Acyclic Carbodications[1]

George A. Olah,* James L. Grant, Robert J. Spear,[2a] J. Martin Bollinger,[2a] Art Serianz,[2a] and Gyorgy Sipos[2b]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received May 9, 1975.

Abstract: Ionization of a series of tetramethyl- and tetraphenyl-substituted diols and dihalides where the two functionalized carbons are separated by an ethylidene, *trans*-ethene, ethyne, *trans*-1,2-dicyclopropyl, and 1,4-phenylene group has been studied under stable ion conditions. In most cases, both hydroxyl (halide) groups are ionized to form dicarbenium ions, although proton elimination, ring opening, and other side reactions lead only to monocarbenium ions in several instances. The tetraphenylethylene dication (**34**) was formed from tetraphenylethylene with SbF₅ in SO₂ClF. The tetrakis(*p*-methoxyphenyl) and -(*p*-*N,N*-dimethylaminophenyl) derivatives of **34** were also studied. **34** undergoes further oxidation at higher temperatures to form the dibenzo[*g,p*]chrysene dication. The ^{13}C NMR parameters of the dicarbenium ions are discussed in relation to charge distributions, and comparison with the corresponding monocarbenium ions reveals distinct differences in a number of cases.

Introduction

The development, in the early sixties, of methods allowing preparation of carbocationic intermediates under long-lived (stable ion) conditions has led to their extensive study during the past decade. Proton (^1H) and carbon-13 (^{13}C) nuclear magnetic resonance studies have been complemented by infrared, Raman, ultraviolet, and ESCA spectroscopy for the determination of structures and charge distributions for these carbocationic species.[3] Whereas monocarbenium ions have been intensively studied, evidence for carbodicationic intermediates has been extremely limited. The earliest examples of carbodications are the isolable bisanthylium[4-6] and bisacridinium[7] salts. However, it was not until 1963 that the first carbodications which did not contain stabilizing heteroatoms were reported,[8] when Hart and Volz independently investigated tetraphenylphenylenedicarbenium ions.[9,10] We reported the first alkyl dications in a preliminary communication in 1967.[11] Since then, a number of cyclic dications,[12,13] cyclobutadiene dications,[14] and Hogeveen's nonclassical $(CCH_3)_6^{2+}$ dication[15] have been reported. Dicarbenium ions have also been prepared from tetrakis(*p*-methoxyphenyl)ethylene[16,17] and tetrakis(*p*-*N,N*-dimethylaminophenyl)ethylene[16,18] by two-electron oxidation processes.

We now report in full our systematic study of alkyl- and aryl-substituted acyclic dicarbenium ions. The majority of dicarbenium ions were formed by ionization of dihalides or diols with the two functionalized centers separated by ethylidene, *trans*-ethene, ethyne, *trans*-1,2-cyclopropane, and 1,4-phenylene groups. Several dicarbenium ions formed by two-electron oxidation of the corresponding tetrakisarylethylene have also been studied. The ^1H and ^{13}C NMR parameters obtained are completely consistent with the dicarbenium nature of these ions. In a number of cases it was not possible to observe dicarbenium ions due to intramolecular rearrangements and other processes, and these are also described. Charge distributions in the dicarbenium ions are assessed from the ^{13}C NMR chemical shifts and are discussed in relation to monocarbenium ions.

Results and Discussion

The majority of dicarbenium ions studied were generated by ionization of the appropriate dihalides or diols with the superacid systems FSO₃H, FSO₃H–SbF₅, or SbF₅ in SO₂ClF as solvent. Dicarbenium ions were also formed from tetraarylethylenes by oxidation with bromine, SbCl₅, or SbF₅. The complete experimental details are described in the Experimental Section. Conditions which did not lead to dicarbenium ions, due to rearrangements or other processes, or were insufficient to afford ionization are described in the following discussion.

^1H NMR data for the dicarbenium ions are summarized in Table I, while the corresponding ^{13}C NMR parameters are listed in Table II. Carbon chemical shift assignments were aided by recording off-resonance spectra. In the case of ions with a number of sp²-hybridized carbon atoms, carbons were assigned on the basis of relative peak intensities.

Tetramethyl-Substituted Dicarbenium Ions. Dissolution of 2,5-dichloro-2,5-dimethylhexane (1) in SbF₅–SO₂ClF at −78 °C yielded a slightly colored solution. The ^1H NMR spectrum (Table I) consisted of a triplet at δ 4.24 and a multiplet at δ 5.04, while the ^{13}C NMR spectrum (Table II) exhibited three peaks, consistent with the symmetrical dicarbenium structure **2**. The ^{13}C shift of the carbenium
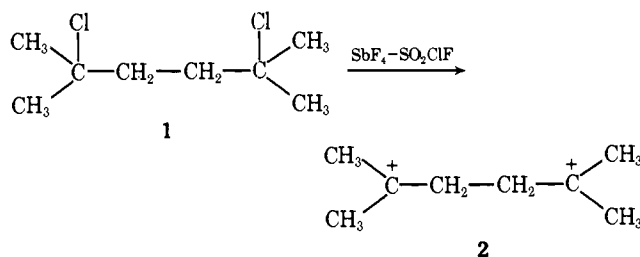
center, δ 331.1 ppm, is almost identical with that for the dimethylethylcarbenium ion, δ 333.8,[19] clearly ruling out the presence of cyclic halonium ions or equilibrating halonium ions even in low concentrations. The large $^4J_{H,H}$ coupling, 3.0 Hz, between the methyl and methylene protons is characteristic of coupling across a carbenium center. Quenching of **2** in methanol at −78 °C yields only 2,5-dimethoxy-2,5-dimethylhexane.

Under the same conditions as **1**, 2,4-dichloro-2,4-dimethylpentane (3) ionizes to the 2,4-dimethyl-2-pentenyl cation [**4**,[20] ^1H NMR: δ 2.96 (singlet, 12 H, 4 × CH₃), 7.89 (singlet, 1 H, H₃)]. The potential dicarbenium ion from **3** would have the two carbenium centers one carbon closer than **2**, and evidently, if this ion does form, it has only a transient existence, rapidly eliminating a proton to give **4**.
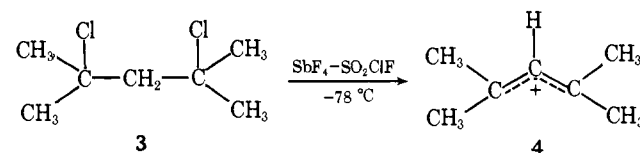
Table I. ¹H NMR Parameters[a] for Dicarbenium Ions

Ion		H_{ortho}	H_{meta}	H_{para}	H_α	H_β	CH_3
	2[b]				5.04 multiplet		4.24 triplet, $J = 3.0$
	18[b]					9.28	4.46
	22[c]	8.05	8.05	8.55	4.70		
	23[d]	8.10	8.10	8.51	8.42		
	24[d]	8.40	8.05	8.50			
	25[e]	8.17	8.17	8.55	4.66 triplet, $J = 8.5$	3.54 triplet, $J = 8.5$	
	26[e]	8.13	8.13	8.58		8.08	
32, X = OCH_3[f]		7.51	6.95				3.79
33, X = $N(CH_3)_2$[g]		7.75	7.34				4.26
34, X = H[b]		8.55	8.55	9.07			

[a] Chemical shifts are in ppm, external (capillary) Me_4Si. Coupling constants are in Hz. [b] In SbF_5–SO_2ClF at −75 °C. [c] In FSO_3H–SbF_5–SO_2 at −60 °C. [d] In FSO_3H–SbF_5–SO_2ClF at −50 °C. [e] In FSO_3H–SO_2ClF at −40 °C. [f] In SO_2 at −30 °C. [g] In Me_2SO-d_6 at 37 °C.

We attempted to block proton elimination by ionizing 2,3,3,4-tetramethylpentane-1,3-diol (5), but a quantitative cleavage reaction occurred, affording the equilibrating dimethylisopropylcarbenium ion (7)[19] and protonated acetone (6).
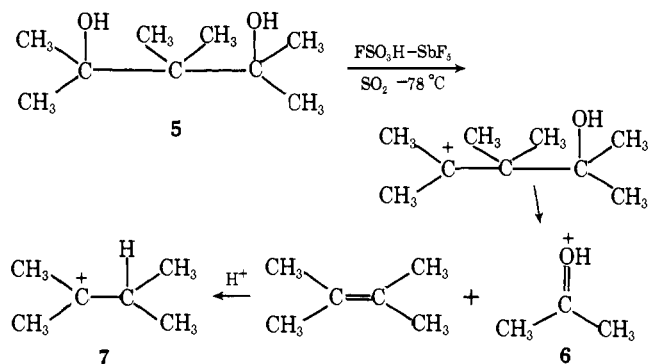
Ionization of 2,3-dichloro-2,3-dimethylbutane (8), where the two potential carbenium centers are adjacent, affords only the cyclic chloronium ion 9.[21] This represents the only instance related to this study where halonium ion formation successfully competes with dication formation.
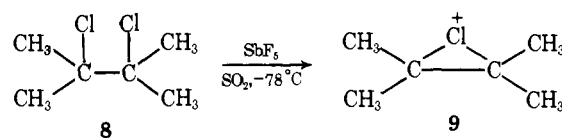
Ionization of either cis- or trans-2,5-dimethyl-3-hexene-2,5-diol (10) under a variety of superacidic conditions (FSO_3H, SbF_5-FSO_3H, SbF_5, HF-SbF_5) in either SO_2 or SO_2ClF at temperatures as low as −125 °C gave only a complex multiline ¹H NMR spectrum. There were no methyl resonances below δ 3.5, ruling out the presence of the dicarbenium ion 11. Side reactions are not completely
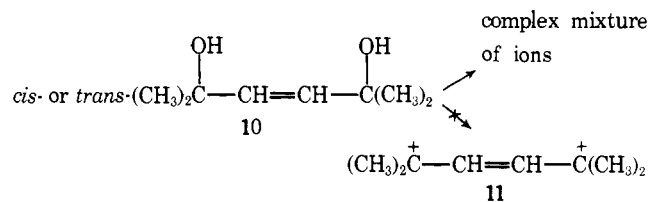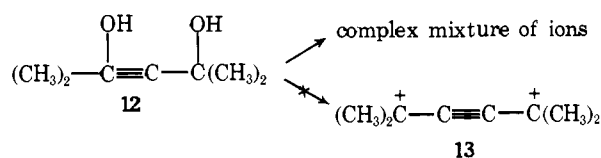

unexpected from 10 since pinacol-type rearrangements and formation of 2,5-dihydrofurans have been reported from 10 and related systems.[22] Similarly, 2,5-dimethyl-3-hexyne-2,5-diol (12) also yielded a complex ¹H NMR spectrum

**Table II.** ^{13}C NMR Parameters[a] for Dicarbenium Ions

Ion	C$^+$	C$_{ipso}$	C$_{ortho}$	C$_{meta}$	C$_{para}$	C$_\alpha$	C$_\beta$	CH$_3$
2[b]	331.1					52.7		47.1
18[b]	240.8					149.1	137.85	42.8
22[c]	222.4	139.95	142.2	132.15	148.65	42.65		
23[d]	198.8	139.75	144.3	132.4	148.75	157.5		
24[d]	183.8	139.1	144.15	133.35	150.55	126.6		
25[e]	220.9	139.1	141.5	131.7	147.4	42.4 $^1J_{CH}$ = 172.5	29.9 $^1J_{CH}$ = 173.6	
26[e]	210.6	140.8	146.15, 143.65	131.7	147.0	146.95	139.75	
[e]	210.7	140.85	144.9	131.7	147.15	147.0	139.55	
32, X = OCH$_3$[f]	181.9	135.3	144.65	119.35	175.3			58.35
33, X = N(CH$_3$)$_2$[g]	168.8	130.75	140.25	116.7	157.8			42.4
34, X = H[b]	198.6	140.1	142.95, 148.4	134.3	152.85			
32a, X = OCH$_3$[h]		137.5	133.1	113.7	158.3	139.0		55.6
33a, X = N(CH$_3$)$_2$[g]		134.4	132.9	112.0	149.0	138.1		37.0
34a, X = H[i]		143.7	131.3	127.6	126.4	141.0		

[a] Chemical shifts are in ppm from external (capillary) Me$_4$Si. Coupling constants are in Hz. [b] In SbF$_5$–SO$_2$ClF at –75 °C. [c] In FSO$_3$H–SbF$_5$–SO$_2$ at –60 °C. [d] In FSO$_3$H–SbF$_5$–SO$_2$ClF at –60 °C. [e] In FSO$_3$H–SbF$_5$–SO$_2$ClF at –60 °C. [f] In SO$_2$ at –30 °C. [g] In Me$_2$SO at 37 °C. [h] In CDCl$_3$ at 37 °C. [i] Data of J. P. C. M. Van Dongen, M. J. A. de Bie, and R. Steur, *Tetrahedron Lett.*, 1371 (1973).

under identical conditions, with no resonances being attributable to the dicarbenium ion **13**. Systems like **12** are well known to undergo a variety of rearrangements, such as the Rupe and Meyer-Schuster rearrangements.[23] We were not able to assign structures to any of the ions derived from **12** or **10**.

$(CH_3)_2\overset{OH}{C}\equiv C\overset{OH}{C}(CH_3)_2$ **12** → complex mixture of ions
→ (no) $(CH_3)_2\overset{+}{C}—C\equiv C—\overset{+}{C}(CH_3)_2$ **13**

trans-α,α,α′,α′-Tetramethylcyclopropane-1,2-dimethanol (**14**) yielded only the diprotonated diol [**15**, ^{1}H NMR: 1.82, 2.02 (singlets, 2 × 6H, 2 × CH$_3$), 1.10, 2.21 (AA′BB′
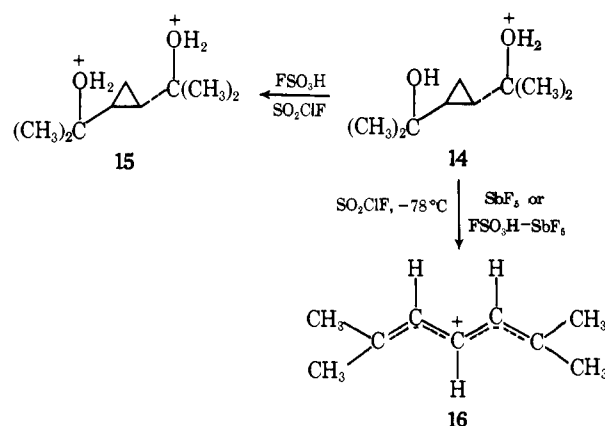
spectrum, 2 × 2H, H$_\alpha$, H$_\beta$ of cyclopropyl), 10.15 (singlet, 4 H, 2 × $^+$OH$_2$)] upon attempted ionization with FSO$_3$H in SO$_2$ClF at −78 °C. Ionization could not be induced even by heating to 5 °C, but under the more forcing conditions of FSO$_3$H-SbF$_5$ or SbF$_5$ in SO$_2$ClF at −78 °C, ionization did occur, but this was accompanied by ring opening to give the 2,6-dimethylhepta-2-dienyl cation [16,[24] ^{1}H NMR: δ 3.98 (singlet, 12 H, 4 × CH$_3$), 7.56 (d, J = 13.5 Hz, H$_{2,4}$), 9.55 (t, J = 13.5 H$_3$); ^{13}C NMR: 24.2, 32.15 (2 × CH$_3$), 135.3 (C$_{2,4}$), 175.0 (C$_3$), 212.6 (C$_{1,5}$)]. Apparently the cyclopropyl group cannot provide sufficient stabilization for the dication, and ring opening with simultaneous proton elimination leads to the more stable ion 16.

α,α,α′,α′-Tetramethyl-1,4-xylene-α,α′-diol (17) dissolves in SbF$_5$ in SO$_2$ClF at −78 °C to yield a slightly colored solution. The ^{1}H NMR spectrum (Table I) consists only of single peaks at δ 4.46 and 9.28, while the ^{13}C NMR spectrum contains only four peaks (Table II), consistent with the symmetrical dicarbenium ion structure 18. Although
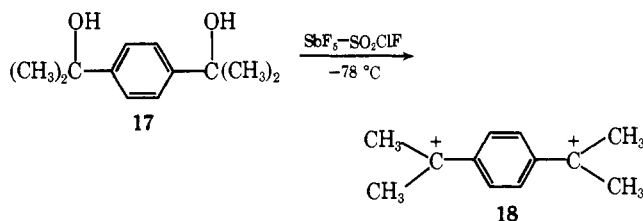

the ^{13}C chemical shifts for 18 are similar to the phenyldimethylcarbenium ion (19),[25] charge distribution differences between 18 and 19 are readily apparent. Most notably, the carbenium carbon in 18 is more shielded than 19, while the reverse is true for the methyl groups.[26] The ipso carbons of 18, which are each para to one $^+$C(CH$_3$)$_2$ group, also resonate at higher field than C$_{para}$ in 19 despite the fact that the latter is unsubstituted, which is usually a shielding influence on ^{13}C shifts.[27]
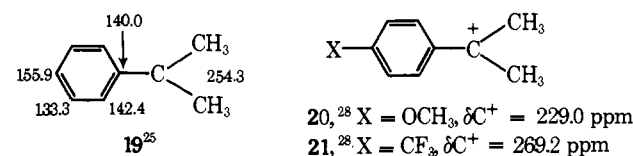
18 can be considered as a derivative of 19 with a powerful electron-withdrawing para substituent. The carbon shifts of a series of para-substituted derivatives of 19 have been reported previously from our laboratories, and it was shown that the carbon shift of the carbenium center (C$^+$) correlated linearly against σ$^+$ of the para substituent,[28] e.g., 20, 21. Note that C$^+$ in 18, δ 240.8, is more shielded than either 21 or 19, despite the fact that the para $^+$C(CH$_3$)$_2$ substituent is much more strongly electron withdrawing than CF$_3$. It seems reasonable to conclude that minimization of charge-charge repulsions in 18 require a much greater demand on the terminal methyl groups to hyperconjugatively delocalize charge than in 19. A clear-cut difference, therefore, exists between the mono- and dicarbenium ions, whereby the latter ion, having only a minimal number of atoms over which to spread the two units of charge, delocalizes more charge to the terminal methyl groups, while charge localization at C$^+$ and the phenyl ring is lowered due to charge repulsions.

Tetraphenyl-Substituted Dicarbenium Ions. Phenyl groups, due to their strong conjugative donation of π-electron density, are exceptionally good stabilizing groups for carbenium ions. We continued our investigation of dicarbenium ions by preparing a series of tetraphenyl diols where the two benzhydrol fragments were separated by ethylidene (22a), trans-ethene (23a), ethyne (24a), trans-1,2-cyclopropane (25a), and 1,4-phenylene (26a) linkages. 22a-26a

all ionized extremely readily using either FSO$_3$H or FSO$_3$H-SbF$_5$ in SO$_2$ClF at −60 °C to yield deep-red to purple solutions of the dicarbenium ions 22-26, respectively. 26 was also prepared from the corresponding dibromide under identical conditions, and preparations reported previously utilized 26a with concentrated H$_2$SO$_4$[9] or the dichloride of 26a with SbCl$_5$.[10]
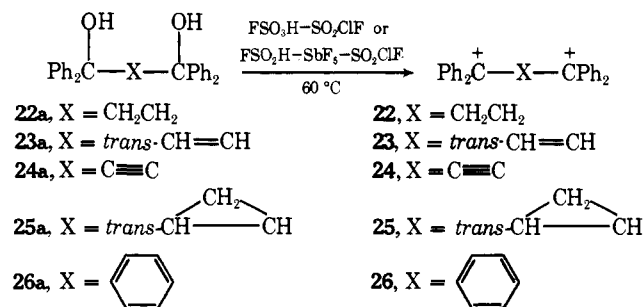
That 22-26 are dicarbenium ions can readily be confirmed by the characteristic chemical shifts of the carbenium centers (C$^+$, Table II), which are very similar to those of the corresponding monocarbenium ions 27-31, and the symmetrical ^{13}C NMR (Table II) and ^{1}H NMR (Table I) spectra. The NMR data for 4 also confirm that the cyclopropyl group has remained intact during the ionization processes. 22-26 give the expected dimethoxy derivatives upon quenching with methanol at −78 °C. The dicarbenium nature of 26, and its ortho and meta isomers, had previously been deduced from cryoscopic and uv absorption spectra measurements, as well as isolation and elemental analysis.[9,10]

It is well known that three electron delocalizing groups about a carbenium center cannot all achieve the geometrical conformation for optimum overlap. This leads to situations such as 30, which has magnetically nonequivalent phenyl groups,[25] and 31, which has a propeller structure[31] with the three phenyl groups being magnetically equivalent.[25] In addition, the ortho and meta carbon atoms for the equivalent phenyl groups in 27-29 and 31 are magnetically equivalent, and this is also observed for 22-25 (Table II). In contrast, 26 (and the tetraphenylethylene dication, to be discussed later) exhibits nonequivalence of the ortho carbon atoms for the four terminal phenyl groups; at temperatures below −10 °C, two resonances are observed which coalesce into a single sharp resonance at −5 °C (Table II). The ^{13}C NMR spectra of 22-25 show no temperature dependence.
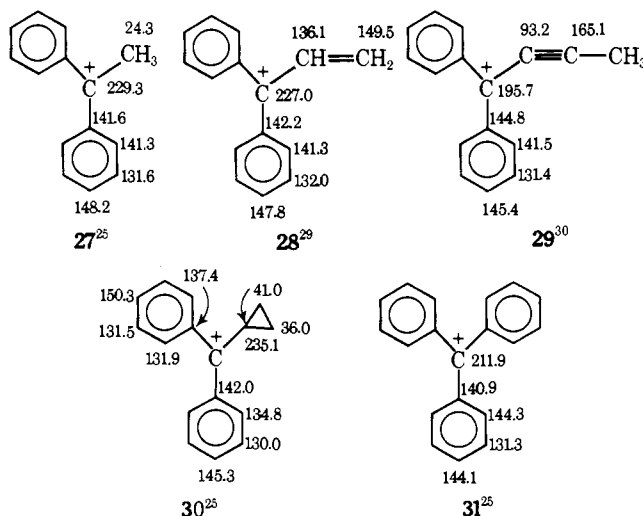
Although these steric differences hinder direct comparison of 22-26 with 27-31, the charge-distribution patterns indicated by the ^{13}C NMR shifts for 22-26 (Table II) are

qualitatively comparable with their analogues **27–31**. In all cases, the positive charge is predominantly localized at the carbenium center and the ortho and para carbons of the directly attached phenyl groups. Quantitative comparisons are limited, in most cases, to the para carbon shifts of the equivalent phenyl groups; the carbon resonances for C^+, C_{ipso}, and C_{ortho}, which are proximate to X in **22–26**, will be affected by variations in X additional to variations due to charge differences.[32]

Not unexpectedly, the ^{13}C shifts for **22** compare almost exactly with **27**, indicating that **22** can be considered as two (virtually) isolated diphenylmethylcarbenium ions. The C_{para} shifts for **23** and **24**, relative to **22**, indicate that the double bond is only as effective, and the triple bond less effective, than the ethane group at competing for charge delocalization against the phenyl groups. Charge obviously is delocalized onto the central group (X) in **23** and **24**, since their carbon atoms are deshielded relative to uncharged systems, e.g., **23a**, $\delta_{C_{vinyl}} = 78.6$ ppm; **24a**, $\delta_{C\equiv C} = 74.6$ ppm. The carbon shifts show that there is less charge delocalized onto the vinyl and acetylene groups in **23** and **24** than onto the corresponding groups in **28**[29] and **29**,[30] respectively.

It is only in **25** and **26**, where the cyclopropyl and phenyl groups represent the central linkages best able to delocalize positive charge, that there is a net loss of charge from the C_{para} positions relative to **22**. Again, as observed for the vinyl and acetylenic groups in **23** and **24**, the carbon shifts of the central phenyl and cyclopropyl groups are deshielded, indicating positive charge delocalization to these functionalities. However, C_β in **25** is more shielded than **30**, and C_β is more shielded than the ortho carbons of the four terminal phenyl groups in **26** (Table II), showing that charge is predominantly delocalized onto these latter functionalities.

Collectively, positive charge in **22–26** is preferentially delocalized onto the terminal phenyl groups, with lesser delocalization provided by the central group (X) between the two carbenium centers. The ability of X to delocalize charge, as defined by the C_{para} shift of the terminal phenyl rings, crudely follows the order expected from monocarbenium ions.[20]

Tetraarylethylene Dications. The dicarbenium ions which should show the largest deviations in charge distribution from the corresponding monocarbenium ions are those with adjacent carbenium centers. The dicarbenium ions formed by a number of tetraarylethylenes by two-electron oxidations formally involve removal of the two electrons from the olefinic double bond and, hence, fit into this category. Tetrakis(p-methoxyphenyl)ethylene (**32a**) and tetrakis(p-N,N-dimethylaminophenyl)ethylene (**33a**) readily undergo such reactions with a variety of oxidizing electrophiles to form stable dicationic salts.[16–18] We accordingly prepared the tetrakis(p-methoxyphenyl)ethylene dications (**32**) as the bis(tribromide) salt by reaction of **32a** with bromine[33] and the tetrakis(p-N,N-dimethylaminophenyl)ethylene dication (**33**) as the bis(hexachloroantimonate) salt by reaction of **33a** with SbCl₅. Stable salts of **32** have been particularly well characterized, including an x-ray structural determination of the bis(dichloroiodo) salt.[17]

The parent tetraphenylethylene dication (**34**) has, so far, not been reported, although the radical cation has been well


32a, X = OCH₃
33a, X = N(CH₃)₂

32, X = OCH₃
33, X = N(CH₃)₂
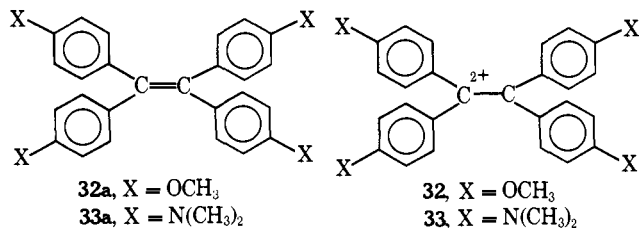
characterized.[34,35] Tetraphenylethylene (**34a**) is oxidized only to the radical cation with SbCl₅,[34] but we have found in recent studies on polycyclic aromatic hydrocarbons that SbF₅ in SO₂ClF is an extremely powerful oxidizing agent.[36] **34a** slowly dissolved in SbF₅ in SO₂ClF at −78 °C to yield a deep-burgundy colored solution. The ^1H NMR spectrum is of the same appearance as those for **22, 23, 25**, and **26**, consisting only of two broadened absorptions for the ortho, meta, and para protons, respectively (Table I). The ^{13}C NMR spectrum contains six resonances, two for tertiary carbons and four, in the ratio 1:1:1:2, for secondary carbons (Table II). The data are consistent with the dicarbenium structure **34**, and, like **26**, nonequivalent ortho carbon atoms are observed.[37] The *total* increase in the carbon

24a → **34**
SbF₅–SO₂ClF
78 °C
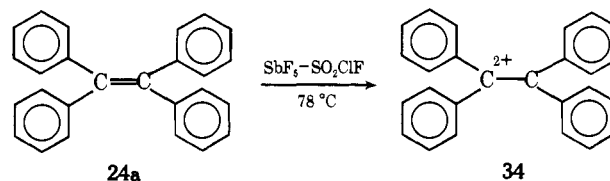
shifts for **34**, relative to **34a** (Table II), is 319.9 ppm, which is exactly twice the 160 ppm per electronic charge predicted from the Spiesecke-Schneider relationship.[31] **34** cannot be generated from either 1,1,2,2-tetraphenylethane-1,2-diol (**35**) or its dichloride (**36**). A previously reported attempt using **36** with SbCl₅ gave only 9,10-diphenylphenanthrene (**37**).[9]


35, X = OH
36, X = Cl

37
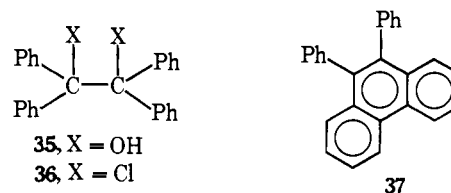
If the solution of **34** is allowed to warm above −40 °C, the burgundy color disappears and a deep blue–black solution forms. Concurrently, the ^1H NMR spectrum for **34** is replaced by a sharp spectrum consisting of four resonances; triplets at δ 8.30 and 7.62 and doublets at δ 7.85 and 7.26, $J = 7–8$ Hz in all cases. The ^{13}C NMR spectrum now consists of seven resonances: three tertiary carbons at δ 210.2, 140.55, and 138.45 and secondary carbons at δ 157.1, 154.1, 135.55, and 134.6 ppm. The symmetry and reso-


34 → [dication of] **37** →
heat above −40 °C

38
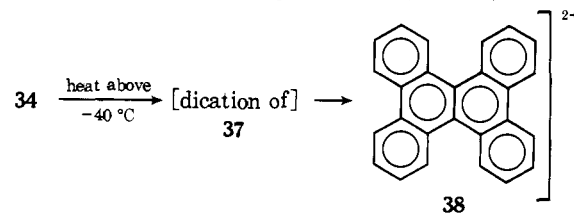
nance positions of these spectra suggested that the new ion was the dication of dibenzo[g,p]chrysene (**38**), formed by a two step oxidation of **34**. This was confirmed by dissolution of dibenzo[g,p]chrysene in SbF₅–SO₂ClF at −20 °C, forming **38** quantitatively.[36] If the dication of **37** is involved as an intermediate in the transformation of **34** to **38**, it apparently has only a transitory existence under these conditions.

Delocalization of the two units of positive charge in **32–34** can readily be seen by comparison with the ^{13}C shifts of the precursors **32a–34a**, respectively (Table II). With respect to the monocarbenium ions **39, 40** (shown below),[38] and **31** (discussed previously), the trends observed for **18** relative to **19** are again followed. This is most apparent for **34**, where the carbenium center (δ 198.6 ppm) is shielded by 13.3 ppm relative to **31**, while the ring carbon atoms are deshielded with the greatest deshielding (8.15 ppm) observed for C_{para}. However, whereas the carbenium carbons

etc.
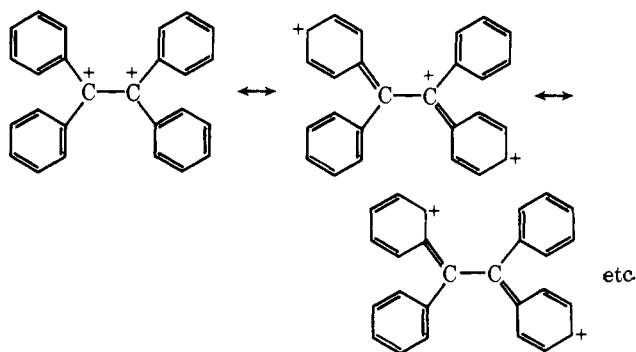
are shielded, by 12.3 and 8.3 ppm in **32** and **33** relative to **39** and **40**, respectively, the stabilization afforded by the heteroatom substituents in the para positions leads to less spectacular differences for the ring carbon shifts.

39[38]

40[38]
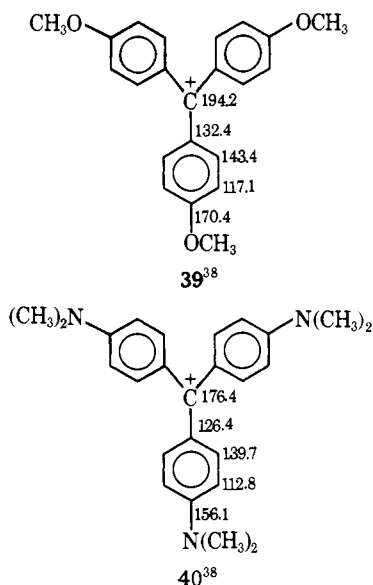
Substantial differences in charge-distribution patterns between the mono- and dicarbenium ions are thus apparent. The effects of charge-charge repulsion cause charge to spread out more from the central carbenium positions, and in the case of **32–34**, a greater demand on the electron-delocalizing ability of the terminal phenyl rings, relative to the monocarbenium ions, is the result.

Experimental Section

2,5-Dimethylhexane-2,5-diol, 2,5-dimethylhex-3-yne-2,5-diol (**12**), 1,1,4,4-tetraphenylbutane-1,4-diol (**22a**), 1,1,4,4-tetraphenylbut-2-yne-1,4-diol (**24a**), tetraphenylethylene (**34a**), 4,4′-bis(dimethylamino)benzophenone (Michler's ketone), 4,4′-dimethoxybenzophenone, diethyl fumarate, and dimethyl terephthalate were commercially available samples. Where dichloride precursors were employed, they were synthesized from the parent diols using standard procedures. SbF$_5$ and FSO$_3$H were both doubly distilled prior to use.

cis- and *trans-***2,5-Dimethylhex-3-ene-2,5-diol (10).** Both isomers were prepared according to the procedure of Johnson and Johnson:[22] cis, mp 67–9 °C (lit.[22] mp 69–70 °C); trans, mp 100–101 °C (lit.[22] mp 101.5–102.5 °C).

*trans-α,α,α′,α′-***Tetramethylcyclopropane-1,2-dimethanol (14).** A solution of diethyl cyclopropane-1,2-dicarboxylate[39] (9.2 g, 0.05 mol) in ether (50 ml) was added dropwise, with stirring, to a solution of methyllithium in hexane (Alfa Inorganics, 0.3 mol) diluted with ether. The mixture was stirred overnight and worked up by addition of ethyl formate then water. The organic layer was separated, dried over MgSO$_4$, and the solvent removed to give a yellow oil which was taken up in 1:1 ether–pentane. **14** crystallized out upon storage at −40 °C as white crystals, mp 70–72 °C (lit.[40] mp 67.5–70 °C).

*α,α,α′,α′-***Tetramethyl-1,4-xylene-α,α′-diol (17).** A solution of dimethyl terephthalate (25 g, 0.129 mol) in ether was added dropwise with stirring to an ethereal solution of methylmagnesium bromide (Alfa Inorganics, 0.516 mol). The reaction was stirred overnight and worked up by addition of concentrated aqueous ammonium chloride. Separation and removal of solvent afforded a crude product containing ester and diol, which was saponified with 5% aqueous sodium hydroxide. Recrystallization afforded **17** as white crystals, mp 139–141 °C (ethanol–water) (lit.[41] 142.4–142.9 °C).

*trans-***1,1,4,4-Tetraphenylbut-2-ene-1,4-diol (23a).** A solution of phenyllithium in 20:30 benzene–ether (Alfa Inorganics, 1.0 mol) was added in portions to a stirred solution of diethyl fumarate (3.8 g, 0.018 mol) in ether at −78 °C under a nitrogen atmosphere. After complete addition, the solution was stirred at −78 °C for 30 min and then allowed to come to room temperature overnight. Workup by dropwise addition of water, followed by separation and removal of solvent, gave **23a** as white crystals, mp 195–197 °C (lit.[42] mp 195–201 °C).

*trans-α,α,α′,α′-***Tetraphenyl-1,2-cyclopropanedimethanol (25a).** A solution of diethyl cyclopropane-1,2-dicarboxylate[39] (9.2 g, 0.05 mol) in ether (70 ml) was added dropwise with stirring to a solution of phenylmagnesium bromide [0.3 mol, from bromobenzene (47.1 g) and magnesium (7.3 g)] in ether. The mixture was refluxed overnight, cooled, and worked up by addition of water. The organic layer was dried over MgSO$_4$ and upon removal afforded a brown oil which slowly crystallized to **25a**, white crystals, mp 191–193 °C (chloroform–hexane) (lit.[43] mp 194–195 °C).

*α,α,α′,α′-***Tetraphenyl-1,4-xylene-α,α′-diol (26a).** Reaction of dimethyl terephthalate with phenylmagnesium bromide as described by Hart[9] gave **5a** as white crystals, mp 170–171 °C (benzene–light petroleum) (lit.[9] mp 169–171 °C). Conversion to the dibromide was achieved using HBr in acetic acid.[44] The dibromide was obtained as white crystals, mp 269 °C (1,2-dibromoethane) (lit.[44] mp 271 °C).

Tetrakis(*p*-methoxyphenyl)ethylene (32a). Reaction of 4,4′-dimethoxybenzophenone with oxalyl chloride, followed by reaction with copper bronze powder according to the procedure of Buckles and Womer[45] gave **32a** as white crystals, mp 184–185 °C (benzene) (lit.[45] mp 183–184 °C).

Tetrakis(*p*-methoxyphenyl)ethylene Dication (32) as the Bis(tribromide) Salt. Bromine (3.1 g, 0.039 mol) in carbon disulfide (30 ml) was added dropwise to a solution of **32a** (1.4 g, 0.003 mol) in carbon disulfide (50 ml). **32** precipitated from the solution as a blue-green solid and was filtered from the reaction. The physical properties were identical with those previously reported.[33]

Tetrakis(*p*-N,N-dimethylaminophenyl)ethylene (33a) was prepared by reductive coupling of Michler's ketone with tin and HCl using the method described by Willstatter and Goldman.[46] **33a** was obtained as yellow crystals, mp 292–295 °C (lit.[46] mp 295–300 °C).

Tetrakis(*p*-N,N-dimethylaminophenyl)ethylene Dication (33) as the Bis(hexachloroantimonate) Salt. Antimony pentachloride (0.30 ml, 0.002 mol) was added dropwise to **33a** (0.50 g, 0.001 mol) in methylene chloride (50 ml). The resulting deep-purple solution was filtered and the volume reduced to about 10 ml. Addition of an equal volume of benzene yielded yellow-brown crystals, which were filtered, washed with cold ether, and dried. The yield was 0.86 g (69%).

1,1,2,2-Tetraphenylethene-1,2-diol (35) was prepared according to the procedure of Bachmann.[47] The dichloride was prepared by chlorination of tetraphenylethylene and was isolated as white crystals, mp 183–184 °C (chloroform) (lit.[48] mp 185°).

Preparation of Ions. Owing to the low solubility of the diols in SO$_2$ClF or SO$_2$, the usual procedure for generating ions was modified. The following describes the method employed for the dicarbenium ions **18** and **22–26**, as well as the unsuccessful attempts at preparing dications from **10**, **12**, and **14**.

The diol (250 mg) was precooled in a test tube at −78 °C and then was added in 15–25-mg portions to a solution of FSO$_3$H or FSO$_3$H–SbF$_5$ or SbF$_5$ (0.75 ml) in SO$_2$ClF (1.25 ml). The mixture was vigorously agitated (Vortex stirrer) until all solid dissolved, then the solution was recooled, and then further solid was added. After complete addition and dissolution, the sample was transferred by a precooled pipet to a precooled NMR tube. The particular superacid for each ion is described in the text. **2** and **4** were prepared by dropwise addition of the precursors **1** and **3**, re-

spectively (250 mg), in SO₂ClF (0.75 ml) to a solution of SbF₅ (0.75 ml) in SO₂ClF (0.75 ml).

The tetraphenylethylene dication (**34**) was prepared by addition of precooled tetraphenylethylene (100 mg) in 10-mg portions to a solution of SbF₅ (1.25 ml) in SO₂ClF (1.25 ml) at −78 °C. The solution was vigorously agitated for about 10–15 s after addition, then at 5-min intervals until all solid dissolved. Conversion of **34** to the dibenzo[*g,p*]chrysene dication (**38**) was achieved by shaking the solution until the SO₂ClF just boiled. The tube was again cooled and the process repeated for about 10 min, giving a deep blue-black solution.

Quenching of Ions. Ions were quenched by dropwise addition of the ion solution to a stirred slurry of excess K₂CO₃ in methanol at −78 °C. After complete addition, the mixture was allowed to come to room temperature, and the dimethoxy derivatives were isolated by standard procedures.

NMR Spectroscopy. ¹H NMR spectra were recorded on a Varian Associates Model A56/60A spectrometer equipped with a variable-temperature probe. Chemical shifts are in ppm from external (capillary) Me₄Si.

¹³C NMR spectra were obtained using a Varian Associates Model XL-100 spectrometer equipped with a broad-band decoupler, variable-temperature probe, and interfaced with a Varian 620-L computer operating with 8192 digital points. Chemical shifts were measured from the ¹³C signal of 5% ¹³C-enriched Me₄Si contained in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube. Coupling constants were obtained directly from the spectra recorded in the gyro-gate mode. Typically, 2000–5000 transients were necessary to obtain acceptable signal to noise levels.

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