

Consanguineous Syntheses of Polymethyl-Substituted 1*H*-, 3*aH*-, and 5*H*-Indenes from Arylallyl Alcohols

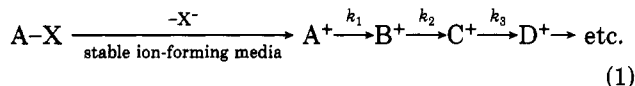
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Starting with specific arylallyl alcohols, via a cascading series of observable carbocations, one can synthesize 1*H*- or 3*aH*-indenes and, in a special case, a 5*H*-indene. The chemistry of the reactive 3*aH*-indenes has been studied in some detail. The 5*H*-indene appears to be the first simple representative of this particular isoindene and has been physically characterized. It is chemically less reactive than the 3*aH*-indenes.

Carbocations are notorious for the ease with which they rearrange. When these cations are of reasonable complexity, the rearrangements often occur via a directly observable cascading sequence in which ever more stable ions are formed (eq 1).¹ However, from a synthetic viewpoint,



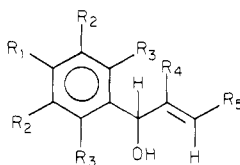
these eq 1 reactions are of limited interest because (1) the steps are not always separated kinetically, (2) the rearrangements are dictated by thermodynamics (molecular stability and interest are often inversely related), and (3) one must recover neutral products from the ions, conveniently and in good yield, and this can prove difficult in many cases.

There is, however, one potentially redeeming feature about the eq 1 sequence, i.e., the possibility of selectively producing any one of a number of products, all from the same starting material.

In this paper we describe reactions of the eq 1 type, leading to the preparation of 1*H*-, 3*aH*-, and 5*H*-indenes, in the last case apparently the first preparation of a simple derivative of this particular isoindene.

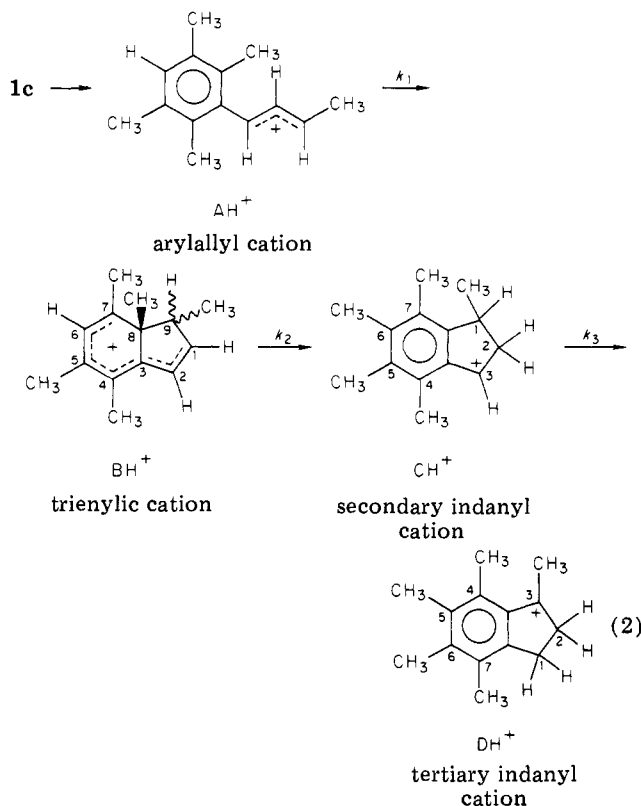
Results

With reference to eq 1, A-X in our present case is represented by a series of arylallyl alcohols 1 (X = OH).



- 1a, R₁ = R₃ = R₅ = CH₃; R₂ = R₄ = H
 b, R₁ = R₃ = R₄ = R₅ = CH₃; R₂ = H
 c, R₂ = R₃ = R₅ = CH₃; R₁ = R₄ = H
 d, R₂ = R₃ = R₄ = R₅ = CH₃; R₁ = H
 e, R₁ = R₂ = R₃ = R₄ = R₅ = CH₃

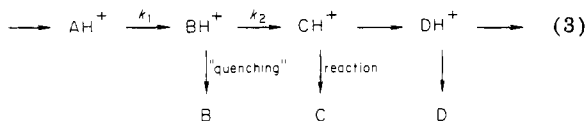
Alcohol 1c turns out to be an almost perfect example of an ideal eq 1 molecule, from the cation rearrangement standpoint, in this case involving four cations in the cascading sequence. The rearrangement series is shown in eq 2. We have previously described² the cyclization step AH⁺ → BH⁺ and have characterized the ions AH⁺ and/or BH⁺ for the complete alcohol series 1a-e. Only in the case of alcohol 1c are all four ions (AH⁺, BH⁺, CH⁺ and DH⁺) observed. Table I summarizes the overall observations for all of the alcohols employed in this study.



The kinetic rate constants for each of the ion to ion transformations have been measured for completeness sake and are listed in Table II. These measurements are of course not strictly necessary for synthetic applications.

The alcohol 1c results, as mentioned, are ideal since each cascading step is well separated (ΔG^\ddagger values of 15.6, 21.0, and 24.0 kcal/mol) and in each case the reaction leads cleanly to a single ion.

The last step in an overall synthesis involves converting the ions back into neutral organic compounds. In principle, one can carry out a variety of "quenching" reactions,³ but in this study we have been interested only in a proton-elimination reaction and have therefore added the ions to aqueous bases (see Experimental Section). The overall "ideal" situation is shown in eq 3, but in practice these



quenching reactions range from giving virtually 100% of

(1) See, for example, Sorensen, T. S. *Acc. Chem. Res.* 1976, 9, 257.
 (2) Dytnerski, D. M.; Ranganayakulu, K.; Singh, B. P.; Sorensen, T. S. *Can. J. Chem.*, in press.

(3) The assumption in using this word is that the ions are rapidly converted to neutral products. Operationally this process is not unlike a number of other organic reaction steps.

Table I. Observable Cations Starting from the Alcohols 1a-e

| alcohol | aryllallyl cation AH ⁺ | triénylic cation BH ⁺ | secondary indanyl cation CH ⁺ | tertiary indanyl cation DH ⁺ | other cations EH ⁺ |
|---------|-----------------------------------|----------------------------------|--|---|-------------------------------|
| 1a | x | | x | x | |
| 1b | | x | | x | |
| 1c | x | x | x | x | |
| 1d | | x | | x | |
| 1e | | x | | | x |

Table II. Kinetic Rate Constants for Ion-Ion Rearrangements

| alcohol | ion-ion rearrangement | k_2 s ⁻¹ | T , °C | ΔG^\ddagger | solvent |
|---------|--|-----------------------|----------|---------------------|--|
| 1a | AH ⁺ → CH ⁺ | 6×10^{-4} | +35 | 22.0 | FSO ₃ H |
| 1a | CH ⁺ → DH ⁺ | 6×10^{-4} | +35 | 22.0 | FSO ₃ H ^a |
| 1b | BH ⁺ → DH ⁺ | 4×10^{-4} | -30 | 18.0 | FSO ₃ H |
| 1c | AH ⁺ → BH ⁺ | 5×10^{-4} | -70 | 15.6 | FSO ₃ H-SO ₂ ClF (1:3) |
| 1c | BH ⁺ → CH ⁺ | 3×10^{-4} | +10 | 21.0 | FSO ₃ H |
| 1c | CH ⁺ → DH ⁺ | 8×10^{-6} | +23 | 24.0 | FSO ₃ H ^a |
| 1d | BH ⁺ → DH ⁺ | 6×10^{-4} | +35 | 23.0 | FSO ₃ H |
| 1e | BH ⁺ → EH ⁺ ^b | 4×10^{-4} | +15 | 21.2 | 96% H ₂ SO ₄ |

^a These rates are dependent upon the acid strength of the medium and will be different in different acid solvents (and probably even at different concentrations since the cation preparation generates water, which then "dilutes" the FSO₃H).

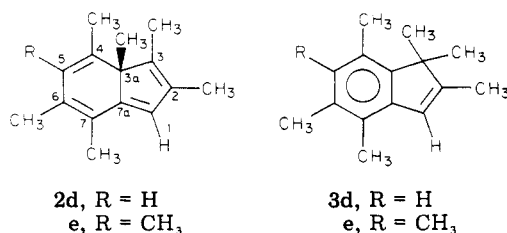
^b Small peaks from another ion are present during the reaction (characterized by a high-field doublet at δ 0.74 ($J = 7$) and the corresponding quartet methine hydrogen at δ 3.1, and possibly also a peak at δ 6.82). This ion does not seem to be an intermediate and disappears at higher temperatures.

a single product to giving none of the expected material, or giving a mixture of products (see later).

There is, of course, no real point in "quenching" AH⁺, since this is the skeleton of the starting material in the present context. For a particular ion and solvent system, time and temperature are the only variables in determining which particular rearrangement ion one has. For preparative-scale reactions, it is convenient to monitor this process by NMR spectroscopy (on an aliquot).

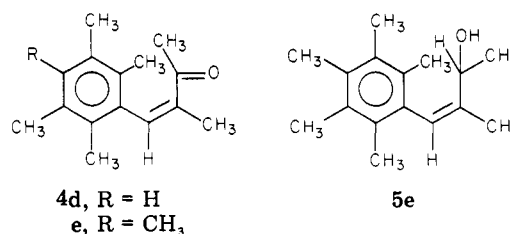
Reaction Products. 3aH-Indenes. Cation BH⁺ (Table I) from alcohol 1d is quenched to give >50% crude yield of a 3aH-indene 2d. This is contaminated with a small amount of an exocyclic tetraene² (proton elimination from the C-7 methyl group) and an even smaller amount of other hydrocarbons of unknown structure. A nearly pure sample of 2d was obtained by column chromatography, but the compound is an unstable oil and difficult to work with. Cation BH⁺ from 1e also gives a 3aH-indene 2e, although in this case the crude quench product is richer in the exocyclic tetraene. For all of the subsequent reactions of 2d or 2e, the mixture of 3aH-indene and exocyclic tetraene could be used, since the latter rapidly isomerizes under most reaction conditions. Cation BH⁺ from alcohol 1c is not quenched to recognizable products so the methyl group at C-1 appears to be necessary here. When this work was underway, simple 3aH-indenes were unknown. However, Gilchrist et al. have since communicated the preparation of a simple methoxy-substituted analogue.⁴

The 3aH-indenes 2d and 2e are both thermally and oxidatively rather unstable. On heating to 100 °C, both are quite cleanly converted to 1H-indenes 3d and 3e, via

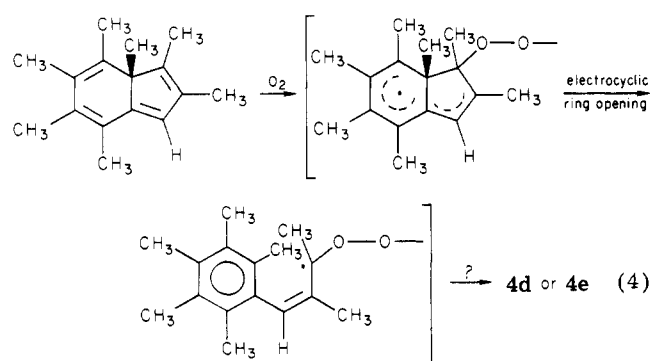


a 3a,3(1,5)sigmatropic methyl shift. As with 2H-indenes,⁵ the methyl shift involves rearomatization and is particularly favorable. This rearrangement has also been observed by Gilchrist et al.⁴

On exposure to air (oxygen) in solution or as an oil, 2d and 2e are converted to a ring-opened ketone, 4d and 4e, respectively. The cis orientation of the aryl and keto



groups follows from the unusually high-field CH₃C=O methyl ¹H resonance (in the face of the aryl ring) and also the weak C=O stretching frequency. The mechanism of this oxidation may be as shown in eq 4, although a 1,4-dioxygen adduct equivalent to 7d (see later) could also be a possible intermediate.



On exposure of 2e to dilute aqueous acid (pH ~1), alcohol 5e was obtained. This structure was correlated with

(4) Gilchrist, T. L.; Rees, C. W.; Tuddenham, D. *J. Chem. Soc., Chem. Commun.* 1980, 689; *J. Chem. Soc., Perkin Trans. 1* 1981, 3214.

(5) (a) Dolbier, W. R., Jr.; McCullagh, L.; Rolison, D.; Anapolle, K. E. *J. Am. Chem. Soc.* 1975, 97, 934. (b) McCullough, J. J.; Yarwood, A. J. *J. Chem. Soc., Chem. Commun.* 1975, 485.

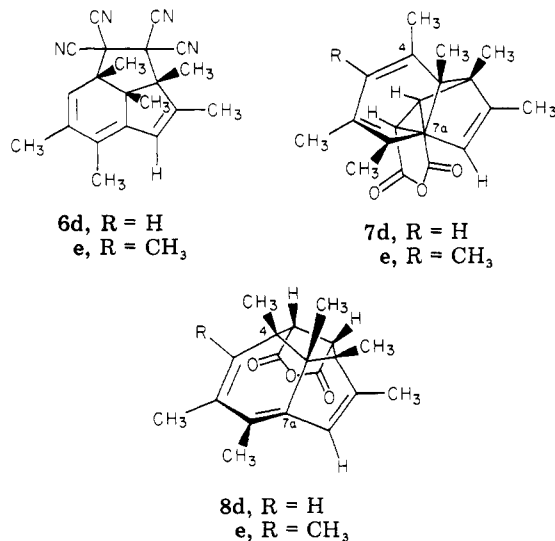
Table III. ^1H NMR Parameters for Cations CH^+ , DH^+ , and EH^+ in the Alcohol Series 1a-e

| alcohol | series | solvent | temp, $^{\circ}\text{C}$ | position ^a | | | | | | |
|---------|---------------|-----------------------------|-----------------------------|--|--|--|-------------------|-------------------|-------------------|-------------------|
| | | | | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1a | CH^+ | FSO_3H | 25 | 1.25 ^c 3.71 ^d | ca. 3.22 ^b ca. 3.69 ^b | 9.81 ^e | 2.51 ^e | 7.30 | 2.55 | 2.25 |
| 1c | CH^+ | FSO_3H | 28 | 1.30 ^c 3.77 ^d | 3.21 ^b 3.67 ^b | 9.84 ^e | 2.58 ^e | 2.29 ^k | 2.61 | 2.27 ^k |
| 1a | DH^+ | FSO_3H | 28 | <i>f</i> | <i>f</i> | 3.17 | <i>f</i> | <i>f</i> | 7.85 | <i>f</i> |
| 1b | DH^+ | FSO_3H | 28 | 3.43 ^g 2.72 ^g | 1.41 ^c 3.58 ^h | 3.11 | 2.55 | 2.30 ^k | 7.85 | 2.23 ^k |
| 1c | DH^+ | FSO_3H | 28 | 3.17 ^e | 3.53 ^e | 3.09 | 2.47 | 2.27 | 2.62 | 2.27 |
| 1d | DH^+ | FSO_3H | 35 | <i>i</i> | 1.37 | 3.01 | 2.42 | 2.23 ^k | 2.57 | 2.20 ^k |
| 1e | EH^+ | 96% H_2SO_4 | 15 | 6.92 | 2.24 ^k | 1.22 ⁿ 3.54 ^m | 2.26 ^k | 1.18 1.20 | 2.30 ^k | 2.06 |

^a The numbering follows that given in the text. Values (δ) are relative to external references, Me_4Si in CDCl_3 for cation EH^+ and Me_4Si in $\text{Me}_4\text{Si}-d_{12}$, with a correction factor of 0.4 ppm, for the remaining cations. ^b AB pattern with further small coupling. J_{gem} is remarkably large at ca. 27 Hz. ^c Doublet, $J = 7$ Hz. ^d Doublet of quartets, $J = 2$ and 7 Hz. ^e Broad. ^f Spectrum is not clean, but the two assignments shown are characteristic for this ion. ^g Doublets, $J_{\text{gem}} = 23$ Hz. ^h Very broad quartet, $J \sim 7$ Hz. ⁱ Complex pattern including peaks at ca. 3.30 and 2.87. ^j Multiplet centered ca. 3.48. ^k These assignments are interchangeable. ^m Quartet, $J = 7$ Hz. ⁿ One-half of a doublet.

4e by reduction of the latter with LiAlH_4 . This ring opening is undoubtedly a reverse of the original cyclization reaction and the compound is isomeric with the starting alcohol.

Finally, 2d and 2e exhibit interesting Diels-Alder behavior. Tetracyanoethylene (TCNE) adds immediately to 2d or 2e to give the 1,8-adducts 6d and 6e. Gilchrist et al. have also observed 1,8-adducts from a methoxy-substituted 3aH-indene and 4-phenyltriazoline-3,5-dione or dimethyl acetylenedicarboxylate. The regioselectivity shown is based on molecular model studies. Maleic anhydride, however, adds initially to give the 1,4-adducts 7d and 7e, which slowly rearrange at 25 $^{\circ}\text{C}$ in solution or the solid state to give the 1,8-adducts 8d and 8e. The endo

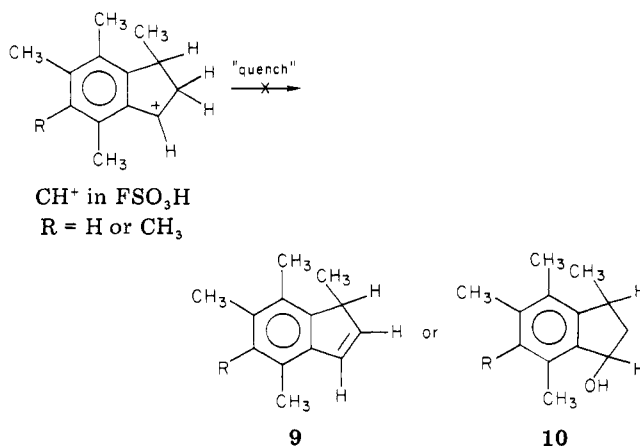


geometry is probably favored in 7d and 7e and we have assigned the same orientation in 8d and 8e, on the assumption that only the C-7a bond is broken in the rearrangement. Gilchrist et al. have also very recently found a 1,4-adduct using maleic anhydride and their methoxy-substituted 3aH-indene and have observed the rearrangement of this to the 1,8-adduct.⁴

The 1,8- and 1,4-adduct assignments are consistent with the ^1H NMR spectra (three high-field methyls vs. two), but the ultraviolet absorptions are perhaps the most definitive. The 1,4-adducts 7d and 7e show λ_{max} 274 and 277 nm, respectively (conjugated diene), while 8d and 8e show λ_{max} 308 and 307 nm, respectively (conjugated triene). The

TCNE adducts 6d and 6e also show λ_{max} 315 (both) (conjugated triene).

Quenching of the Secondary Indanyl Cations (CH^+). Quenching the CH^+ cations from alcohols 1a and 1c (^1H and ^{13}C spectra are reported in Tables III and IV) led to unexpected results. On the basis of the clean recovery of 1H-indenes from the tertiary (DH^+) cations, one might likewise assume a similar result for the CH^+ cations. One can indeed obtain a near-quantitative recovery of an unstable organic product on quenching, but analysis of this shows that little, if any, of the expected 1H-indene 9 is formed, nor is there any sign of the secondary alcohol 10. The recovered hydrocarbon, on readdition to acid, regenerates at least 50% of the starting ion, showing that the basic skeleton of at least one-half of the quench material is unchanged.



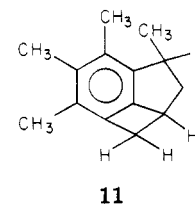
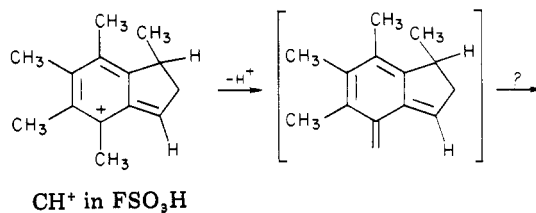
The most reasonable explanation for this unexpected behavior is that ions CH^+ are probably not well represented by the secondary indanyl structure (as shown) and should be thought of as having most of the charge delocalized into the aryl ring. Thus, proton elimination to give 9 would be less likely and rather unstable products such as 11 might be formed instead. Because the recovered material is a complex mixture, no further work was done.

Quenching of Tertiary Indanyl Cations (DH^+) to 1H-Indenes. Tertiary indanyl cations DH^+ , from alcohols 1a-d (^1H and ^{13}C NMR spectra, Tables III and IV), are quenched to give 1H-indenes 12a-d. The yields are virtually quantitative for 12c and 12d, but 12a is only obtained in about 40% yield. All of these crystalline products

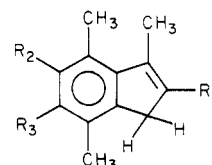
Table IV. ^{13}C NMR Parameters for Cations CH^+ and DH^+ in the Alcohol Series 1a-d

| alcohol series | ion | temp, $^{\circ}\text{C}$ | solvent ^a | position ^{b,c} | | | | | | | | | |
|----------------|---------------|--------------------------|------------------------|-------------------------|------|------|-------|-------|-------|-------|-------|-------|--|
| | | | | 1 | 2 | 3 | 3a | 4 | 5 | 6 | 7 | 7a | methyls |
| 1a | CH^+ | 28 | FSO_3H | 209.0 | 51.2 | 42.2 | 153.2 | 145.9 | 184.4 | 136.1 | 178.4 | 133.7 | 23.5, 18.1, 17.8, 14.1 |
| 1c | CH^+ | 20 | FSO_3H | 206.5 | 50.2 | 41.7 | 148.4 | 144.7 | 179.5 | 141.6 | 177.2 | 135.8 | 20.5, 17.6, ^d 16.1, 15.0 ^d |
| 1b | DH^+ | -20 | FSO_3H | 247.7 | 55.6 | 40.7 | 148.4 | 144.0 | 157.2 | 142.3 | 176.3 | 132.6 | 27.2 (C-1), 19.1, 18.3, 17.35 (2) |
| 1c | DH^+ | 28 | FSO_3H | 233.7 | 47.9 | 31.8 | 146.0 | 141.8 | 174.5 | 140.8 | 168.8 | 134.7 | 26.0 (C-1), 19.6, 17.9, 15.0 (2) |
| 1d | DH^+ | 28 | FSO_3H | 238.2 | 54.2 | 41.2 | 147.3 | 142.2 | 173.8 | 142.0 | 170.2 | 135.8 | 26.2 (C-1), 20.9, 19.6, 18.2, 16.2, 16.0 |

^a In contrast to the H_2SO_4 solvent preparative work, the NMR spectra of these cations were measured in FSO_3H solvent. ^b Referenced with respect to external Me₄Si in $\text{CDCl}_3 = \delta$ 0.00. ^c The numbering system follows that shown in eq 2. The assignment for positions 3a, 4, 5, 6, 7, 7a is tentative in most cases. Peaks for carbons 3a and 7a are often very weak because of long relaxation times. ^d One of these peaks corresponds to two carbons.

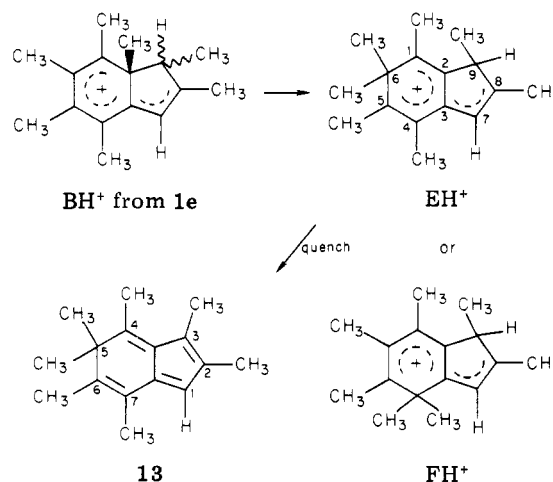


have been characterized by ^1H and ^{13}C NMR spectroscopy, etc.



- 12a, $\text{R}_1 = \text{R}_3 = \text{H}$; $\text{R}_2 = \text{CH}_3$
 b, $\text{R}_3 = \text{H}$; $\text{R}_1 = \text{R}_2 = \text{CH}_3$
 c, $\text{R}_1 = \text{H}$; $\text{R}_2 = \text{R}_3 = \text{CH}_3$
 d, $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{CH}_3$

5H-Indene. Alcohol 1e follows a different overall cation rearrangement route compared to 1a-d. After the initial steps $\text{AH}^+ \rightarrow \text{BH}^+$, one gets a much slower second rearrangement leading very cleanly to a second nonaromatic cation (see Table III for the tabulated ^1H assignments). This difference occurs because it is not possible by 1,2 methyl shifts to rearomatize the "aryl ring", there already being a methyl group at each carbon of this six-membered ring in the BH^+ ion. However, 1,2 methyl shifts can evidently lead to a more stable ion and two "conjugated" structures were possible, EH^+ or FH^+ . The latter is



conjugated (a trienylic cation like the BH^+ ion), while the former is cross-conjugated (a "trivinylmethyl" cation). It has previously been found⁶ that an extra vinyl group does not enhance the λ_{max} in a cross-conjugated dienyl cation, whereas a linear extension to give a trienyl cation most certainly does.⁷ Experimentally, the trienylic cation BH^+ has λ_{max} 483 nm (the longest wavelength peak) (cf. 473 nm for an acyclic example),⁷ whereas the rearranged ion has λ_{max}

(6) Sorensen, T. S.; *Can. J. Chem.* **43**, 1965, 2745.

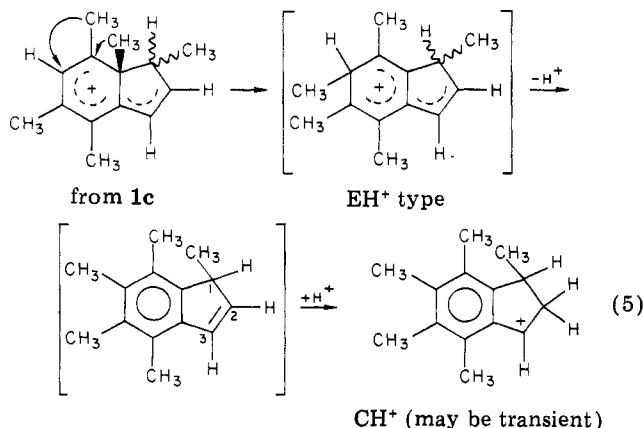
(7) Sorensen, T. S.; *J. Am. Chem. Soc.* **1965**, *87*, 5075.

380 nm (cf. 397 nm for the heptamethylbenzenonium ion⁸). Hence the rearranged ion was assigned the structure EH^+ , rather than FH^+ .

On quenching, EH^+ leads in good yield to the orange-red crystalline 5*H*-indene 13, the first simple example of this particular isoindene. The ¹H and ¹³C NMR spectra, MS, and C, H analyses are consistent with this structure (both quaternary methyls are equivalent, for example). The UV-visible spectrum shows λ_{max} 420, 265, 253, 248, 220 nm (ϵ_{max} 1.06×10^3 , 5.6×10^3 , 1.97×10^4 , 2.19×10^4 , 1.31×10^4). The 5*H*-indene 13 does not add maleic anhydride and mild heating causes no sigmatropic rearrangements. The latter result is expected since rearomatization would not occur until after two 1,9 methyl shifts and a 1,5 methyl shift had occurred.

Discussion

Cation Rearrangement Mechanisms. The cyclization of arylallyl cations AH^+ has been discussed previously.² The rearomatization of the BH^+ to CH^+ cations involves either a simple 1,2 methyl shift of the bridgehead methyl, i.e., alcohols 1a and 1b, or two 1,2 methyl shifts in the case of 1c and 1d. Proton loss leads to an indene intermediate that is then reprotonated at C-2 (eq 5). In the case of



alcohol 1e, there is no possible proton elimination and the EH^+ ion is the end product.

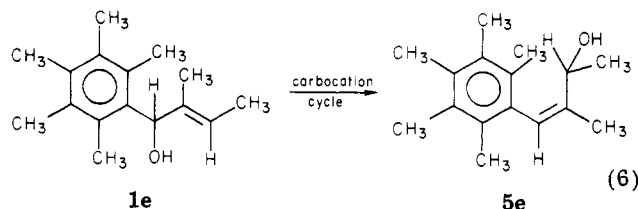
Pittman and Miller have extensively⁹ discussed the rearrangement of secondary to tertiary indanyl cations. In our examples, where a methyl group is present at C-2, one does not even see the secondary CH^+ ion, since a double 1,2 H shift process now goes through a low-energy intermediate involving a tertiary ion at C-2. Where C-2 is a methylene group, a secondary C-2 ion would be involved and the rearrangement is much slower (and directly observable). In H_2SO_4 solvent, in contrast to FSO_3H , a deprotonation-reprotonation mechanism may intervene,¹⁰ since the rearrangement is experimentally faster in the weaker acid solvents.

Synthetic Aspects. There are undoubtedly more straightforward ways to prepare polymethylated 1*H*-indenes, but the cation route to some specific 3*aH*- and 5*H*-indenes is interesting, if only because there are limited alternatives. One can also note that two different 1*H*-indenes can be made in some cases from the same starting alcohol. The cationic rearrangement route $\text{BH}^+ \rightarrow \text{DH}^+$ shifts the bridgehead methyl into the six-membered ring,

while quenching BH^+ and heating the resulting 3*aH*-indene gives a 1*H*-indene with this same methyl group shifted to the five-membered ring.

Energetics. It may seem unexpected that unstable isoindenes should be produced in this thermodynamically governed synthetic approach. However, one is to a large extent making use of the latent energy inherent in the aryl ring. Benzene and toluene are both kinetically and thermodynamically stable molecules, but a kinetically stable (and prosaic) molecule like 1-hexylbenzene is thermodynamically unstable relative to a more exotic isomer such as ethanoadamantane,¹¹ there being, however, no known way of using this thermodynamic advantage. Carbocations (because of their innate ease of rearrangement) challenge one, therefore, to mechanistically make use of this latent energy inherent in the aryl ring.

A second factor is probably also involved here, as illustrated by the fact that one can isomerize a starting alcohol, e.g., 1e, into what is almost certainly a thermodynamically less stable isomer, e.g., 5e, via a sequence involving observable carbocations (eq 6). This energy



“pumping” probably occurs because the extra σ -bond formation is *more energetic* in the intermediate carbocation BH^+ than in the neutral 3*aH*-indene 2e.

Experimental Section

General Methods. Proton NMR were recorded at 60, 90, 100, or 200 MHz, using a Perkin-Elmer R-24B, Bruker WH-90, Varian HA-100, or Varian XL-200 spectrometer. Carbon NMR were recorded at 22.63 or 50.28 MHz, using the above instruments. Chemical shifts of neutral compounds are reported in δ units from internal Me_4Si , using deuteriochloroform solvent and are run at 200-MHz fields unless noted. IR spectra were taken with a Perkin-Elmer 467 spectrophotometer and electronic spectra were measured on a Cary 219 spectrophotometer. Melting points and boiling points are uncorrected. The arylallyl alcohols used as starting materials are conveniently prepared in high yield and have been reported.² Specific details concerning the NMR spectra of the cations are given in Tables III and IV. In general, ¹³C spectral assignments relied on off-resonance decoupled spectra and proton assignments on specific decoupling.

2,3,3a,4,6,7-Hexamethyl-3a*H*-indene (2d). A solution of carbocation BH^+ (from alcohol 1d) was prepared from 1.00 g (4.6 mmol) of (*Z*)-1-duryl-2-methyl-2-buten-1-ol by dissolving this alcohol in 10 cm³ of methylene chloride and adding the resulting solution dropwise to a stirred solution of 96% H_2SO_4 (10 mL at 0 °C). The carbocation solution, kept at 0 °C, was added to a vigorously stirred mixture of water- Na_2CO_3 -ethylene glycol-pentane (200 mL, 60 g, 200 mL, 200 mL) kept at -20 °C. After addition, the mixture was warmed to 20 °C, the pentane layer separated, and the aqueous layer extracted with another 200 mL of pentane. The combined organic layers were washed with Na_2CO_3 solution and water and then dried over anhydrous K_2CO_3 . Removal of the solvent yielded a residue (0.90 g, 98% recovery) of a light-yellow oil whose ¹H NMR spectrum indicated a mixture of two products in a ratio of 2-3:1 favoring the title compound. The other product is an exocyclic tetraene.² Both compounds are air and heat sensitive. The 3*aH*-indene 2d was obtained as a nearly pure (by NMR) yellow oil by rapid chromatography of the mixture (25 g of neutral alumina, elution with pentane): ¹H

(8) von E. Doering, W.; Saunders, M.; Boyton, H. G.; Earhart, H. W.; Wadley, E. F.; Edwards, W. R.; Laber, G. *Tetrahedron* 1958, 4, 178.

(9) Pittman, C. U., Jr.; Miller, W. G. *J. Am. Chem. Soc.* 1973, 95, 2947.

(10) (a) Sorensen, T. S.; Miller, I. J.; Urness, C. M. *Can. J. Chem.* 1970, 48, 3374. (b) Chiu, N. W. K.; Sorensen, T. S. *Ibid.* 1973, 51, 2783.

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NMR δ 5.29 (br, 1 H, H-5), 5.94 (1 H, H-1), 1.75 (d, $J = 2$ Hz, 3 H, CH₃ on C-4), 1.71 (3 H), 1.82 (6 H), 1.93 (3 H) (CH₃'s on C-2, -3, -6, and -7), 1.12 (3 H, CH₃ on C-3a); ¹³C NMR δ 155.8, 144.7, 138.3, 132.7, 126.2, 123.2 (all alkene carbons), 125.9 and 125.3 (CH alkene), 59.9 (q, C-3a), 28.3 (CH₃ on C-3a), 23.7, 20.4, 13.2, 12.0, 11.8 (CH₃'s on alkene carbons).

2,3,3a,4,5,6,7-Heptamethyl-3aH-indene (2e). Using the above procedure with (*Z*)-1-(pentamethylphenyl)-2-methyl-2-buten-1-ol (1e), one obtains the title indene as a yellow, oily mixture together with an exocyclic tetraene (ratio ca. from 1:1 to as much as 1:3 disfavoring the title indene, using ¹H NMR). For reactions, this crude mixture was used, since the mixture yields products that are apparently derived only from 2e. 2e: ¹H NMR δ 5.96 (1 H, H-1), 1.98, 1.89, 1.81, 1.78, 1.66 (all 3 H, five of the six methyls, one being hidden by the exocyclic tetraene peaks), 1.07 (3 H, CH₃ on C-3a).

1,1,2,4,5,6,7-Heptamethyl-1H-indene (3e). The quench mixture containing 3aH-indene 2e (0.50 g, 2.3 mmol) was heated at 100 °C in an argon atmosphere for 48 h. The ¹H NMR spectrum of the crude material corresponds almost entirely to that of 3e, although considerable base-line absorption is also present. The pure indene was obtained by preparative GLC (SE-30 on Chromosorb G) and subsequent sublimation, mp 41–42 °C; ¹H NMR δ 6.43 (br, 1 H, H-3), 2.41, 2.32, 2.24, 2.23 (each 3 H, aromatic CH₃'s), 1.945 (d, $J = 2$ Hz, 3 H, CH₃ at C-2), 1.33 (6 H, C-1 CH₃'s); ¹³C NMR δ 153.5, 147.4, 139.7, 133.0, 131.3, 128.8, 125.4 (all q, aromatic carbons), 122.2 (C-3), 51.3 (C-1), 21.9 (at least 2 C), 16.1, 15.9 (probably 2 C), 12.5, one uncertain (methyl carbons). Anal. Calcd for C₁₆H₂₂: C, 89.71; H, 10.28. Found: C, 89.67; H, 10.56.

1,1,2,4,6,7-Hexamethyl-1H-indene (3d). This indene was obtained in a similar way to 3e, using the 3aH-indene 2d mixture. The crude product was distilled, bp 92–94 °C (0.15 mm), and further purified by preparative GLC: mp 53–55 °C; ¹H NMR δ 6.73 (1 H, H-6), 6.44 (q, $J = 1.6$ Hz, H-3), 2.41 and 2.21 (3 H and 6 H, respectively, aromatic CH₃), 1.93 (d, $J = 1.5$ Hz, 3 H, CH₃ at C-2), 1.28 (6 H, C-1 CH₃); ¹³C NMR δ 154.6, 147.7, 142.2, 134.5, 129.3, 125.2 (all q), 128.3 (C-6), 122.4 (C-3), 51.2 (C-1), 22.0 (C-1 CH₃), 19.4, 18.2, 14.8, 12.4 (CH₃). Anal. Calcd for C₁₅H₂₀: C, 89.94; H, 10.06. Found: C, 89.42; H, 9.72.

(Z)-4-Duryl-3-methyl-3-buten-2-one (4d). The indene mixture 2d (0.50 g) was left in an open flask for 3–4 days at room temperature. The crude ketone was distilled, bp 145–150 °C (1.0 mm), and then sublimed: a white crystalline solid; mp 45–46 °C; yield ca. 200 mg, ca. 35%; ¹H NMR δ 5.99 (br, 1 H, H-4), 5.94 (1 H, aromatic), 2.21 (6 H) and 2.16 (6 H) (aromatic CH₃), 2.06 (d, $J = 2$, 3 H, C-3 CH₃), 1.67 (3 H, CH₃ at C-1); ¹³C NMR δ 202.7 (C=O), 139.3 (2 C, q), 137.3 (C H), 136.8 (2 C, q), 133.9 (2 C, q), 131.0 (q), 130.9 (CH), 29.3 (C-1), 20.1 (methyl on C-3), 19.95 and 16.6 (2 C, aromatic methyls). Anal. Calcd for C₁₅H₂₀O: C, 83.33; H, 9.26. Found: C, 82.78; H, 9.34.

(Z)-4-(Pentamethylphenyl)-3-methyl-3-buten-2-one (4e). The indene mixture 2e was treated as above, using several sublimations for purification, mp 58–60 °C. Characterized by ¹H NMR: δ 6.0 (br, 1 H, H-4), 2.20, 2.16, and 2.10 (3 H, 6 H, 6 H, aromatic CH₃); 2.04 (d, $J = 2$, 3 H, CH₃ at C-3); 1.64 (3 H, CH₃ at C-1).

(Z)-4-(Pentamethylphenyl)-3-methyl-3-buten-2-ol (5e). If ion BH⁺ from alcohol 1e is quenched in water and the solution mixture left for 12 h at 20 °C, a flocculent precipitate forms. This precipitate was filtered and purified by several sublimations in vacuo: mp 95–97 °C; ¹H NMR δ 6.17 (br, 1 H, H-4), 4.24 (1 H, q, $J = 6$ Hz, H-2), 2.22, 2.19, 2.10 (3 H, 9 H, 3 H, CH₃ on aromatic ring, restricted rotation indicated), 1.94 (3 H, d, $J = 2$ Hz, CH₃ at C-3), 1.12 (3 H, d, $J = 6$ Hz, C-1). The structure of 5e was proven by reducing 4e with LiAlH₄ to produce 5e, identical in all respects, mp 98–99 °C. If the quench mixture is left for even longer periods before workup, a second isomer is slowly formed, having distinctive ¹H NMR peaks at δ 6.44 (1 H, br), 4.52 (1 H, q, $J = 6$ Hz), and 1.22 (3 H, d, $J = 6$ Hz). These peaks very probably correspond to the H-4, H-2, and C-1 CH₃ of the *E* isomer of the title compound.

Tetracyanoethylene Adduct 6e. The indene mixture 2e (0.25 g, 1.32 mmol) was treated with 0.128 g (1.1 mmol) of tetracyanoethylene in 20 mL of methanol at –50 °C. The mixture was warmed to 20 °C and left for 0.5 h. After solvent removal, the

crude adduct was purified by column chromatography (silica gel, eluting solvent CHCl₃–pentane, 1:10), greenish-gray crystals, 200 mg (63%), recrystallized from CHCl₃–pentane (1:5), mp 168–170 °C dec. The numbering system in these adducts is arbitrarily taken as that in the 3aH-indene. 6e: ¹H NMR δ 6.51 (br, 1 H, H-1), 2.12 (d, $J = 1$, CH₃ at C-2), 2.02, 1.97, 1.86 (all 3 H, CH₃ at C-6, -6, -7), 1.71 (3 H, CH₃ at C-4), 1.61 (3 H, CH₃ at C-3), 0.74 (3 H, CH₃ at C-3a); ¹³C NMR δ 146.3, 140.3, 135.1, 126.9 (q, C-2, -5, -6, -7, -7a), 130.9 (C-1), 112.0, 111.6, 111.2 (CN), 69.6 (CCN), 58.9, 56.4, 53.3 (C-3, -3a, -4), 21.6, 18.2, 18.0, 17.0, 15.9, 15.4, 14.7 (CH₃); electronic spectrum in acetonitrile, λ_{\max} 315 nm (ϵ_{\max} 7700). Anal. Calcd for C₂₂H₂₂N₄: C, 77.19; H, 6.43; N, 16.37. Found: C, 77.38; H, 6.43; N, 15.87.

Tetracyanoethylene Adduct 6d. With use of the same procedure as above with indene 2, whitish-grey crystals, mp 128–131 °C dec. were obtained: ¹H NMR (60 MHz) δ 6.40 (br, 1 H, H-1), 6.25 (br, 1 H, H-5), 2.04, 1.90 (d, $J = 1.2$), 1.78 (CH₃ on C-2, -6, -7), 1.58 (3 H, CH₃ on C-4), 1.46 (3 H, CH₃ on C-3), 0.70 (3 H, CH₃ on C-3a); electronic spectrum in acetonitrile, λ_{\max} 215 nm, 315 (ϵ_{\max} 9900, 6950). Anal. Calcd for C₂₁H₂₀N₄: C, 76.82; H, 6.09; N, 17.07. Found: C, 76.94; H, 6.19; N, 16.86.

Maleic Anhydride Adduct 7e. The 3aH-indene mixture 2e (0.50 g, 2.64 mmol) was treated with 0.230 g (2.35 mmol) of freshly sublimed maleic anhydride in 20 mL of dry CHCl₃ and the reaction mixture allowed to stand for 2 h at 20 °C. The solvent was removed under reduced pressure and the residue purified by crystallization from pentane at low temperature: white crystals; 600 mg (88%); mp 103–104 °C dec; ¹H NMR δ 5.97 (q, $J = 2$ Hz, 1 H, H-1), 3.14, 3.68 (AB, $J = 8$ Hz, "maleic anhydride" protons), 2.06, 1.80, 1.78, 1.70 (CH₃ at C-4, -5, -6, -7), 1.69 (d, $J = 2$ Hz, 3 H, CH₃ at C-2), 1.57 (CH₃ at C-3), 0.65 (CH₃ at C-3a); ¹³C NMR δ 173.6, 171.6 (CO), 147.1, 133.1, 130.4, 128.0, 127.2 (C-2, -4, -5, -6, -7), 125.4 (C-1), 71.4, 64.1, 63.4 (C-3, -3a, -7a), 55.2 and 50.9 (CH of "maleic anhydride"), 16.7, 15.6, 15.3, 15.1, 14.1, 13.3, 12.1 (CH₃); UV spectrum in acetonitrile, λ_{\max} 274 nm (ϵ_{\max} 4400). Anal. Calcd for C₂₀H₂₄O₃: C, 76.9; H, 7.7. Found: C, 77.1; H, 7.9.

The adduct 7e rearranges on heating in CHCl₃ (60 °C) to the thermodynamically preferred adduct 8e, characterized only by ¹H NMR but completely analogous to adduct 6e: ¹H NMR (60 MHz) δ 6.09 (br, 1 H, H-1), 3.10 (2 H, "maleic anhydride" protons), 1.91, 1.82, 1.68 (3 H, 6 H, 3 H, CH₃ at C-2, -5, -6, -7), 1.42 and 1.30 (both 3 H, CH₃ at C-3, -4), 0.56 (3 H, CH₃ at C-3a); UV spectrum in acetonitrile, λ_{\max} 308 nm (ϵ_{\max} 8300).

Maleic Anhydride Adduct 7d. With use of the same procedure as above, white crystals, mp 93–94 °C dec, were obtained ¹H NMR (60 MHz) δ 5.92 (1 H, br q, H-1), 5.44 (br, 1 H, H-5), 3.60 and 3.05 (AB, $J = 9$ Hz, "maleic anhydride" protons), 2.03, 1.81, (3 H, 6 H, CH₃ at C-4, -6, -7), 1.69 (d, $J = 2$ Hz, CH₃ at C-2), 1.51 (3 H, CH₃ at C-3), 0.65 (3 H, CH₃ at C-3a); UV spectrum in acetonitrile, λ_{\max} 277 nm (ϵ_{\max} 3700). Anal. Calcd for C₁₉H₂₂O₃: C, 76.5; H, 7.4. Found: C, 76.9; H, 7.5.

The above adduct rearranges on standing for several days at 20 °C. The new adduct was characterized by 60 MHz. 8d: ¹H NMR δ 6.12 (1 H, H-1), 5.3 (br 1 H, H-5), 3.10 (2 H, "maleic anhydride" protons), 1.95, 1.89 (d, $J = 2$ Hz), 1.70 (CH₃ at C-2, -6, -7), 1.40 (CH₃ at C-4), 1.30 (CH₃ at C-3), 0.58 (CH₃ at C-3a); UV spectrum in acetonitrile, λ_{\max} 217 nm, 307 (ϵ_{\max} 10300, 8100).

2,3,4,5,6,7-Hexamethyl-1H-indene¹² (12d). A solution of 2.00 g (9.2 mmol) of alcohol 1d in 20 mL of pentane was added dropwise with stirring to 20 mL of 96% H₂SO₄ kept at 0 °C. The resulting ion solution was warmed to 20 °C and then quenched by adding dropwise to a vigorously stirred solution of Na₂CO₃ (60 g of Na₂CO₃ in 300 mL of water) covered with pentane and kept at 0 °C. The organic layer was separated and the aqueous layer further extracted (2 × 200 mL) with pentane. The combined organic layers were dried over anhydrous MgSO₄. After solvent removal, the residue was recrystallized from pentane: yield 1.60 g (90%); mp 141.5 °C; ¹H NMR δ 3.11 (br, 2 H, H-1), 2.49, 2.02, 2.23 (3 H, 3 H, 12 H, CH₃ protons); ¹³C NMR δ 141.7, 139.1, 137.1, 134.0, 133.5, 130.2, 128.2, 126.3 (all q), 41.9 (C-1), 16.2 (2 C), 15.7, 15.1 (2 C), 14.0 (CH₃). Anal. Calcd for C₁₅H₂₀: C, 89.9; H, 10.1. Found: C, 90.0; H, 10.35.

2,3,4,5,7-Pentamethyl-1H-indene (12c). This indene was prepared as above with 2.00 g of 1c: yield 1.40 g (83%); mp 97.5

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°C; $^1\text{H NMR}$ δ 6.74 (1 H, H-5), 3.06 (2 H, H-1), 2.45, 2.03, 2.28, 2.23 (3 H, 3 H, 3 H, 6 H, CH_3); $^{13}\text{C NMR}$ δ 144.5, 139.2, 138.0, 135.1, 134.1, 129.1, 126.3 (all q), 126.9 (C-6), 40.9 (C-1, 20.3, 18.1, 14.8 (2 C), 14.0 (CH_3)). Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.3; H, 9.7. Found: C, 89.8; H, 9.7.

3,4,5,6,7-Pentamethyl-1H-indene (12b). This indene was prepared as for **12d** using 1.00 g of **1b**: yield 0.80 g (88%); mp (after sublimation) 133-34 °C (lit.¹³ mp 104 °C); $^1\text{H NMR}$ δ 6.15 (br, 1 H, H-2), 3.17 (br, 2 H, H-1), 2.53 and 2.29 (3 H, 9 H, CH_3 on C-4, -5, -6, -7), 2.41 (m, $J_{1,3}$ and $J_{2,3} \sim 1$ Hz, 3 H, CH_3 at C-3); $^{13}\text{C NMR}$ δ 142.1, 141.9, 140.5, 133.7, 131.6, 129.0, 127.5 (q), 129.7 (C-2), 36.6 (C-1, 19.1 (2 C), 16.4 (2 C), 15.9 (CH_3)). Anal. Calcd for $\text{C}_{14}\text{H}_{18}$: C, 90.3; H, 9.7. Found: C, 90.2; H, 9.4.

3,4,5,6,7-Tetramethyl-1H-indene (12a). This indene was prepared as for **12b**, except that 100% H_2SO_4 was used and the ion solution was kept at 20 °C for 4 h before quenching. From 1.00 g (5.3 mmol) of alcohol **1a**, there was obtained 0.40 g (47%) of **12a**, purified in this case by sublimation of the crude residue (0.1 mm, bath 45 °C): mp 59-60 °C; $^1\text{H NMR}$ δ 6.90 (1 H, H-6), 6.23 (br, 1 H, H-2), 3.16 (br, 2 H, H-1), 2.52, 2.34, 2.32 (all 3 H, CH_3 at C-4, -5, -7), 2.42 (m, 3 H, CH_3 at C-3); $^{13}\text{C NMR}$ δ 143.0, 135.1, 129.7, 127.3 (all q), 130.3 and 127.8 (CH aromatic), 35.6 (C-1), 20.1, 18.5, 18.1, 14.7 (CH_3). Anal. Calcd for $\text{C}_{13}\text{H}_{16}$: C, 90.7; H, 9.3. Found: C, 90.8; H, 9.2.

2,3,4,5,5,6,7-Heptamethyl-5H-indene (13). The cation solution described for the preparation of **2e**, using 0.50 g (2.2 mmol) of the alcohol **1e**, was allowed to warm to 20 °C, resulting after 2 h in the formation of cation EH^+ . After quenching in the usual way, the crude residue was purified by sublimation, yield 0.30 g of red crystals (65%), mp 42-43 °C (some decomposition occurs during the purification since the yield of the nearly pure crude product is virtually quantitative). The compound slowly polymerizes on contact with air. **13**: $^1\text{H NMR}$ δ 6.00 (1 H, H-3), 2.32, 2.04, 1.94, and 1.87 (all sharp 3 H singlets, CH_3 at C-3, -4, -6, -7),

2.20 (d, $J = 1$, CH_3 at C-2), 1.13 (6 H, C-5 CH_3 's); $^{13}\text{C NMR}$ δ 150.6, 140.0, 138.5, 135.2, 133.1, 123.4, 121.2 (all q), 120.1 (CH alkene), 44.4 (q, C-5), 23.9 (2 C, CH_3 's on C-5), 15.7, 14.8, 14.5, 13.9, 13.3 (CH_3); electronic spectrum (acetonitrile), 220 nm, 248, 253, 265, 420 (ϵ_{max} 13 100, 21 900, 19 700, 5600, 1060). Anal. Calcd for $\text{C}_{16}\text{H}_{22}$: C, 89.7; H, 10.3. Found: C, 88.9; H, 10.5.

Electronic Spectra of Cations BH^+ and EH^+ from Alcohol **1e.** Cation BH^+ was prepared at 0 °C in 96% H_2SO_4 . The spectrum was recorded at 5.2 °C [λ_{max} 483 nm, 351, 313, 260 (ϵ_{max} 9350, 4600, 5000, 15 200, respectively)]. On warming to 20 °C, the rearrangement of BH^+ to EH^+ slowly takes place. The spectrum of EH^+ shows λ_{max} 380 nm, 352 (ϵ_{max} 11 850, 25 200). On leaving cation EH^+ for 24 h at 20 °C, there was no change in the spectrum.

Kinetic Measurements. The first-order rate constants shown in Table II were obtained by $^1\text{H NMR}$ integration of the area decrease of a reactant peak and the accompanying increase of a product peak. The temperature calibration and other NMR details follows that given previously.¹⁴

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Registry No. **1a**, 74705-62-7; **1a**· AH^+ , 84012-09-9; **1a**· CH^+ , 84012-07-7; **1a**· DH^+ , 84000-52-2; **1b**, 84000-28-2; **1b**· BH^+ , 84000-48-6; **1b**· DH^+ , 84000-53-3; **1c**, 84000-29-3; **1c**· AH^+ , 84012-08-8; **1c**· BH^+ , 84000-49-7; **1c**· CH^+ , 84000-46-4; **1c**· DH^+ , 84000-54-4; **1d**, 84000-30-6; **1d**· BH^+ , 84000-50-0; **1d**· DH^+ , 84000-56-6; **1e**, 84000-31-7; **1e**· BH^+ , 84000-51-1; **1e**· EH^+ , 84000-47-5; **2d**, 84000-32-8; **2e**, 84000-33-9; **3d**, 84000-35-1; **3e**, 84000-34-0; **4d**, 84000-36-2; **4e**, 84000-37-3; **5e**, 84000-38-4; **6d**, 84000-40-8; **6e**, 84000-39-5; **7d**, 84000-42-0; **7e**, 84000-41-9; **12a**, 84000-44-2; **12b**, 84000-43-1; **12c**, 36230-98-5; **12d**, 21866-46-6; **13**, 84000-45-3.

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Kinetics and Mechanism for the Alkaline Homogeneous Hydrolysis of 1,1,1-Trimethylolethane Trinitrate

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The kinetics for the alkaline homogeneous hydrolysis of 1,1,1-trimethylolethane trinitrate (MTN) in 95% ethanol-water with sodium hydroxide concentrations between 0.25 and 2.1 M and temperatures between 50.0 and 60.0 °C have been investigated. One mole of MTN was found to react with 3 mol of base and to hydrolyze by a series of consecutive and competitive bimolecular and internal cyclization reactions involving three nitrate ester intermediates to form the cyclic alcohol ether 3-methyl-3-oxetanemethanol (AE) as the final major product with only trace amounts of the expected triol 1,1,1-tris(hydroxymethyl)ethane (TA). MTN and its intermediates showed good second-order rate constants for the expression $-\text{d}(\text{MTN})/\text{d}t = k_1(\text{MTN}) = k_2(\text{B}^-)(\text{MTN})$, where k_1 is the first-order rate constant with excess base, B^- . Relative k_2 values in 95% ethanol-water, 95% methanol-water, and water were found to be 1.0, 0.1, and 0.01, respectively. Hydrolysis kinetics and product formation for each nitrate ester intermediate have been determined, and an overall hydrolysis mechanism for MTN is presented.

Introduction

Highly energetic nitrate esters such as nitroglycerine (NG) and 1,1,1-trimethylolethane trinitrate (MTN) are widely used in propellant and explosive compositions. It is essential, therefore, that a thorough knowledge of their chemical reactions be known, including hydrolytic stability, for safety as well as environmental concerns. An excellent historical summary of the alkaline hydrolyses of nitrate

esters has been presented by Urbanski¹ with 24 references covering work from 1885 through 1955. None of these investigations, however, included MTN. Baker and co-workers' kinetic studies of the alkaline hydrolyses of nitrate esters are classic²⁻⁴ and led to the conclusion that three

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