**) (1.81 g, 0.012 mol) and 75 ml of 0.5 M sodium acetate in acetic acid were kept at room temperature for 3 days and extracted with a small amount of ether. The contents were filtered through a Büchner funnel to remove the excess sodium acetate, and the mixture was transferred to a separatory funnel containing a mixture of water and pentane. A work-up similar to that described above gave 1.58 g of residue. Gas chromatography showed one peak with a retention time of 5 min, and one broad peak with a retention time of 18 min.

Separation by chromatography on neutral alumina gave 1-isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**), corresponding to peak one. The fraction eluted with pentane–ether (9:1), corresponding to peak two, was a mixture of **9**, **10**, and **11** in the ratio of 2.2:3.4:1 (pmr).

Treatment of 7 with Sodium Acetate in Acetic Acid at 10°. Another reaction using the same amount of reagents as stated in the preceding experiment was carried out at a temperature of 10°. After a similar work-up, the crude material obtained showed two peaks on gas chromatography as well as absence of resonances at δ 3.92 and 6.16 in the pmr spectrum of the second fraction after chromatography. The second fraction contained **9** and **10** in the ratio of 1:1.75. None of the monocyclic acetate **11** was detected either by gas chromatography or pmr spectroscopy.

Tricyclic Alcohol (14 and 15). *cis*- (or *trans*-) Umbellulol (**6** or **5**) (3.5 g, 0.023 mol) and methylene iodide (7.7 g, 0.029 mol) were added dropwise to zinc–copper couple[18] (2.9 g) in ether containing methylene iodide (2.8 g) at 36°. The reaction mixture was stirred at reflux for 30 hr and cooled and saturated ammonium chloride was added. The ether was separated from the inorganic salts, and the salts were washed with ether. The combined ether extracts were washed with ammonium chloride, sodium bicarbonate, and sodium chloride solutions and dried and the ether was removed. Purification by column chromatography gave tricyclic alcohol: *cis*-**14** (1.34 g, 35%) bp 138–139° (7 mm); ir (neat) 2.98, 9.50, and 9.70 μ; pmr (CCl_4) δ 4.50 (d, 1, J = 7.0 Hz), 1.25 (s, 3), 0.28–1.5 (complex, 14); *trans*-**15** (1.27 g, 33%) bp 123–124° (10 mm); ir (neat) 2.94, 9.50, and 9.70 μ; pmr (CCl_4) δ 4.58 (d, 1, J = 7.0 Hz), 1.28 (s, 3), 0.20–1.30 (complex, 14).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: **14**, C, 79.30; H, 11.06. **15**, C, 79.72; H, 11.11.

Tricyclic Ketone (16 and 17). To chromium trioxide–pyridine complex prepared from chromium trioxide (2.01 g, 0.02 mol) and pyridine (18 ml) was added tricyclic alcohol (**14** or **15**) (1.34 g, 0.008 mol) in pyridine (12 ml) and the reaction mixture was stirred at room temperature overnight. Addition of water was followed by extraction with ether. The ether extract was washed with water, 3% hydrochloric acid, and sodium bicarbonate solution and dried and the ether was removed. The crude product was purified by column chromatography: **17**, 1.20 g, 91%; ir (neat) 5.85, 9.68, and 9.84 μ; pmr (CCl_4) δ 0.87 (d, 3, J = 7.0 Hz), 0.90 (d, 3, J = 7.0 Hz), 1.43 (s, 3); mass m/e 164; **16**, 1.08 g, 82%; ir (neat) 5.85, 9.68, and 9.84 μ; pmr (CCl_4) δ 0.81 (d, 3, J = 7.0 Hz), 0.93 (d, 3, J = 7.0 Hz), 1.27 (s, 3).

The pmr spectrum, gas chromatographic retention time, and tlc R_f value of **17** were identical with those of a ketone prepared from umbellulone by Eastman's procedure.[9]

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: **17**, C, 80.53; H, 9.91. **16**, C, 80.30; H, 9.79.

Acknowledgment. We thank Mr. L. Strausser of Beckman Instruments for the preliminary analysis of the cymene mixture (24 ft 5% Bentone-34 plus 5% OS-124 column at 110°).

(18) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

Bridged Polycyclic Compounds. LXXII. Salt Effects in Acetolysis of *syn*-7-Chlorobenzonorbornadiene[1]

Stanley J. Cristol, Allen L. Noreen, and Guenter W. Nachtigall

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received February 23, 1971*

Abstract: *syn*-7-Chlorobenzonorbornadiene (**1**-Cl) solvolyzes in acetic acid to **1**-OAc about 10^3 times as fast as its anti epimer **2**-Cl gives **2**-OAc. Acetolysis of **1**-Cl, but not of **2**-Cl, is accelerated dramatically by potassium acetate. Possible bimolecular mechanisms and salt effects are considered, but in view of results with lithium perchlorate, which is more effective at rate acceleration than is potassium acetate, bimolecular mechanisms are excluded. The results are interpreted as "special salt" effects.

It was recently reported[2] that acetolyses of *syn*- (**1**-Cl) and *anti*-7-chlorobenzonorbornadiene (**2**-Cl) proceed with retention of configuration. Acetolysis of **1**-Cl is faster than that of **2**-Cl by a factor of 10^3, not including accelerative effects of potassium acetate, and the rate of acetolysis of **1**-Cl, but not that of **2**-Cl,

(1) Paper LXXI: S. J. Cristol, J. K. Harrington, T. C. Morrill, and B. E. Greenwald, *J. Org. Chem.*, **36**, 2773 (1971).

(2) S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7132 (1968).