# Pyramidal Bishomo $(CH)_5^+$-Type Carbocations. Effects of Phenyl Substitution at Basal Positions

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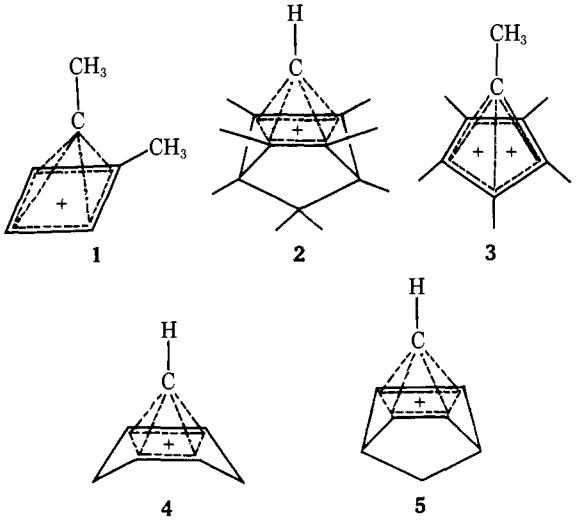
**Abstract:** When two adjacent methyl substituents at the base of the pyramidal bishomo $(CH)_5^+$-type carbocation **2** are replaced by phenyl substituents, the resulting ion is destabilized with respect to rearrangement. Thus carbocation **18** could only be prepared from the tetracyclic alcohol *exo*-2,3-diphenyl-1,5,6,7,7,8-hexamethyltetracyclo[3.3.0.$0^{2,8}$.$0^{3,6}$]octan-4-ol (**11**) or hydrocarbon 8-methylene-2,3-diphenyl-1,5,6,7,7-pentamethyltetracyclo[3.2.1.$0^{2,4}$.$0^{3,6}$]octane (**15**) and $FSO_3H$-$SO_2ClF$ if the temperature was kept well below −100°, whereas **2** can be prepared from analogous precursors at temperatures as high as −50°. NMR chemical shift data on **18** suggest that the methyl-bearing carbons at the "base" of the pyramid are more positive than the corresponding atoms in **2**. Above −100°, **18** rearranges to the bicyclo[3.3.0]octyl allylic carbocations **24** and **25** in the ratio 7:3. The structures of these ions were deduced by trapping experiments at −78° with $CH_3ONa$-$CH_3OH$; ion **24** gave *exo*- and *endo*-methyl ethers **20** and **21**, whereas ion **25** gave the triene **22**. The tetracyclic alcohol **11** is converted to the corresponding chloride (**12**) or trifluoroacetate (**13**) only under more vigorous reaction conditions than are necessary in the analogous all-methyl system. Chloride **12** methanolyzes more slowly (by about $10^2$) than the corresponding all-methyl substituted chloride (**26**); whereas **26** gives only substitution products, **12** gives the elimination product **15** as well as the expected methyl ether **14** (the latter with retention of configuration). Elimination is favored by added base. All these data support the conclusion that substitution of phenyl groups for methyl groups at C-2 and C-3 in the tetracyclic alcohol (**11**) or related compounds destabilizes the resulting carbocation.

The effect of phenyl substitution on carbonium ion stability is complex and not easily predicted[1] since the factors at play (steric, inductive, and conjugative) may act in opposing ways. Theoretical calculations which overemphasize one of these factors or neglect another may lead to erroneous conclusions. Consequently there is a need for experimental studies of the problem.

During the past two years, the predictions of Stohrer and Hoffmann[2] that the $(CH)_5^+$ carbocation may assume a square pyramidal geometry have been verified with the synthesis and characterization of ions **1**,[3] **2**,[4] **3**,[5] **4**,[6] and **5**.[7] In



each case, NMR evidence, both $^1H$ and $^{13}C$, shows that the carbons at the base of the pyramid bear more of the positive charge than does the carbon at the apex. Theoretical calculations[8] predict that ions of type **1** should be stabilized by methyl or phenyl substitution; stabilization is predicted to be greater for "basal" than for "apical" substituents, and greater for phenyl than for methyl.

We describe here the synthesis of ion **18**, in which two of the methyl substituents at the base of the pyramid in **2** are replaced by phenyl groups. Contrary to what might have been predicted from an extrapolation of theoretical calculations,[8] such phenyl substitution resulted in an ion which was only stable at a much lower temperature than is **2**, and which was more prone to thermal rearrangement. Furthermore, the unequal charge distribution at the "basal" carbons in **18** resulted in reactions not observed with **2**.

## Results and Discussion

**Synthesis and Characterization of Tetracyclic Alcohol 11.** The precursor of ion **18** was the tetracyclic alcohol **11**, whose synthesis is outlined in Scheme I.[9] Diels-Alder addi-

**Scheme I**

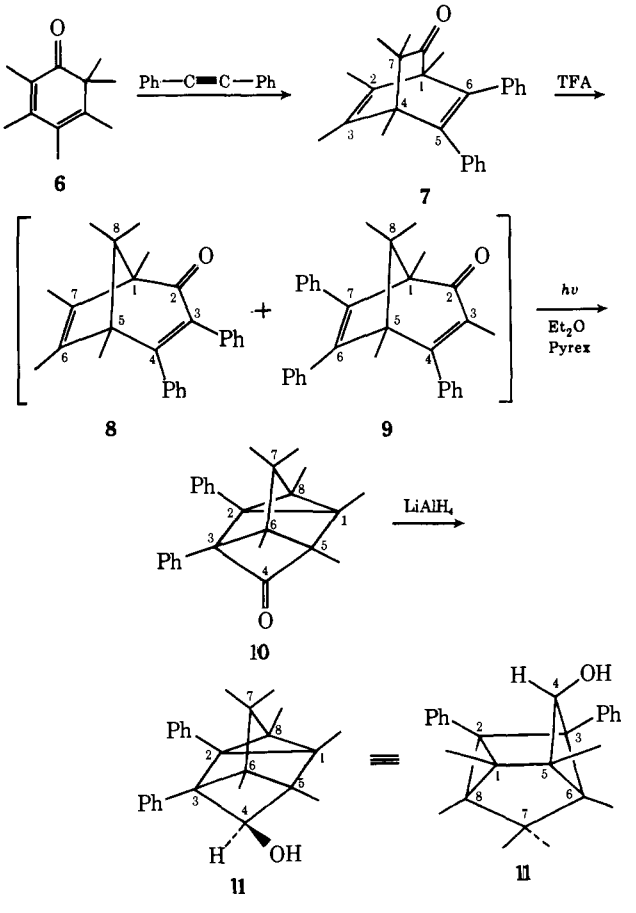


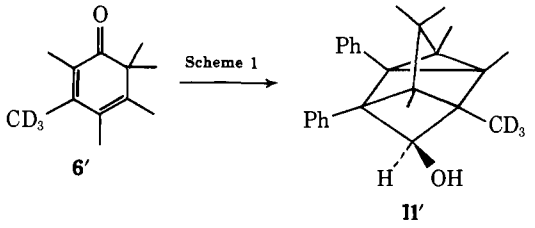
Table I. $^1$H NMR Spectra of 7–15

| Compd | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 1.10 (3.9) | 1.78 (1.4) | 1.88 (1.0) | 1.15 (1.4) | Ar | Ar | 1.22 (3.3)<br>0.98 (3.1) | | |
| 8 | 1.10 (4.0) | | Ar | Ar | 0.78 (1.3) | 1.75 (1.3) | 1.55 (1.4) | 1.02 (1.0)<br>1.28 (2.3) | |
| 9 | 1.02 (3.6) | | 1.82 (2.6) | 1.70 (1.4) | 1.08 (1.0) | Ar | Ar | 1.22 (1.0)<br>1.02 (1.4) | |
| 10 | 1.00 (1.5) | Ar | Ar | | 1.17 (2.1) | 0.92 (2.3) | 0.92 (1.2)<br>0.85 (1.1) | 1.35 (1.0) | |
| 11 | 1.27 (1.2) | Ar | Ar | 4.40 (8.3) | 1.09 (3.8) | 1.40 (4.0) | 1.05 (1.5)<br>0.80 (1.2) | 0.80 (1.0) | OH 1.40 (44.8) |
| 12 | 1.32 | Ar | Ar | 4.57 | 1.18 | 1.47 | 1.08<br>0.82 | 0.82 | |
| 13 | 1.37 | Ar | Ar | 3.62 | 1.08 | 1.40 | 1.12<br>0.85 | 0.85 | |
| 14 | 1.27 (1.0) | Ar | Ar | 4.00 (3.0) | 1.05 (1.7) | 1.40 (3.3) | 0.98 (1.3)<br>0.77 (1.3) | 0.77 (1.3) | $OCH_3$<br>4.12 (3.0) |
| 15 | 1.17 | Ar | Ar | 2.60 | 1.22 | 0.75 | 1.05<br>0.53 | 4.30, 4.35 | |

tion of diphenylacetylene to hexamethyl-2,4-cyclohexadienone[11] gave the crystalline adduct **7**, mp 150°, in 70% yield. On standing at room temperature in trifluoroacetic acid (TFA), **7** gave a mixture of **8** and **9** (92:8) which was irradiated without purification, in ether solution through a Pyrex filter, to give the crystalline tetracyclic ketone **10** (mp 147–148°, sublimes) in 64% yield.[12] The structures of **7** → **10** follow clearly from their $^1$H NMR (Table I) and other spectra (see Experimental Section).

Lithium aluminum hydride reduction of **10** gave a nearly quantitative yield of a single crystalline secondary alcohol, mp 137–138°, assigned the configuration shown in structure **11**. Jones' oxidation[13] of **11** gave an 80% yield of **10**, confirming that the tetracyclic ring structure established[12] for **10** was also present in **11**. The geometry of **11** is clear from the large and nearly equal relative Eu-shift[14] slopes (Table I) of the C-5 and C-6 methyl substituents. Apparently hydride attack is only possible from the face of the cyclobutanone ring in **10** opposite the phenyl (at C-3) and methyl (at C-5 and C-6) substituents. Similar specificity was observed previously in the all-methyl analog of **10**.[4]

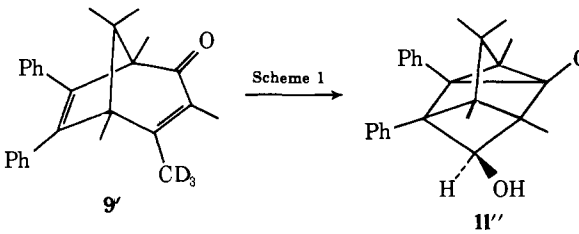
When the reaction sequence shown in Scheme I was carried through starting with deuterium labeled[11] dienone **6′**, the resulting **11′** had an NMR spectrum identical with that




**6′** **11′**

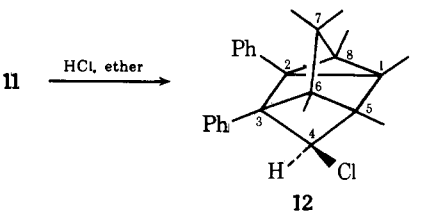
of **11** except that the singlet at δ 1.09 was absent, allowing this signal to be assigned to the C-5 methyl substituent. This assignment is consistent with the large Eu-shift slope for this signal.

When the latter part of Scheme I was carried through using deuterium-labeled **9′** (prepared from **9**, sodium methoxide, and $CH_3OD$), the resulting **11″** had an NMR spectrum identical with that of **11** except that the singlet at δ 1.27 was absent, allowing this signal to be assigned to the C-1 methyl substituent. The low Eu-shift relative slope of this signal (1.2) reinforces the conclusion that **11** has the structure shown, and not the epimeric geometry at C-4. These labeling results, taken together with the Eu-shift data, also allow the unambiguous assignment of the lowest field methyl singlet (δ 1.40) to the C-6 substituent, whose chemical shift is undoubtedly affected by the nearby hydroxyl and phenyl groups. Other features of the NMR assignment are discussed in the supplement to this paper.

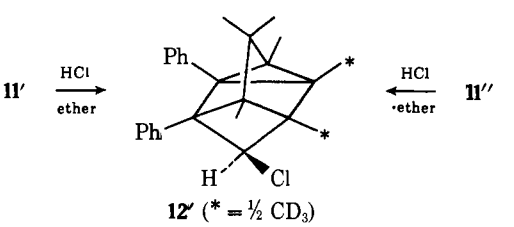



**9′** **11″**

**Reactions of 11.** Treatment of **11** with an ether solution of hydrogen chloride for 6 hr at room temperature gave (80%) the crystalline chloride **12**, mp 141°. These conditions are considerably more rigorous than those required for the all-methyl analog,[4] where the corresponding transformation was complete in 5 min at 0°.[15] However, as with the all-methyl analog, the "front" and "back" of the molecule interconvert during the reaction. Thus treatment of either **11′** or **11″** with hydrogen chloride in ether gave **12′**, with




**12**

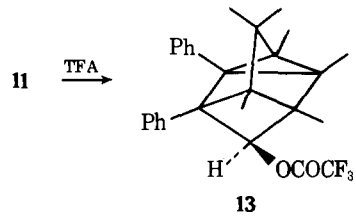



**12′** (* = ½ $CD_3$)

the deuterium label equally distributed between the C-1 and C-5 methyl groups (the singlets at δ 1.18 and 1.32 integrated for 1.5 protons each).

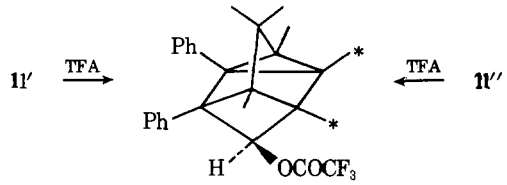
The reaction of **11** with trifluoroacetic acid (30% in $CCl_4$, 1 hr, room temperature) proceeded in a similar manner, to give the trifluoroacetate **13** (an oil). Once again, the conditions required are more severe than those needed for the all-methyl analog (1 min at room temperature). However, the labeling results were similar to those with the chloride (**11′** or **11″** gave **13′**).

The stereochemistry of **12** and **13** is assumed but appears



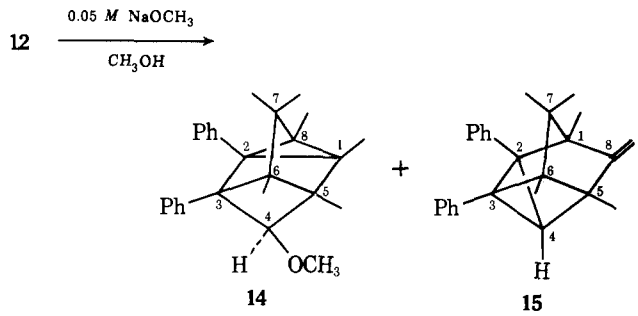

13

reasonable not only on mechanistic grounds[4] but also as a consequence of comparing their NMR spectra with that of **11** (Table I).



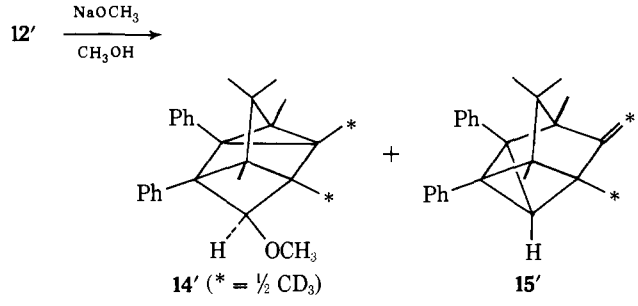

13′ (* = ½ $CD_3$)

Still another difference from the all-methyl system showed up when **12** was refluxed overnight with 0.05 *M* sodium methoxide in methanol. In addition to the expected methyl ether **14** (formed in 45% yield), a hydrocarbon was also obtained (55% yield), to which we assign structure **15**.




14 15

In the all-methyl system, only the ether was produced. The structure of the crystalline ether **14**, mp 96–97°, follows from its spectra, particularly the NMR spectrum (Table I), which is similar to those of **11–13**. Treatment of **12′** with sodium methoxide in methanol gave labeled **14′** whose



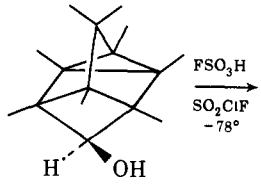

14′ (* = ½ $CD_3$) 15′

NMR spectrum showed only 1.5 H for the signals at δ 1.27 and 1.05, allowing these signals to be assigned to the methyls at C-1 and C-5 (respectively, if one compares chemical shifts with **11**). Consequently the large relative slope (Eu-shift data) for the methyl group at C-6 (δ 1.40) allows us to conclude that **11** and **14** have the same configuration at C-4. Since **14** was also obtained from **12** and neutral or acidified methanol (vide infra)—that is, under SN1 conditions—we conclude that **12** also has the same configuration as **11** and **14**, and that, in fact, all of these displacements go with retention of configuration at C-4.

The NMR spectrum (Table I) of **15** (an oil) showed two vinyl protons, a methine singlet, and five methyl singlets, in addition to the aryl protons. In the NMR spectrum of **15′**, the areas of the vinyl protons and the methyl singlet at δ 1.22 were reduced by 50%; this allows the methyl signal at C-5 to be assigned unequivocally. The remaining methyl assignments follow by chemical-shift comparisons with the all-methyl analog of **15**[4b] (i.e., **17**).

Treatment of **15** with hydrogen chloride in ether (room temperature, 30 min) or with trifluoroacetic acid in carbon tetrachloride (room temperature, 5 min) gave **12** and **13**, respectively, confirming the structure of **15**.

**Stable Ions in $FSO_3H$–$SO_2ClF$.** As described previously,[4] stable solutions of the pyramidal ion **2** were readily obtained by dissolving either the alcohol **16** or hydrocarbon **17**[4b] in $FSO_3H$–$SO_2ClF$ (1:4) at −78°. Such solutions were

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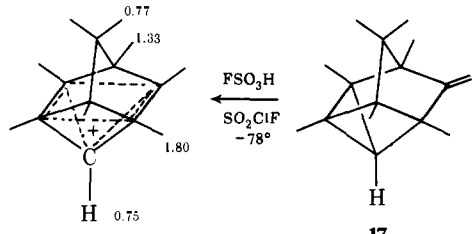
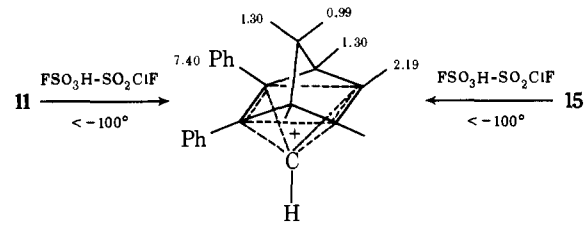



2 17

stable over the temperature range −50 to −120°, and the $^1H$ NMR spectrum of **2** consisted of four singlets at δ 1.80, 1.33, 0.77, and 0.75 with relative areas 12:6:6:1.

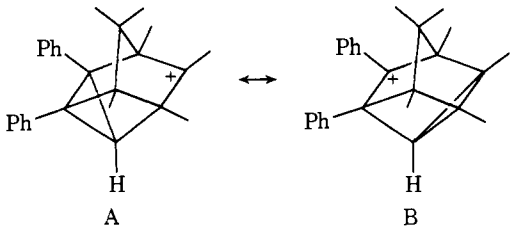
It seemed likely, from the results described above (deuterium label scrambling and retention of configuration), that the interconversions of **11–14** proceed through an analog of **2** in which two of the methyl groups at the base of the pyramid are replaced by phenyl substituents. However, when attempts were made to prepare stable solutions of the ion by treating either **11** or **15** with $FSO_3H$–$SO_2ClF$ at −78°, the resulting NMR spectrum was complex and not consistent with expectation for the diphenyl analog of **2**. Only when **11** was carefully treated with $FSO_3H$–$SO_2ClF$ (ca. 1:5 v/v) at −125°, and the temperature was kept below −100°, while determining the NMR spectrum, could a simplified spectrum be obtained. It consisted of four singlets at δ 7.40, 2.19, 1.30, and 0.99 with relative areas of approximately 10:6:9:3. We obtained the identical spectrum from **15** and attribute it to the pyramidal ion **18**.




18

The methyl signals in the NMR spectrum of **18** can be compared with those of **2** and may be interpreted in the following way. In **2**, charge is equally distributed over all four atoms at the base of the pyramid whereas, in **18**, charge will be differently distributed between the phenyl- and methyl-bearing carbons. Since this signal occurs at lower field in **18** (δ 2.19) than in **2** (δ 1.80), one might conclude that the methyl-bearing carbons in **18** carry a somewhat larger positive charge than do those in **2**. In resonance terms, we could say that structures such as A contribute more to the reso-

nance hybrid **18** than do structures B. The rearrangement of **18**, to be discussed below, is consistent with this conclusion.



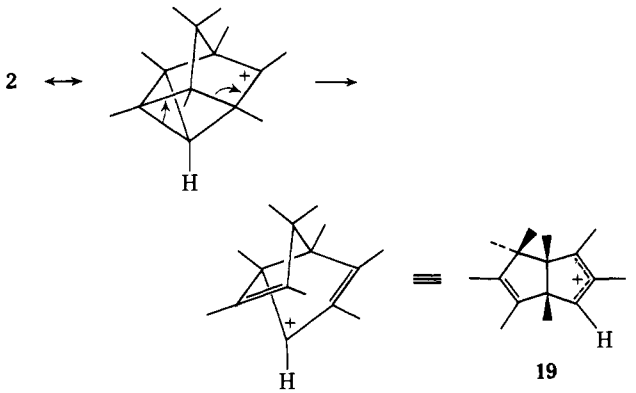
A B

The bridgehead methyls have approximately the same chemical shifts in both ions ($\delta$ 1.30 in **18**, $\delta$ 1.33 in **2**).

Although the symmetry of **2** requires that the *gem*-dimethyl protons be equivalent, this is not so for **18**. We attribute the signal at $\delta$ 1.30 to the methyl syn to and presumably deshielded by the phenyl substituents. Models show that the phenyl groups assume a canted face-to-face rather than edge-to-edge geometry with respect to each other. This presents their deshielding region to the *syn*-methyl group and also explains why the phenyl groups are less effective than methyl groups at stabilizing positive charge on the "basal" carbons to which they are attached. The remaining methyl signal in **18** occurs at lower field ($\delta$ 0.99) than that of the corresponding *gem*-dimethyl signal in **2** ($\delta$ 0.77), probably because the "basal" carbons which it is "over" (or syn to) are more positive. Finally, we have been unable to locate the signal for the proton at the apex of the pyramid; it is probably buried under one of the peaks at $\delta$ 0.99, 1.30, or 2.19. We note that, in **2**, this signal was also difficult to locate since it had nearly the same chemical shift as the *gem*-dimethyl protons.

Despite several attempts, we have thus far been unsuccessful in obtaining a $^{13}C$ NMR spectrum of **18** since the ion rearranges so easily, even at $-100°$.

**Rearrangement of 18.** We showed earlier[4b] that ion **2** rearranges, at about $-55$ to $-40°$, to the allylic ion **19**. At much lower temperatures, ion **18** undergoes a similar but more complex rearrangement (more complex because of the lower symmetry of **18**).



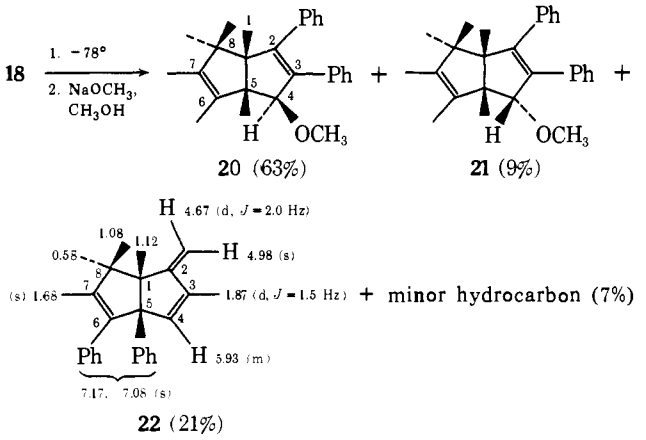
**19**

When solutions of **18** in $FSO_3H$-$SO_2ClF$ were allowed to warm above $-100°$, the simple NMR spectrum ascribed to **18** became more complex. Two different sets of new peaks appeared, which had the approximate areas of 7:3. The product ion which gave rise to the major peaks was stable up to about $-40°$, but the minor product ion was stable only to about $-70°$, whereupon its NMR pattern changed even further.

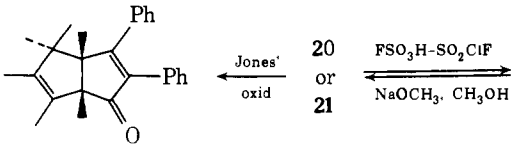
Solutions of **18** in $FSO_3H$-$SO_2ClF$ were warmed to $-78°$ for 30 min, then carefully quenched at that temperature with excess sodium methoxide in methanol. Four products were isolated, two ethers and two hydrocarbons. The former were separated by preparative thin-layer chromatography, and the latter by gas chromatography. The minor hydrocarbon product has not been positively identified, but the other products are assigned structures **20–22** on mechanistic, spectroscopic, and chemical evidence.

Table II. The NMR Spectra of 20, 21, and 23

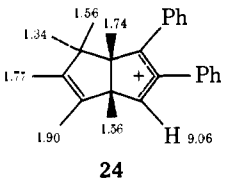
| | 20 | 21 | 23 | Assignment |
|---|---|---|---|---|
| $CH_3O$ | 3.15 (13.0) | 3.12 | | |
| $CH_3OCH$– | 4.28 (15.0) | 3.97 | | |
| $CH_3C$= | 1.72 (1.5) | 1.58 | 1.75 (2.6) | C-6 |
| | 1.52 (1.0) | 1.58 | 1.55 (1.0) | C-7 |
| $CH_3C$ | 1.27 (5.0) | 1.28 | 1.28 (1.6) | C-1 |
| | 1.07 (7.0) | 1.14 | 1.22 (3.5) | C-5 |
| | 0.92 (1.5) | 1.05 | 1.10 (1.1) | C-8 |
| | 0.82 (3.0) | 0.78 | 0.92 (1.5) | C-8 |
| Ar (10 H) | 7.00, 7.07 | 7.08 | 7.27, 7.08 | |




The NMR spectra of **20** and **21** were very similar, as shown in Table II.[16] Furthermore, Jones' oxidation[13] of either **20** or **21** gave the same ketone, assigned structure **23**, and dissolution of either **20** or **21** in $FSO_3H$-$SO_2ClF$ at $-78°$ gave the same carbonium ion, assigned structure **24**. Consequently **20** and **21** must be stereoisomers. Presumably both are formed by attack of methanol, exo or endo, on ion **24**, which must be the major rearrangement product of **18**. The major product is assigned the geometry shown for **20** because (a) exo attack should be favored, and (b) the large Eu-shift slopes for the C-1 and C-5 methyls are consistent with this assignment.




**23**



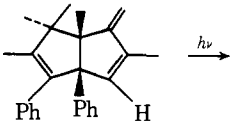

**24**

The NMR spectrum of ion **24** strongly supports the assigned structure. The one-proton singlet at $\delta$ 9.06 is typical of a proton at the terminus of an allyl cation in a five-membered ring.[17] The absence of any methyl signals below $\delta$ 2.0 requires that the other two carbons of the allyl cation be substituted with phenyl, not methyl groups. Other assignments shown in the structure are based in part on labeling experiments described below, and in part on comparison of chemical shifts with those of similar ions.[18]

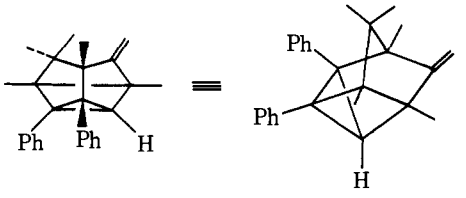
The structure of **23** is based on spectral evidence. The $\nu_{C=O}$ 1690 $cm^{-1}$ and $\lambda_{max}$ (EtOH) 294 nm ($\epsilon$ 8300), 231 (17,400) are consistent with the cyclopentenone moiety.[19] The chemical shifts of the allylic methyl groups ($\delta$ 1.55, 1.75) and their Eu-shift slopes are consistent only with their location in the five-membered ring that does not contain the carbonyl group. The other methyl shifts and slopes (see Table II) compare well with those of **20** and **21.**

The structure of **22** is based on mechanistic, spectral, and chemical evidence. The ir spectrum had a strong terminal methylene band at 880 $cm^{-1}$. The uv spectrum [$\lambda_{max}$ (EtOH) 236 nm ($\epsilon$ 16,800)] was similar to those of other compounds with the same chromophore.[20] The NMR spectrum (see structure) showed three vinyl protons, two allylic methyl groups with coupling patterns that place them on different double bonds, and three unsplit aliphatic methyl singlets. Double irradiation of the vinyl proton at $\delta$ 5.93 caused collapse into singlets of the doublets at $\delta$ 1.87 and 4.67.

Finally, the structure of **22** was confirmed by irradiation of an acetone solution (Corex), to give **15.** A preliminary account of several similar photoisomerizations was recently published.[21,22]

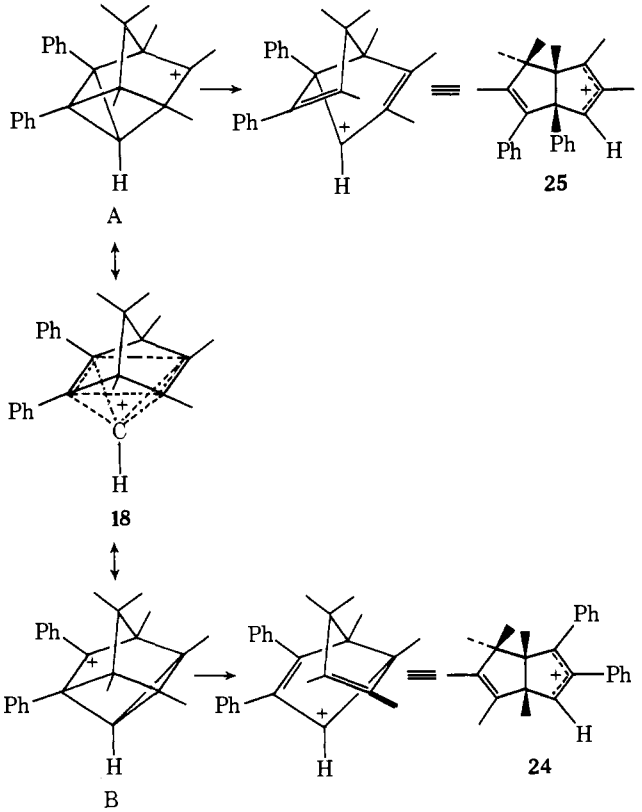



**22**




**15**

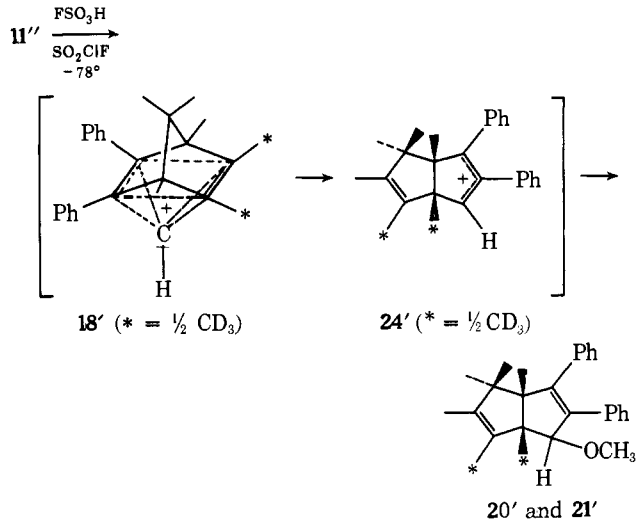
**Mechanism of the Rearrangement of 18.** The mechanism for the rearrangement of **18** is similar to that of **2**; however, because of the lower symmetry of **18,** two different rearrangement paths are possible, depending upon whether rearrangement occurs from resonance contributor A or B. The expected[4] products would be allylic ions **24** or **25.** The observed quenching products **20** and **21** arise from attack of methanol on **24,** whereas **22** is formed by proton loss from **25.**




**25**

**24**

A labeling experiment is consistent with this scheme. Alcohol **11″** was treated with $FSO_3H$-$SO_2ClF$ at −78°, then quenched with sodium methoxide in methanol. If the above scheme is correct, the resulting **20′** and **21′** should be labeled as shown (the hydrocarbon product was ignored). Consistent with expectation, the peaks at $\delta$ 1.07 and 1.72 in **20′** were reduced in area to 1.5 H each, and the peaks at $\delta$ 1.14 and 1.58 in **21′** were reduced in area to 1.5 H and 4.5 H, respectively.



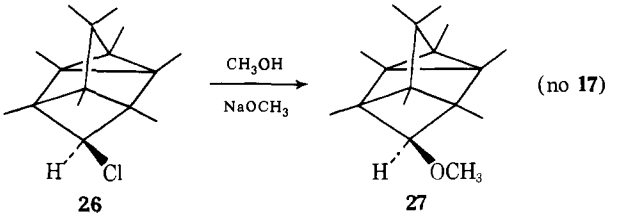

**18′** (* = ½ $CD_3$)

**24′** (* = ½ $CD_3$)

**20′** and **21′**

The predominant formation of ethers **20** and **21** over hydrocarbon **22** (and the unidentified product) indicates that the preferred rearrangement product of **18** is **24,** not **25,** by a factor of approximately 7:3. Yet the chemical-shift data on **18** indicate that A is a more important contributor to the structure of **18** than is B. Thus the transition state leading to **24** must have a lower energy than that leading to **25,** possibly as a consequence of somewhat greater stabilization of the positive charge by a phenyl than by a methyl substituent; this is more likely in the [3.3.0] allylic system than it is in **18.**[23]

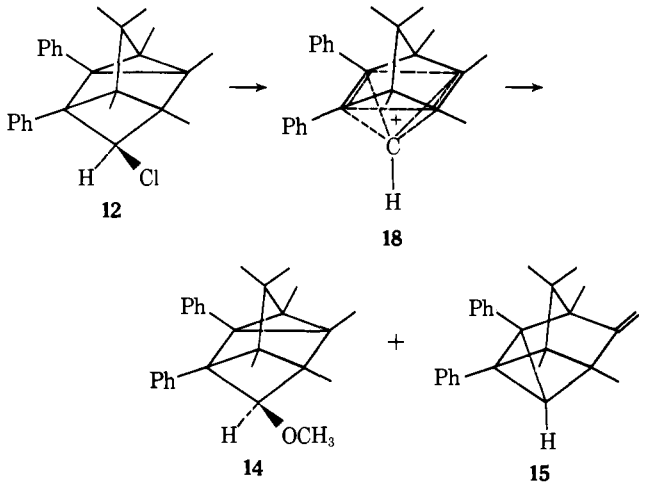
**Further Discussion of the Solvolytic Reactions.** In a previous section (vide supra), it was shown that the secondary chloride **12,** on treatment with dilute sodium methoxide in methanol, gave not only the corresponding ether **14** but the elimination product **15** as well. In contrast, **26** gave[4b] only the methyl ether **27.** Presumably this reaction proceeds via




(no **17**)

**26** **27**

ion **18,** which then partitions between the substitution and elimination paths. To further explore the elimination reaction, which does not occur in the all-methyl analog of **12,** we studied the reaction of **12** with methanol under a variety of conditions, as summarized in Table III. Under acidic conditions, only the ether **14** was formed. Separate experiments showed that, under the conditions of expt 1, **15** was converted entirely to **14.** Thus the product of thermodynamic con-




trol is clearly **14**.

Although some **15** (4%) was formed from **12** in neutral methanol, the yield of **15** was markedly increased, to a maximum of 82%, by added sodium methoxide.[24] Separate experiments showed that **14** and **15** are not interconverted under the conditions of expt 2-6 (Table III). Consequently, **15** must be a product of kinetic control.

It seems reasonable to conclude that in the polar media used in these reactions, **12** readily ionizes to **18** which then either reacts with methanol (or methoxide) at the apical carbon to give **14** (an SN1 process, thermodynamic control) or eliminates a proton from one of the "basal" methyl groups, the latter process being analogous to the ElcB mechanism, and involving kinetic control. The reason for the difference in behavior of **18** and **2** is that there is more positive charge on the methyl-bearing "basal" carbons in **18** (as judged from the NMR data); thus, the protons of the "basal" methyls in **18** are more acidic than those in **2**, and consequently they are more readily removed by base.

Finally, the methanolysis rates of **12** and **26** were compared. At 25°, using 0.0025 *M* solutions, the first-order rate constants were $3.1 \times 10^{-4}$ sec$^{-1}$ for **26** and $3.7 \times 10^{-6}$ sec$^{-1}$ for **12** (the products were **27** from **26**, and 96% **14**, 4% **15** from **12**). Thus the phenyl substituents cause an approximately $10^2$ retardation in methanolysis rate.

**A Comparison of the Phenyl-Substituted System with the All-Methyl System.** In the previous sections of this paper, the following facts have been established which bear on the relative stabilities of ions **18** and **2**: (a) the conversion of the phenyl-substituted tetracyclic alcohol **11** to the corresponding chloride **12** or trifluoroacetate **13** requires more vigorous conditions than the corresponding conversions in the all-methyl system but, in both systems, these reactions involve a symmetric intermediate, as shown by label scrambling; (b) phenyl substitution retards the first-order methanolysis of the tetracyclic chloride (**12** vs. **26**) by a factor of approximately $10^2$; (c) the phenyl-substituted chloride **12** undergoes elimination (to **15**) as well as substitution in neutral or basic methanol, the elimination being favored by increased concentrations of base, whereas all-methyl chloride **26** does not eliminate (to **17**) even in strongly alkaline methanol; (d) ion **18** can be formed from its alcohol (**11**) or hydrocarbon (**15**) precursors in $FSO_3H$-$SO_2ClF$ only at temperatures below −100°; above that temperature, it rearranges rapidly to the [3.3.0] allylic ions **24** and **25**, whereas **2** does not rearrange similarly until the temperature is raised above −50°; (e) the preferred rearrangement product of **18** is **24**; and (f) the "basal" methyl protons in **18** are shifted downfield by about 0.39 ppm from the corresponding protons in **2**.

All of these data are consistent with the conclusion that phenyl substitution at the "basal" positions of pyramidal $(CH)_5^+$-type carbonium ions of the type **2** destabilizes the ion and places a greater positive charge on the remaining methyl-bearing "basal" carbon atoms. The most likely explanation for this result is that the phenyl rings must be unable to exert their usual conjugative stabilizing effect and in fact exhibit a destabilizing electron-withdrawing inductive effect. This result is in contrast to theoretical predictions for the $(CH)_5^+$ ion[8] and is probably a consequence of twisting of the phenyl rings in a canted face-to-face orientation as a result of steric crowding.

Table III. Methanolysis of **12**

| Expt | Conditions | % yield 14 | % yield 15 |
|---|---|---|---|
| 1 | 80% aq MeOH, trace of HCl | 100[a] | 0 |
| 2 | $CH_3OH$ | 96 | 4 |
| 3 | 0.01 *M* $NaOCH_3$–$CH_3OH$ | 67 | 33 |
| 4 | 0.05 *M* $NaOCH_3$–$CH_3OH$ | 45 | 55 |
| 5 | 0.5 *M* $NaOCH_3$–$CH_3OH$ | 20 | 80 |
| 6 | Suspension of $NaOCH_3$–$CH_3OH$ | 18 | 82 |

[a] Includes some 11.

## Experimental Section

Proton NMR spectra of neutral compounds were obtained on a Varian Associates T-60 spectrometer, usually in $CCl_4$ using $Me_4Si$ as an internal reference. Decoupling experiments were done on a Varian Associates HA-100 spectrometer. Spectra of carbonium ions were obtained on a Varian Associates A56-60 or HA-100 spectrometer equipped with a variable-temperature probe; the solvent was $FSO_3H$-$SO_2ClF$ (ca. 1:5) and either $(CH_3)_4NBF_4$ (δ 3.13) or $CH_2Cl_2$ (δ 5.30) was used as an internal standard. The temperature control was calibrated with a methanol standard sample.

Ir spectra were measured on a Unicam SP-200 spectrophotometer. Uv spectra were measured in 95% ethanol using a Unicam SP-800 spectrophotometer. Mass spectra were obtained at 70 eV on a Hitachi Perkin-Elmer RMU-6 spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and by Clark Microanalytical Laboratories, Urbana, Ill. Varian Aerograph gas chromatographs were used. Melting points are uncorrected.

**5,6-Diphenyl-1,2,3,4,7,7-hexamethylbicyclo[2.2.2]octa-2,5-dien-8-one (7).**[9] A mixture of 5.0 g (28.1 mmol) of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone[25] and 10.7 g (60.1 mmol) of diphenylacetylene was heated at about 200° for 20 hr. On cooling, the mixture became crystalline, and an NMR spectrum of the crude mixture showed only the desired product **7** and excess diphenylacetylene (no unreacted 6). Fractional crystallization from methanol gave 6.1 g of **7** as colorless crystals, mp 150°, and 3.7 g of recovered diphenylacetylene. An additional 0.9 g of **7** and 1.2 g of diphenylacetylene were obtained from the mother liquors (total yield of **7**, 70%) by column chromatography over silica gel using methylene chloride as the eluent: ir ($CCl_4$) 1703 (s), 1630 (w), 1600 (m), 700 (s) cm$^{-1}$; uv (EtOH) $\lambda_{max}$ 220 nm (ε 14,130), 207 (17,200); NMR ($CCl_4$) see Table I; all methyl peaks were sharp singlets except those at δ 1.78 and 1.88, which were broadened because of homoallylic coupling of approximately 1 Hz.

Anal. Calcd for $C_{26}H_{28}O$: C, 87.60; H, 7.92. Found: C, 87.66; H, 7.89.

When the above procedure was carried out with 3-$CD_3$ dienone[11] (**6'**), the resulting **7'** had an NMR spectrum identical with that of **7** except that the peak at δ 1.78 was absent, and that at δ 1.88 became a sharp singlet.

**3,4-Diphenyl-1,5,6,7,8,8-hexamethylbicyclo[3.2.1]octa-3,6-dien-2-one (8) and 6,7-Diphenyl-1,3,4,5,8,8-hexamethylbicyclo[3.2.1]octa-3,6-dien-2-one (9).**[9] The ratio of **8**:**9** formed on acid-catalyzed rearrangement of **7** depends on the reaction conditions. A good procedure for obtaining mainly **8** is as follows (procedure A). A solution of 1.0 g (2.81 mmol) of powdered **7** in 10 ml of trifluoroacetic acid was allowed to stand for 2 hr at room temperature, then poured onto ice-water. The resulting yellow solid was extracted with methylene chloride, and combined extracts were

washed successively with sodium carbonate solution and water and dried ($Na_2SO_4$). Evaporation of the solvent in vacuo left a yellow oil whose NMR spectrum showed that the ratio of **8**:**9** was about 92:8 (traces of other isomers were also present). The oil could be crystallized, and recrystallization from 95% ethanol gave 0.82 g (82%) of **8** as yellow crystals: mp 136–137°; ir (KBr) 1660 $cm^{-1}$; uv (EtOH) $\lambda_{max}$ 300 nm ($\epsilon$ 2190), 226 (8690), 213 (8690); NMR ($CCl_4$), see Table I; all methyl signals were sharp singlets except those at $\delta$ 1.75 and 1.55, which were mutually homoallylically coupled, $J$ = 1.0 Hz.

Anal. Calcd for $C_{26}H_{28}O$: C, 87.60; H, 7.92. Found: C, 87.51; H, 7.72.

Procedures for obtaining **9** are as follows (procedure B). A solution of 1.0 g (2.81 mmol) of powdered **7** in 10 ml of trifluoroacetic acid is heated at reflux (76°) for 10 hr, then quenched in ice-water and worked up as in procedure A. The NMR spectrum of the crude product showed it to be almost pure **9**, as a viscous yellow liquid, >0.9 g (90%), contaminated only with a little **8**. Further purification was rather difficult. The product was distilled under reduced pressure to give **9**, bp 173° (0.75 Torr), slightly contaminated with **8** (NMR): ir (neat) 1660 $cm^{-1}$; NMR ($CCl_4$) see Table I. No analysis was obtained since the sample was always contaminated with **8**, and since both **8** and **9** gave **10** on irradiation.

**4-Methyl-$d_3$-6,7-diphenyl-1,3,5,8,8-pentamethylbicyclo[3.2.1]-octa-3,6-dien-2-one (9′).** A solution of 1 g of **9** in 10 ml of $CH_3OD$ containing 50 mg of $NaOCH_3$ was refluxed overnight. After removal of the excess methanol (in vacuo), the residue was treated with water and extracted with methylene chloride. The organic layer was washed with water, dried ($Na_2SO_4$), and evaporated under reduced pressure to give an essentially quantitative yield of **9′**, whose NMR spectrum differed from that of **9** (Table I) only in that the peak at $\delta$ 1.70 was absent, and that at $\delta$ 1.82 sharpened to a singlet.

**2,3-Diphenyl-1,5,6,7,7,8-hexamethyltetracyclo[3.3.0.0$^{2,8}$.0$^{3,6}$]-octan-4-one (10).**[10] The 92:8 mixture of **8**:**9** obtained by rearrangement of 1.0 g of **7** in trifluoroacetic acid according to procedure A above was irradiated in ether (300 ml) through Pyrex for 1 hr with a Hanovia 450-W lamp. The pale-yellow color of the solution was discharged during the irradiation. The resulting colorless solution was concentrated to dryness in vacuo to give almost colorless crystals which recrystallized from petroleum ether to give 640 mg (64% overall yield from **7**) of pure **10**: mp 148° (sublimes); ir ($CCl_4$) 1760 (s, br), 1508 (m), 1450 (m), 1390 (m), 1255 (m), 880 (s), 710 (s); NMR ($CCl_4$) see Table I, all methyl signals were sharp singlets.

Anal. Calcd for $C_{26}H_{28}O$: C, 87.60; H, 7.92. Found: C, 87.56; H, 7.84.

The same results were obtained when either pure **8** or **9** was similarly irradiated.

Irradiation of the crude product obtained from rearrangement of **7′** gave labeled **10** whose NMR spectrum was identical with that of **10** (Table I) except that the peak at $\delta$ 1.17 was absent. Similar irradiation of **9′** (300 mg in 100 ml of ether, Pyrex, 450-W Hanovia lamp, 20 min) gave 250 mg (83%) of labeled **10** whose NMR spectrum was identical with that of **10** (Table I) except that the peak at $\delta$ 1.00 was absent.

***exo*-2,3-Diphenyl-1,5,6,7,7,8-hexamethyltetracyclo[3.3.0.0$^{2,8}$.0$^{3,6}$]octan-4-ol (11).** To a suspension containing 34 mg of lithium aluminum hydride in 10 ml of ether was added dropwise a solution of 500 mg (1.40 mmol) of **10** in 10 ml of ether. After the reaction mixture was stirred at room temperature for 6 hr, water was added. The ether layer and extracts were washed with saturated sodium chloride and dried ($MgSO_4$). The residue obtained by removal of the ether in vacuo had an NMR spectrum identical with that of pure **11** (0.46 g, 92%). Recrystallization from petroleum ether (30–60°) gave 350 mg (70%) of pure **11** as colorless crystals: mp 137–138°; ir (KBr) 3550 (m), 1605 (m), 1580 (w) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 358 (10), 340 (10), 325 (12), 288 (18), 261 (15), 260 (14), 229 (15), 228 (15), 215 (24), 203 (23), 191 (17), 179 (39), 178 (54), 165 (43), 151 (34), 150 (30), 135 (20), 129 (33), 128 (44), 115 (52), 105 (69), 97 (65), 91 (100); NMR ($CCl_4$) see Table I; all methyl signals were sharp singlets; the peak at $\delta$ 1.40 was removed by equilibration with $D_2O$.

Anal. Calcd for $C_{26}H_{30}O$: C, 87.10; H, 8.44. Found: C, 86.99; H, 8.36.

Similar reduction of deuterated **10** which lacked a methyl signal at $\delta$ 1.17 gave **11′** whose NMR spectrum was identical with that of **11** except for the absence of the singlet at $\delta$ 1.09. Analogous reduction of deuterated **10** which lacked a methyl signal at $\delta$ 1.00 gave **11″** whose NMR spectrum was identical with that of **11** except for the absence of the singlet at $\delta$ 1.27.

**Oxidation of 11.** An equimolar amount of Jones' reagent[13] was added to a solution of 200 mg (0.56 mmol) of **11** in 10 ml of acetone. After 2 hr at room temperature, saturated sodium bisulfite solution was added. The acetone layers were evaporated in vacuo, and the residue was taken up in methylene chloride, washed with water, and dried ($Na_2SO_4$). Removal of the solvent in vacuo left 155 mg (77%) of **10** whose NMR spectrum was identical with that of an authentic sample.[26]

**4-Chloro-2,3-diphenyl-1,5,6,7,7,8-hexamethyltetracyclo[3.3.0.-0$^{2,8}$.0$^{3,6}$]octane (12).** Hydrogen chloride was bubbled into a solution of 500 mg (1.40 mmol) of **11** in 20 ml of ether at 0° until saturation. The solution was allowed to warm to room temperature and remain for 6 hr. The solution was poured onto ice-water and salted out with sodium chloride, and the ether layer was washed with saturated sodium chloride solution and dried ($MgSO_4$). The residue obtained by concentration of the ether in vacuo was recrystallized from petroleum ether (30–60°) to give 420 mg (80%) of **12**: mp 141°; ir (KBr) 1610 (m), 1585 (w) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 376 (3), 340 (100), 325 (92), 310 (14), 297 (14), 283 (13), 269 (13), 247 (12), 221 (21), 183 (13), 178 (11), 165 (14), 143 (31), 128 (16), 115 (16), 105 (35), 91 (39); the peaks at *m/e* 376, 377, and 378 were in the ratio 1:0.30:0.37; NMR ($CCl_4$) see Table I; all aliphatic proton peaks were sharp singlets. The product gave a positive Beilstein test.

Anal. Calcd for $C_{26}H_{29}Cl$: C, 82.87; H, 7.70. Found: C, 82.89; H, 7.80.

Treatment of 100 mg of **11′** with hydrogen chloride in 10 ml of ether, as described above for **11**, gave 79 mg (76%) of **12′** which had an NMR spectrum identical with that of **12** (Table I) except that the peaks at $\delta$ 1.18 and 1.32 were reduced in area to 1.5 H each. The identical result was obtained starting with 100 mg of **11″**.

**2,3-Diphenyl-1,5,6,7,7,8-hexamethyltetracyclo[3.3.0.0$^{2,8}$.0$^{3,6}$]-oct-4-yl Trifluoroacetate (13).** To approximately 300 $\mu$l. of a carbon tetrachloride solution which contained 70 mg (0.20 mmol) of **11** was added dropwise, in an NMR tube, approximately 100 $\mu$l. of trifluoroacetic acid. The reaction was monitored by NMR. After 1 hr at room temperature, the solution was poured onto ice-water and extracted with methylene chloride. The methylene chloride solution, combined with washings, was washed successively with sodium bicarbonate solution and water and dried ($Na_2SO_4$). Removal of solvent in vacuo left 75 mg (83%) of **13** as a pale-yellow oil; further purification by VPC was difficult: ir (neat) 1775 (s), 1605 (m) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 454 (22), 439 (18), 340 (21), 339 (14), 325 (100), 310 (10), 298 (15), 297 (49), 143 (20), 105 (40), 97 (39), 91 (45); NMR ($CCl_4$) see Table I; all aliphatic proton signals were sharp singlets.

Treatment of **11′** (50 mg) with trifluoroacetic acid in carbon tetrachloride (0.4 ml, 1:3) as above gave **13′** whose NMR spectrum was identical with that of **13** except that the peaks at $\delta$ 1.08 and 1.37 were reduced in area to 1.5 H each. The identical result was obtained starting with **11″**.

**4-Methoxy-2,3-diphenyl-1,5,6,7,7,8-hexamethyltetracyclo[3.3.-0.0$^{2,8}$.0$^{3,6}$]octane (14) and 8-methylene-2,3-diphenyl-1,5,6,7,7-pentamethyltetracyclo[3.2.1.0$^{2,4}$.0$^{3,6}$]octane (15).** A solution of 376 mg (1.0 mmol) of **12** and 270 mg (5 mmol) of sodium methoxide in 100 ml of methanol was refluxed for 10 hr. The reaction mixture was concentrated to dryness in vacuo, and the residue was treated with water and extracted with methylene chloride. The combined organic layers were washed with water, dried ($Na_2SO_4$), and evaporated in vacuo. An NMR spectrum of the residue showed it to be a 45:55 mixture of **14** and **15**. The residue was resolved by thin-layer chromatography (2.0 mm silica gel, methylene chloride eluent), and each component was extracted from the silica gel with acetone. The acetone was removed in vacuo, and the residue was taken up in methylene chloride and dried ($Na_2SO_4$), and the solvent was evaporated.

The residual colorless oil thus obtained from the first TLC band was identified as **15** (150 mg, 44%). Further purification was effected by preparative VPC (5 ft × 0.25 in. column, 10% SE-30 on

Chromosorb W, 200°, 100 ml of He/min, retention time 8 min): ir (neat) 1670 (m), 1602 (m), 890 (s) $cm^{-1}$; uv (EtOH) $\lambda_{max}$ 231 nm ($\epsilon$ 14,200): mass spectrum (70 eV) *m/e* (rel intensity) 340 (69), 325 (56), 310 (8), 297 (8), 283 (8), 269 (10), 247 (9), 221 (14), 183 (10), 178 (8), 143 (12), 128 (13), 115 (18), 105 (12), 91 (100); NMR ($CCl_4$) see Table I.

Anal. Calcd for $C_{26}H_{28}$: C, 91.71; H, 8.29. Found: C, 91.61; H, 8.33.

The residual colorless oil from the second TLC band crystallized. Recrystallization from petroleum ether (30-60°) gave 105 mg (30%) of **14** as colorless crystals: mp 96-97°; ir (KBr) 1603 (m), 1585 (w) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 372 (100), 357 (12), 341 (20), 340 (46), 325 (68), 310 (13), 297 (20), 286 (18), 276 (15), 275 (40), 213 (15), 189 (16), 179 (13), 157 (18), 133 (19), 127 (35), 113 (80), 105 (33), 91 (35); NMR ($CCl_4$) see Table I; all aliphatic proton signals were sharp singlets.

Anal. Calcd for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 86.99; H, 8.67.

A solution of **12′** (75 mg) in 100 ml of methanol containing 54 mg of sodium methoxide was refluxed for 10 hr, then worked up as above. The ratio of the resulting **14′** and **15′** was 2:1. The NMR spectrum of **14′** was identical with that of **14** except that the singlets at $\delta$ 1.05 and 1.27 were reduced in area to 1.5 H each. The NMR spectrum of the resulting **15′** was identical with that of **15** except that the singlet at $\delta$ 1.22 was reduced in area to 1.5 H, and the peaks at $\delta$ 4.30 and 4.35 were reduced in area to 0.5 H each.

The yield data presented in Table III were obtained from NMR spectra of the crude product, using the spectra of pure **14** and **15** for analysis. The relative solvolysis rates of **12** and **26** were obtained by withdrawing aliquots periodically and analyzing them by NMR.

**Preparation of 12 from 15.** A solution of **15** (50 mg) in 10 ml of ether saturated at 0° with hydrogen chloride was allowed to warm to room temperature. After 30 min, the reaction was worked up as in the preparation of **12** from **11**. The NMR spectrum of the crude reaction product was identical with that of **12** prepared from **11**.

**Preparation of 13 from 15.** To 36 mg of **15** in an NMR tube was added a solution of 100 $\mu$l. of trifluoroacetic acid in 300 $\mu$l. of carbon tetrachloride. After 5 min, the product had an NMR spectrum identical with that of authentic **13** prepared from **11**.

**Carbonium Ion 18.** All of the following operations were carried out under a blanket of dry nitrogen. An NMR tube containing 50 $\mu$l. of fluorosulfonic acid was cooled to −78°, and 200 $\mu$l. of sulfuryl chlorofluoride was condensed in the tube (the tube was previously marked by pencil for the various volumes). The contents were mixed using a "super-mixer" (Matheson Scientific, Cat. No. 60100-05), and a thin glass rod needed for stirring later was inserted in the NMR tube. The entire mixture was cooled to −132° (liquid nitrogen-pentane slush bath) and another 50 $\mu$l. of sulfuryl chlorofluoride was condensed on the surface of the mixture. A solution containing 40 mg of either **11** or **15** in 100 $\mu$l. of dideuteriomethylene chloride was added carefully to the surface of the mixture in the tube. When the contents were all cooled to −132°, they were mixed using the glass rod, to give a light-brown solution of carbonium ion **18**. For the NMR spectrum, see the structure and accompanying text.

**Rearrangement of 18.** A solution of **18** was prepared as described above except on a larger scale, using a 10-mm diameter reaction tube, 0.5 ml of fluorosulfonic acid, 2.5 ml of sulfuryl chlorofluoride, and a solution of 200 mg of **11** in 1 ml of dideuteriomethylene chloride. After preparation of the ion at −132°, the tube was transferred to a −78° bath (isopropyl alcohol-Dry Ice) and allowed to stand at that temperature for 30 min. The solution, which had become dark reddish brown, was then quickly added dropwise to a vigorously stirred suspension of sodium methoxide in methanol, maintained at −78°. The contents were allowed to slowly warm to room temperature.

The residue obtained by evaporating the methanol in vacuo to dryness was treated with a little water, saturated with sodium chloride, and extracted with ether. Combined ether extracts were washed with saturated sodium chloride solution and dried ($MgSO_4$), and the solvent was removed under vacuum. An NMR spectrum of the residue showed the presence only of **20, 21, 22,** and an unidentified minor product. The ratio of **20:21** was approximately 7:1, and the ratio of **20:22** was 3:1.

The product mixture was submitted to preparative TLC using a 2.0-mm silica gel plate with methylene chloride as eluent, to give three separate product bands.

The first band was extracted from the silica gel with acetone, after which the acetone was removed in vacuo, and the residue was taken up in methylene chloride and dried ($Na_2SO_4$). Removal of the solvent in vacuo left a pale-yellow oil, the NMR spectrum of which showed it to be a 3:1 mixture of **22** and the unidentified hydrocarbon product. VPC (5 ft × 0.25 in. column, 10% SE-30 on Chromosorb W, 200°, 100 ml of He/min, retention time 14 min) gave pure **2-methylene-5,6-diphenyl-1,3,7,8,8-pentamethylbicyclo[3.3.0]octa-3,6-diene (22)**: ir ($CCl_4$) 1615 (w), 1600 (w), 880 (s) $cm^{-1}$; uv (EtOH) $\lambda_{max}$ 236 nm ($\epsilon$ 16,800); mass spectrum (70 eV) *m/e* (rel intensity) 340 (100), 325 (65), 310 (10), 297 (11), 283 (9), 269 (8), 221 (13), 165 (8), 143 (17), 91 (11); NMR ($CCl_4$), See structure and text.

Anal. Calcd for $C_{26}H_{28}$: C, 91.71; H, 8.29. Found: C, 91.67; H, 8.32.

The unidentified hydrocarbon had a retention time under the above VPC conditions of 5 min and had the following properties: ir 1608 (w), 1502 (m), 1455 (m), 1395 (w), 1370 (w) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 340 (100), 325 (97), 310 (23), 295 (8), 157 (20), 105 (14), 91 (20); NMR ($CCl_4$) $\delta$ 0.62, 1.08, 1.19 (s, 3 H each), 1.73 (q, 3, H, $J$ = 1 Hz), 1.82 (s, 3, H), 1.92 (q, 3 H, $J$ = 1 Hz).

The second TLC band was worked up as the first, to give ***endo*-4-methoxy-2,3-diphenyl-1,5,6,7,8,8-hexamethylbicyclo[3.3.0]octa-2,6-diene (21)**, which was further purified by VPC (5 ft × 0.25 in. column, 10% SE-30 on Chromosorb W, 200°, 100 ml of He/min, retention time 10 min): ir ($CCl_4$) 1600 (w) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 372 (25), 357 (9), 341 (35), 340 (100), 297 (16), 275 (23), 127 (55), 105 (26), 91 (31); NMR ($CCl_4$) see Table II.

Anal. Calcd for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 86.88; H, 8.40.

The third TLC band was worked up as the first, and the product was further purified by VPC (same conditions as for **21**, retention time 12 min) to give ***exo*-4-methoxy-2,3-diphenyl-1,5,6,7,8,8-hexamethylbicyclo[3.3.0]octa-2,6-diene (20)**: ir ($CCl_4$) 1600 (w) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 372 (16), 357 (7), 341 (18), 340 (50), 325 (41), 297 (18), 275 (17), 215 (15), 191 (20), 179 (21), 178 (34), 165 (21), 129 (20), 128 (25), 127 (100), 105 (48), 91 (70); NMR ($CCl_4$) see Table II.

Anal. Calcd for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 87.13; H, 8.51.

A similar experiment starting with 11″ gave **20′** (NMR peaks at $\delta$ 1.07 and 1.72 reduced in area to 1.5 H each) and **21′** (NMR peaks at $\delta$ 1.14 and 1.58 reduced in area to 1.5 H and 4.5 H, respectively).

**2,3-Diphenyl-1,5,6,7,8,8-hexamethylbicyclo[3.3.0]octa-2,6-dien-4-one (23).** Jones' reagent[13] was added dropwise to 20 ml of acetone containing 100 mg of **20** until the color of the solution remained reddish orange, and the whole was allowed to stand at room temperature for 6 hr. Sodium bisulfite solution was added until the solution turned greenish blue. The acetone layer was separated by decantation and, combined with acetone washings, was concentrated almost to dryness in vacuo. The residue was diluted with water and extracted with methylene chloride, and the combined extracts were washed with water and dried ($Na_2SO_4$). An NMR spectrum showed that the residue obtained by removal of the methylene chloride in vacuo was primarily one product, **23**. This was purified first by TLC (2.0 mm silica gel plate, methylene chloride eluent) to give 80 mg (84%) of **23** as a pale-yellow oil, which was purified further by VPC (5 ft × 0.25 in. column, 10% SE-30 on Chromosorb W, 210°, 100 ml of He/min, retention time 16 min): ir (neat) 1690 (s), 1615 (w), 1595 (w) $cm^{-1}$; uv (EtOH) $\lambda_{max}$ 294 nm ($\epsilon$ 8300), 231 (17,400); mass spectrum (70 eV) *m/e* (rel intensity) 356 (37), 341 (100), 288 (7), 178 (9), 135 (10), 105 (13), 91 (15); NMR ($CCl_4$) see Table II.

Anal. Calcd for $C_{26}H_{28}O$: C, 87.60; H, 7.92. Found: C, 87.51; H, 7.80.

Similar oxidation of **21** (30 mg in 5 ml of acetone) gave 18 mg (63%) of **23** (identical by ir, NMR).

**Carbonium Ion 24.** A 50 $\mu$l. solution containing 40 mg of **20** was added to an NMR tube containing 50 $\mu$l. of fluorosulfonic acid and 200 $\mu$l. of sulfuryl chlorofluoride at −78° according to procedures previously described.[4b] The resulting deep-brown solution had the

NMR spectrum shown on the structure of **24** (see text). The ion was stable, and the spectrum was unchanged up to about −40°. The identical spectrum was obtained starting with 30 mg of **21** (in place of **20**).

**Irradiation of 22.** A solution containing 34 mg of **22** in 10 ml of acetone was irradiated through a Corex filter with a 450-W Hanovia lamp for 2 hr. After evaporation of the solvent, the residue was taken up in methylene chloride, washed with water, dried ($MgSO_4$), and purified by VPC (5 ft × 0.25 in. column, 10% SE-30, 200°, 100 ml of He/min, retention time 8 min) to give 14 mg (40%) of **15**, identical (ir, NMR) with a sample obtained from **12**. There was also recovered 60% of unreacted **22** (retention time 14 min).

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**Supplementary Material Available.** A comparison of the NMR assignments of the phenyl-substituted compounds in this paper with the all-methyl compounds previously described[4b] will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2450.

## References and Notes


(1) Stabilization of carbocations by aryl substituents is well known (see H. H. Freedman in "Carbonium Ions", Vol. 4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972). Examples of aryl destabilization (relative to alkyl) include cyclopropenyl cations [R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962)], cycloalkenyl cations [N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, ibid., **87**, 4533 (1965)], and the trishomocyclopropenyl cation [S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, **8** (11) 621 (1966), have described the phenyl group as a "treacherous . . . . probe for positive charge development at a carbon atom"]; see also G. D. Sargent, *Q. Rev., Chem. Soc.*, **20**, 301 (1966).

(2) W-D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 1661 (1972).

(3) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *J. Am. Chem. Soc.*, **94**, 8956 (1972).

(4) (a) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **94**, 8958 (1972); (b) ibid., **96**, 6436 (1974).

(5) (a) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973); (b) *J. Am. Chem. Soc.*, **96**, 2208 (1974).

(6) S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakashima, *Angew. Chem., Int. Ed. Engl.*, **12**, 769 (1973); see also R. K. Lustgarten, *J. Am. Chem. Soc.*, **94**, 7602 (1972).

(7) A. V. Kemp-Jones, N. Nakamura, and S. Masamune, *J. Chem. Soc. D*, 109 (1974).

(8) W. J. Hehre and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5837 (1973).

(9) The preparation of **7**, **8**, and **9** is described in the M.S. thesis (Michigan State University, 1966) of T. Kakihana, and the preparation of **10** was first carried out by Love.[10] However, the experimental details have not been readily accessible before so we include them in the present paper (see Experimental Section).

(10) H. Hart and G. M. Love, *J. Am. Chem. Soc.*, **93**, 6266 (1971).

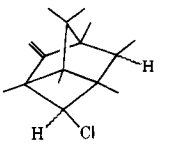
(11) H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

(12) An X-ray crystal structure of **10** has been published: C. G. Biefeld, H. A. Eick, and H. Hart, *Tetrahedron Lett.*, 4507 (1973); C. G. Biefeld and H. A. Eick, *Acta Crystallogr., Sect. B*, **30**, 1172 (1974).

(13) A. Bowers, I. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(14) R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, **93**, 1522 (1971); D. R. Kelsey, ibid., **94**, 1764 (1972).

(15) Furthermore, prolonged treatment (3 hr, 0°) with hydrogen chloride in the all-methyl case caused appreciable opening of the cyclopropane ring to give a product thought to have structure i. The analogous reaction was not observed with **11** (or **12**), even after 24 hr with HCl–ether at room temperature.



i

(16) Unfortunately even a large excess of Eu-shift reagent was rather ineffective with **21**, causing only small shifts of the methoxyl and methine signals. This negative result actually supports the structural assignment, however, since the methoxyl is tucked under the carbon framework in a hindered position which prevents coordination with the europium.

(17) 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. See also K. Rajeswari and T. S. Sorensen, *J. Am. Chem. Soc.*, **95**, 1239 (1973), and *Can. J. Chem.*, **50**, 1293 (1972), for further examples.

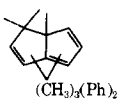
(18) Compare **24** particularly with structures **24** and **35** in ref 4b.

(19) R. M. Silverstein, G. C. Bassler, and T. C. Morrill, "Spectrometric Identification of Organic Compounds", 3rd ed., Wiley, New York, N.Y., 1974, pp 96–99, 244–246.

(20) Compare **22** particularly with structures **26** and **38** in ref 4b.

(21) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 3709 (1974).

(22) The unidentified minor hydrocarbon produced from **18** probably arises from further rearrangements during the quenching process. These rearrangements are analogous to those previously observed[4b] for ion **19**. The NMR spectrum showed three aliphatic methyls and three allylic methyls (one isolated and two adjacent on one of the double bonds). There were no vinyl protons. Thus the structure must be ii, but the exact location of the phenyls and methyls is not known (compare ii with structure **37**, ref 4b).



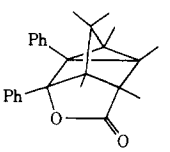
ii

(23) It should be noted that no methyl ether corresponding to the trapping of **25** was observed, even on NMR examination of the crude quenching product. Possible reasons are that approach is hindered by the phenyl substituent at the ring juncture. Likewise, it was not possible to obtain an NMR spectrum of **25** by adding **22** to acid; protonation did not occur exclusively at the methylene carbon (as is true in the all-methyl system), but at other double bonds as well.

(24) In expt 3–6, $NaOCH_3$ was present in excess over the amount of **12** present.

(25) H. Hart, R. M. Lange, and P. M. Collins, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 598.

(26) Treatment of either **10** or **11** with excess Jones' reagent leads to a product of further oxidation, which is tentatively assigned the lactone structure iii. The product, mp 175° from petroleum ether, had the following properties: ir (KBr) 1760 (s, br), 1605 (w) $cm^{-1}$; mass spectrum (70 eV) *m/e* (rel intensity) 372 (4), 328 (23), 178 (43), 165 (26), 150 (78), 135 (43), 128 (19), 115 (30), 105 (75), 91 (44), 77 (98), 51 (31), 41 (100); NMR ($CCl_4$) δ 0.85 (3 H, s), 0.88 (3 H, s), 0.93 (3 H, s), 0.97 (3 H, s), 1.30 (3 H, s), 1.38 (3 H, s), 2.70 (10 H, m).



iii