(Hexaphenyltrimethylene)methane Dication and Related Carbocations[1]

Nicholas J. Head, George A. Olah,* and G. K. Surya Prakash*

Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California, 90089-1661

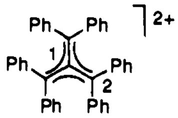
Received July 10, 1995[⊗]

Abstract: By ionization of the respective alkenediol (**8a**), the (hexaphenyltrimethylene)methane dication (**2**) has been prepared and found stable in solution under superacidic stable ion conditions (FSO_3H/SO_2ClF) up to at least −20 °C. The spectroscopic data and AM1 theoretical modeling indicate that although the entire π-system is twisted, phenyl groups stabilize the positive charges in **2** to a similar degree as those in the trityl cation. The hexa-*p*-CF_3 derivative of **2** was also observable but only at very low temperatures (−90 °C). Disruption of the 3-fold symmetry and reduction of the number of stabilizing phenyl rings even to five resulted in intramolecular allylation and subsequent formation of the corresponding indenyl cations. In all the cases studied no evidence for "Y-aromatic" stabilization was found.

Introduction

Trimethylenemethane systems of type **1** (dicationic (**1a**), diradical (**1b**), or dianionic (**1c**)) have been of theoretical and practical interest for years. Diradical **1b** (4π-electrons) was found to exist as a highly reactive triplet species detectable by ESR only at temperatures below −150 °C.[2] Complexation with various metals[3] greatly enhances the stability of **1b**, and palladium[3g] and iron tricarbonyl complexes[3i] have even found use as valuable synthetic reagents along with derivatives of the free diradical itself.[4] Other theoretical aspects and chemistry of **1b** and its derivatives have been reviewed.[5] In contrast the dianionic counterpart, **1c**, was found to be unusually stable.[6] The enhanced stability of **1c** was first thought to be due to "Y-aromaticity" [7] as a result of its 6π-electrons and Y-conjugated framework. However, more recently the stability of **1b** has been ascribed to maximally distant localization of the π-systems by virtue of its D_{3h} symmetry.[8]

1a * = +
1b * = •
1c * = -



2

The trimethylenemethane dication (**1a**) (a 2π-electron system) is still unknown,[9] and only a handful of highly stabilized derivatives have been prepared.[10–14] Although such doubly charged, potentially Y-aromatic, systems were originally suggested on the basis of MNDO calculations[15] to possess enhanced stability over their cyclic counterparts, available experimental observations[10] have not shown this to be the case. Of the few trimethylenemethane dication derivatives known, most are stabilized by three (oxygen[10]) or six (nitrogen[11] or sulfur[12]) heteroatoms. Other approaches to introduce additional stability to **1a** have been the use of aromatic tropylium units[13] and the employment of thiophene spacers.[14] Practical interest in compounds stabilized by sulfur atoms stems from their potential use as acceptors in charge transfer based organic ferromagnetic materials.[12,16]

Another possible method for stabilization of **1a** is by multiple phenyl substitution, the ultimate case of such substitution being the (hexaphenyltrimethylene)methane dication (**2**). However,

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

(1) Stable Carbocations. 296. Part 295: Heagy, M. D.; Prakash, G. K. S.; Olah, G. A.; Lomas, J. *J. Org. Chem.*, in press.

(2) (a) Dowd, P.; Gold, A.; Sachdev, K. *J. Am. Chem. Soc.* **1968**, *90*, 2715. (b) Dowd, P.; Sachdev, K. *J. Am. Chem. Soc.* **1967**, *89*, 715. (c) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

(3) (a) Louguet-Higgens, H. C.; Orgel, L. E. *J. Chem. Soc.* **1956**, 1969. (b) Ehrlich, K.; Emerson, G. F. *J. Am. Chem. Soc.* **1972**, *94*, 2464. (c) Ward, J. S.; Pettit, R. *J. Chem. Soc., Chem. Commun.* **1970**, 1419. (d) Allen, S. G.; Barnes, S. G.; Green, M.; Morn, G.; Trollope, L.; Murrall, N. W.; Welch, A. J.; Sharaiha, D. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1157. (e) Su, G.-M.; Lee, G.- H.; Peng, S.-M.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1992**, 215. (f) Jones, M. D.; Kemmit, R. D. W.; Platt, A. W. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1411. (g) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 3. (h) Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993. (i) Donaldson, W. A.; Hossain, M. A.; Cushnie, C. D. *J. Org. Chem.* **1995**, *60*, 1611.

(4) Little, R. D. *Chem. Rev.* **1986**, *86*, 875.

(5) (a) Weiss, F. *Q. Rev., Chem. Soc.* **1970**, *24*, 278. (b) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. (c) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. (d) Dowd, P.; Chow, M. *Tetrahedron* **1982**, *38*, 799.

(6) (a) Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275. (b) Mills, N. S.; Hollingsworth, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 1236.

(7) (a) Gund, P. *J. Chem. Educ.* **1972**, *49*, 100. (b) Phelan, N. F.; Orchin, M. *J. Chem. Educ.* **1968**, *45*, 633. (c) Inagaki, S.; Hirabayashi, Y. *Chem. Lett.* **1982**, 709. (d) Finnigan, R. A. *Ann. N. Y. Acad. Sci.* **1969**, *152*, 242. (e) Inagaki, S.; Kawata, H.; Hirabayashi, Y. *J. Org. Chem.* **1983**, *48*, 2928. (f) Agranat, I.; Skancke, A. *J. Am. Chem. Soc.* **1985**, *107*, 867.

(8) (a) Gobbi, A.; MacDougall, P. J.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1001. (b) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 4177.

(9) Our efforts to prepare and observe **1a** as a stable species by treatment of 2-(chloromethyl)-3-chloropropene with SbF_5 in SO_2ClF at −120 °C were unsuccessful.

(10) Schotz, K.; Clark, T.; Schaller, H.; Schleyer, P. v. R. *J. Org. Chem.* **1984**, *49*, 733.

(11) Schwesinger, R.; Mibfeldt, M.; Peters, K.; Schnering, H. G. *Angew. Chem.* **1987**, *99*, 1210.

(12) (a) Sugimoto, T.; Ikeda, K.; Yamauchi, J. *Chem. Lett.* **1991**, 29. (b) Adams, F.; Gompper, R.; Hohenester, A.; Wagner, H.-U. *Tetrahedron Lett.* **1988**, *29*, 6921.

(13) Mizumoto, K.; Kawai, H.; Okada, K.; Oda, M. *Angew. Chem.* **1986**, *98*, 930.

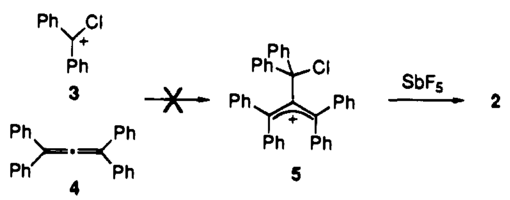
(14) Kawase, T.; Wei, C.; Ueno, N.; Oda, M. *Chem. Lett.* **1994**, 1901.

(15) Clark, T.; Wilhelm, D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1982**, *23*, 3547.

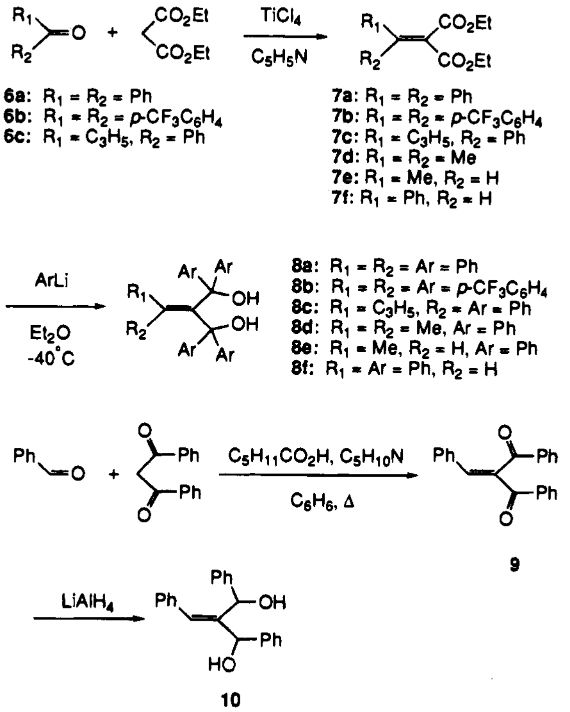
(16) (a) McConnell, H. M. *J. Phys. Chem.* **1963**, *39*, 1910. (b) LePage, T. J.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 2594. (c) Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O. Jr.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594. (d) Miller, J. S.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3850. (e) Torrance, J. B.; Oostra, S.; Nazzal, A. *Synth. Met.* **1987**, *19*, 709.

0002-7863/95/1517-11205$09.00/0

Scheme 1



Scheme 2



as pointed out by Kawase *et al.*[14] "the resulting steric congestion would hinder coplanarity of the molecule and hence disfavor maximal stabilization through conjugation". Nevertheless, as part of our continuing interest in carbocations with unusual or unique structures, we now present our findings on the (hexaphenyltrimethylene)methane dication (**2**) and other related carbocations.

Results and Discussion

Our initial attempts to prepare **2** centered upon addition of the chlorodiphenylmethenium cation[17] (**3**) (generated by *in situ* ionization of dichlorodiphenylmethane with SbF$_5$) to tetraphenylallene[18] (**4**) and subsequent ionization of **5** as illustrated in Scheme 1. However, allene **4** proved reactive toward SbF$_5$ under the conditions employed (SO$_2$ClF, −80 °C), and only **3** could be detected as the sole identifiable stable species. This prompted us to adopt a more straightforward and general approach to substituted trimethylenemethane dications based on ionization of diol precursors **8**.

The diols of interest were prepared according to the sequences shown in Scheme 2. Condensation of the required ketones **6**, in the cases where the diesters **7** were not commercially available, with diethyl malonate was carried out with the TiCl$_4$/pyridine based Knoevenagel procedure of Lenhert.[19] Further reaction of the ester groups in **7** with phenyllithium (or in the case of **7b** with 4-lithiobenzotrifluoride) afforded the diols **8** after recrystallization or trituration. Interestingly the addition of phenyllithium to the diesters **7** was found to be highly dependent on temperature and could not be effected in THF as solvent. Preparation of **10** was achieved by reduction of the corresponding diketone **9**, which in turn was obtained by condensation of benzaldehyde with dibenzoylmethane as reported.[20]

Interestingly the ^{1}H NMR spectra of the precursors **8a–f** displayed two shifts for the alcohol protons regardless of whether the diol was symmetric or not. We have examined this in more detail for two of the more soluble precursors, **8d** and **8f**. For **8d** at low concentrations two shifts are seen at 3.9 and 1.6 ppm. Increasing the concentration resulted in an increase of the more downfield peak while increasing the temperature resulted in an increase of the upfield shift. At concentrations above 0.17 M the upfield shift could not be detected. Similarly for **8f** the area of the upfield peak decreases with increasing concentration. In this case, however, two upfield shifts are seen (always in the same ratio) presumably due to the nonsymmetric nature of **8f**. For both compounds the chemical shifts showed only a very minor temperature dependence (ca 0.1 ppm) over the temperature range 20–60 °C. That the alcohol proton shifts show a concentration dependence suggests that the diols **8a–8f** exist in solution as intermolecularly hydrogen bonded dimers and that the observed upfield shifts belong to the alcohol protons of the dimer. Furthermore, the bonding is strong with 35% of **8d** and 30% of **8f** existing in dimeric form (as determined from the ^{1}H NMR integrations at 20 °C) at concentrations of 0.017 and 0.015 M, respectively. The presence of dimeric and monomeric forms of the diols **8a–8f** was also seen in their ^{13}C NMR spectra which showed two carbinol signals in each case (see the Experimental Section).

On treatment of **8a** with FSO$_3$H in SO$_2$ClF at −78 °C,[21] a dark green solution was obtained, the NMR spectra of which are displayed in Figure 1. As can be seen from these spectra, ionization of **8a** gave rise to a highly symmetric species with only eight peaks in the ^{13}C NMR spectrum, δ 208.5 (s, C2), 145.5 (s, C1), 144.1 (d, *ortho*), 142.4 (d, *ortho′*), 141.5 (s, *ipso*), 137.5 (d, *para*), 131.21 (d, *meta*), 131.18 (d, *meta′*), which we have accordingly assigned as the (hexaphenyltrimethylene)methane dication (**2**). Assignment of the ^{13}C and ^{1}H NMR spectra to dication **2** was made on the basis of the observed multiplcities, and by a 2D HETCOR experiment. The assignments are consistent with those of other known benzylic cations.[22]

The dication **2** was found to be stable from −80 to at least −20 °C, through which temperature range the ^{13}C NMR shifts remained essentially unchanged, although considerable line broadening at the lower temperatures was observed. Interestingly the steric congestion in **2** results in the nonequivalence of both the *ortho* and, to a lesser extent, the *meta* carbons of the phenyl rings. This nonequivalence can be seen in both the ^{13}C NMR and, quite clearly, ^{1}H NMR which shows separate peaks for each of the five possible phenyl hydrogens. Although **2** was cleanly prepared (Figure 1) and quite stable, quenching of the NMR sample with NaHCO$_3$-buffered methanol at −40 °C afforded a complex mixture of products.

---

[17] (a) Olah, G. A.; Svoboda, J. J. *Synthesis* **1972**, 307. (b) Barton, D. H. R.; Magus, P. D.; Garbarino, J. A.; Young, R. N. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2101.

[18] We found the most convienient procedure for the preparation of tetraphenylallene to be that of Vorlander, D.; Siebert, C. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 1024.

[19] Lenhert, W. *Tetrahedron* **1973**, *29*, 635.

[20] Pratt, E. F.; Werble, E. *J. Am. Chem. Soc.* **1950**, *72*, 4638.

[21] Attempts to prepare **2** with SbF$_5$ (SO$_2$ClF, −78 °C) were unsecessful. We believe this is due to the strong oxidizing ability of SbF$_5$ and the highly electron rich nature of the precursor. Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985; Chapter 3, p 112.

[22] Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Org. Chem.* **1977**, *42*, 2666.

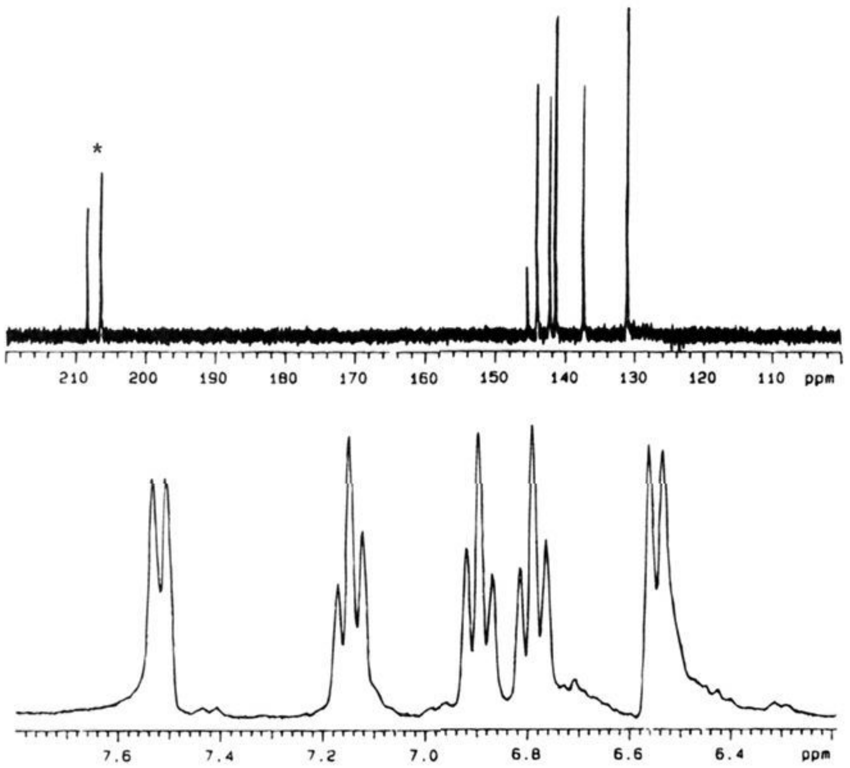


Figure 1. ^{13}C and ^{1}H NMR spectra in SO_2ClF at −20 °C of the (hexaphenyltrimethylene)methane dication (**2**): (upper spectrum) ^{13}C NMR, (lower spectrum) ^{1}H NMR. The asterisk indicates a peak for acetone-d_6 (CO). Chemical shifts are in ppm relative to external acetone-d_6 (CD_3, 29.8 ppm in ^{13}C NMR; CHD_2, 2.04 ppm in ^{1}H NMR).

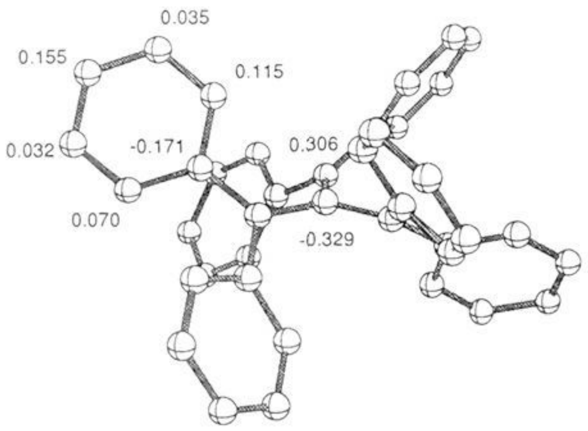
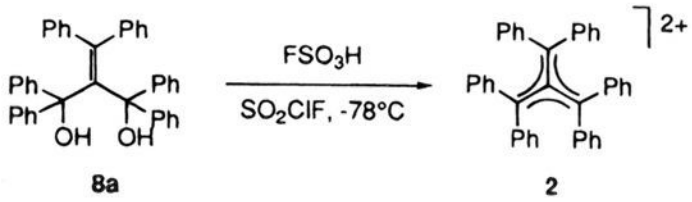


Figure 2. AM1 optimized geometry and charge distribution in the (hexaphenyltrimethylene)methane dication (**2**). Hydrogen atoms were omitted for clarity.

The dication **2** has also been subjected to theoretical modeling at the AM1 level.[23] Both the C1−C2 and C2−C*i* bond lengths are predicted at this level to be of almost identical length at 1.436 and 1.439 Å, respectively. Structurally **2** was found to possess C_3 symmetry and a propeller like structure (Figure 2) with each of the C2−C*i* bonds, by rotation about the C1−C2 bonds, at 37° above (and below) the plane of the central four sp^2 carbon atoms. Furthermore, the phenyl groups themselves are twisted such that the π-system of each phenyl ring is no longer in optimum overlap with the vacant p-orbitals at the three C2 carbons. The nonequivalence of the *ortho* and *meta* carbons in **2** and their lack of discernable temperature dependence indicate that exchange between the two possible chiral forms of **2** is very slow on the NMR time scale, and accordingly the energy barrier for the interconversion must be large.[24] This is probably a consequence of the steric conjestion in **2** which nessecitates that the flipping from one diastereomer to the other occur by syncronous rotation of each C1−C2 bond.

Scheme 3



The calculated charge density distributions (Figure 2) and the ^{13}C NMR data themselves, which do not show C1 to be significantly deshielded for an sp^2 carbon, indicate that the three C2 carbons and their pendant phenyl groups bear the charge of dication **2**. Therefore, statistically each C2 carbon should have approximately two-thirds of a unit positive charge to be accommodated by itself and its two phenyl groups. The resultant ratio of charge per phenyl group (one-third) is the same as that in the well-studied trityl cation.[25,26] As the trityl cation is also known to possess a propeller type structure,[26b] in which the degree of p−π overlap should be similar to that predicted for **2**, it is perhaps not surprising that the ^{13}C NMR chemical shifts for C2 in **2** and for C$^+$ in the trityl cation are remarkably similar at 208.5 and 210.9 ppm, respectively. Although ^{13}C NMR chemical shifts cannot be quantitatively correlated to charge densities, there is considerable evidence[22,25,27,28] indicating that the chemical shifts for carbon atoms of similar hybridization and substitution in hydrocarbon molecules significantly reflect electron densities. Hence, the similar shifts observed indicate that each phenyl group in **2** accommodates a similar degree of positive charge as do those in the trityl cation. This is also supported mainly by the ^{13}C NMR shifts of the phenyl ring carbons of **2** which are extremely similar to those of the trityl cation[25] for the *ipso*, *ortho*, and *meta* sites (averaged shift for the *ortho/ortho′* and *meta/meta′* carbons in **2**); however, the *para* carbons in **2** are somewhat more shielded by 5.6 ppm.

In order to decrease the amount of aryl stabilization to the central Y-conjugated "core" of **2**, suitably modified systems were studied under superacid conditions. The first approach adopted was to decrease the ability of each phenyl ring in **2** to conjugatively stabilize the positive charge by the introduction of electron-withdrawing trifluoromethyl groups.[29] Treatment of the required hexaaryl diol **8b** with FSO_3H/SO_2ClF at −80 °C gave a solution whose ^{13}C NMR was highly complex and could not be readily interpreted. However, careful ionization at −120 °C gave a deep indigo colored solution whose ^{13}C NMR indicated the presence of dication **11** along with a minor species, most probably the indenyl based cation **12** (Scheme 3; see also below). Again, as with **2**, **11** displays a high degree of symmetry with only nine peaks in the ^{13}C NMR, δ 209.8 (s, C2), 146.7 (s, C1), 145.6 (d, *ortho*), 143.1 (s, *ipso*), 142.4 (q, *para*), 138.8 (d, *ortho′*), 128.4 (d, *meta*), 128.1 (d, *meta′*), 121.4 (q, CF_3), and nonequivalence for the *ortho* and *meta* aryl carbons. Surprisingly, although the formation of **12** strongly implies a decreased stability for **11** *vs* **2** and more electrophilic C2 carbons as a result of the *p*-CF_3 substituents, the ^{13}C NMR shifts for both the C1 and C2 carbons are nearly identical in **2** and **11**. On the basis of the ^{13}C chemical shift−electron density

---

(23) AM1 calculations were performed with the Spartan program (*SPARTAN*, Version 2.0.0; Wavefunction Inc.: Irvine, CA, 1991) on an IBM RISC/6000 Model 560 computer.

(24) Due to the size of **2** we were unable to obtain the transition structure for this interconversion by calculational means (ref 23). As exchange was unobservable up to −20 °C, we estimate the activation barrier to be greater than 12 kcal mol^{-1}.

(25) Ray, G. J.; Kurland, R. J.; Colter, A. K. *Tetrahedron* **1971**, *27*, 735.

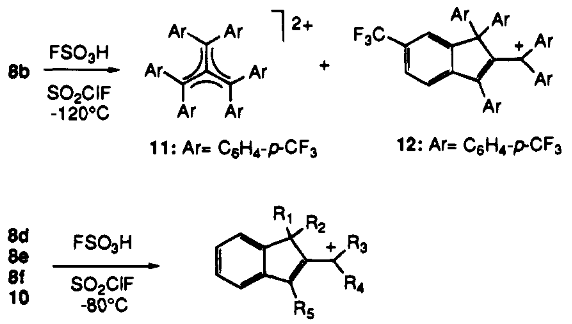
(26) (a) Schuster, I. I.; Colter, A. K.; Kurland, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 4679 and references therein. (b) Gomes de Mesquita, A. H.; MacGillvary, C. H.; Eriks, K. *Acta. Crystallogr.* **1965**, *18*, 437.

(27) (a) Lautebur, P. C. *J. Am. Chem. Soc.* **1961**, *83*, 1838. (b) Spiesecke, H.; Schnieder, W. G.; *Tetrahedron Lett.* **1961**, 468. (c) Lalancette, E. W.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 1941. (d) Olah, G. A.; Bollinger, J. M.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3667 (e) Olah, G. A.; Mateescu, D. *J. Am. Chem. Soc.* **1970**, *92*, 1430. (f) Olah, G. A.; Westerman, P. W.; Forsyth, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 3419.

(28) (a) Ditchfield, R.; Miller, D. P.; Pople, J. A. *Chem. Phys. Lett.* **1970**, *6*, 573. (b) Ditchfield, R.; Miller, D. P.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 4186.

(29) Olah, G. A.; Berrier, A. L.; Prakash, G. K. S. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1998.

Scheme 4



11: Ar= C_6H_4-*p*-CF_3 **12**: Ar= C_6H_4-*p*-CF_3

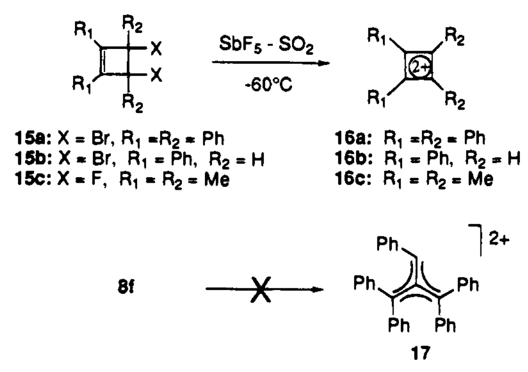
14d: $R_1 = R_2 = Me$, $R_3 = R_4 = R_5 = Ph$
14e: $R_1 = Me$, $R_2 = H$, $R_3 = R_4 = R_5 = Ph$
14f: $R_1 = R_3 = R_4 = R_5 = Ph$, $R_2 = H$
14g: $R_1 = R_4 = Ph$, $R_2 = R_3 = R_5 = H$

relationship referred to earlier and the results of Hammet type relationships established between σ^+ ($\sigma_R{}^+$ [22]) parameters and ^{13}C NMR shifts (C^+) in trityl cations,[25] we expected to observe significant deshielding of the C2 carbons in **11** relative to **2**. Anomolous behavior of the CF_3 group in other tertiary benzylic cations has been previously observed.[22,29] In those cases, as in the case of **11**, the *p*-CF_3 substituent was found to have very little influence on the benzylic carbocationic carbon shift relative to the unsubstituted case, despite its strongly electron-withdrawing nature.

In a second approach we turned our attention to systems with fewer phenyl groups to delocalize the positive charge, **8c–f** and **10**, and thus a break in symmetry. Treatment of **8c** with FSO_3H at −80 °C gave rise to a green solution, the ^{13}C NMR spectrum of which was quite complex as expected due to the distortion in symmetry and resulting nonequivalence of the five phenyl groups. The species obtained was stable up to −50 °C, above which the spectrum degraded rapidly. Throughout this temperature range the ion displayed four sharp singlets at δ 203.9, 195.5, 153.5, and 152.6, suggestive of the C1 and three (now nonequivalent) C2 carbons of the (cyclopropylpentaphenyltrimethylene)methane dication. However, the only two signals in the aliphatic region, δ 76.5 and 30.0, were found to be methylenes, and the expected cyclopropyl methine resonance could not be detected. Consequently we have been unable to determine the nature of the ion formed from **8c**. We can suggest that the cyclopropyl moiety undergoes ring opening, possibly to a homoallylic cation, and subsequent reactions. It should be stressed, however, that peaks characteristic of indenyl ion formation (see below) were entirely absent. That **8c** failed to afford the corresponding trimethylenemethane dication on ionization is surprising in view of the stabilizing ability of the cyclopropyl group,[30] which is able to accommodate positive charge to much the same extent as a phenyl group.[22,31]

The remaining precursors **8d–f** and **10** on treatment with FSO_3H/SO_2ClF at −80 °C gave solutions of varying color (see the Experimental Section) which displayed ^{13}C NMR spectra of varying complexity (see the Experimental Section for the ^{1}H and ^{13}C NMR data) although certain characteristics were common to all. On the basis of their ^{13}C NMR spectra, it was concluded that each of the precursors **8d–f** and **10** gave the corresponding indenyl based cations **14d–g** as the stable observable ions (Scheme 4). Further attempts to prepare the (pentaphenyltrimethylene)methane dication by ionization of **8f** with different superacids (Magic Acid or FSO_3H/SbF_5, ca. 4:1) in different solvents (SO_2ClF or SO_2) and at lower temperatures (−120 °C) also failed.

Scheme 5



15a: X = Br, $R_1 = R_2 = Ph$
15b: X = Br, $R_1 = Ph$, $R_2 = H$
15c: X = F, $R_1 = R_2 = Me$

16a: $R_1 = R_2 = Ph$
16b: $R_1 = Ph$, $R_2 = H$
16c: $R_1 = R_2 = Me$

17

Formation of **14d–g** arises via intramolecular attack of an allylic cation[31a,32] on one of the phenyl groups (Friedal–Crafts intramolecular allylation). Similar ring closures are well known; for example, phenylallyl cations have previously only been observable at low temperature if the 2-position is unsubstituted.[33,34] In each of the above cases the attacking cationic center possess the least stabilizing groups. At this time it cannot be decided whether the cyclizations in the above cases occur via the respective trimethylenemethane dications or in a stepwise manner, i.e., ionization of one hydroxyl group, intramolecular attack, and ionization of the second hydroxyl group to **14**. Ionization of a precursor in which the substituents at each of the two carbinol centers are different may shed some light on this problem.

On the basis of our results, the stability of **2** is exceptional and most likely due to steric (kinetic) as well as conjugative stabilization of the double positive charge, but not to Y-aromaticity.[6,7] We have previously found that certain cyclobutadienyl dications **16**, the cyclic analogues of system **1a**, are stable under superacidic conditions (Scheme 5).[35] Cyclobutadienyl dications stabilized by four (**16a**) or two (**16b**) phenyl groups or even only by methyl groups (**16c**) have been observed[35] and, in accordance with Huckel π molecular orbital theory,[36] have been found to be aromatic due to their cyclic delocalized 2π-electron system. In the phenyl-substituted cases considerable conjugative stabilization is afforded by these electron-donating groups. That even the (pentaphenyltrimethylene)methane dication (**17**) could not be prepared as a stable species under a variety of superacidic conditions clearly reinforces and extends the earlier findings of Schleyer *et al.*[10] that Y-conjugated dications do not possess any enhanced thermodynamic stability and cannot be considered as aromatic.

Conclusions

We have successfully prepared the (hexaphenyltrimethylene)methane dication (**2**) which was found to be quite stable. However, as even **8f**, with only one less phenyl group than **8a** and one more phenyl group than **15a**, failed to give the corresponding trimethylenemethane dication even at −80 °C,

---

(30) Olah, G. A.; Reddy, V. P.; Prakash, G. K. S. *Chem. Rev.* **1992**, *92*, 69.

(31) (a) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1539. (b) Olah, G. A.; Westerman, P. W. *J. Am. Chem. Soc.* **1973**, *95*, 7530. (c) Olah, G. A.; Westerman, P. W.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548.

(32) Deno, N. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, Chapter 18.

(33) (a) Dytnerski, D. M.; Ranganayakulu, R.; Singh, P. B.; Sorenson, T. S. *Can. J. Chem.* **1982**, *60*, 2993. (b) Olah, G. A.; Asenio, G.; Mayr, H. *J. Org. Chem.* **1978**, *43*, 1518.

(34) Cyclization of **10** → **14h** has been previously observed on treatment of **10** with Magic Acid at −115 °C. See ref 8.

(35) Olah, G. A.; Staral, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 6290.

(36) Huckel, E. *Z. Phys.* **1931**, *70*, 204. (b) Huckel, E. *Z. Phys.* **1932**, *76*, 628.

it is clear that the stabilities of the dications described in this paper are delicately poised on electronic and/or steric stabilization and confirm the earlier findings of Schleyer *et al.*[10] that trimethylenemethane dications are not energetically stabilized by Y-aromaticity.

Experimental Section

Unless otherwise specified all reagents and starting materials were obtained from commercial sources and used as received. Diethyl ether and THF were distilled from sodium/benzophenone ketyl immediately prior to use. Benzene was distilled from sodium immediately prior to use. Pyridine was stored over KOH. Benzaldehyde was distilled prior to use. Doubly distilled FSO_3H, SbF_5, and SO_2ClF were used for the preparation of the ions. ^{13}C and ^1H NMR were obtained on a Varian Unity-300 instrument equipped with a variable temperature probe.

p,p'-Bis(trifluromethyl)benzophenone (6b). Ketone **6b** was prepared according to a modified version of Olah's procedure.[37] To a solution of 4-bromobenzotrifluoride (5.0 g, 22.2 mmol) in diethyl ether (50 mL) at −65 °C and under a nitrogen atmosphere was added dropwise *t*-BuLi (1.7 M in pentane, 26.1 mL). The mixture was stirred for 4 h, during which time it was allowed to warm to −20 °C. To the aryllithium was then added a solution of *N*-carboethoxypiperidine (1.74 g, 11.1 mmol) in diethyl ether (25 mL). The mixture was stirred overnight and then refluxed for 1 h before being quenched with HCl (5 M). The ether phase was then washed with concentrated HCl (30 mL), water (30 mL), saturated $NaHCO_3$ (aq) (30 mL), and brine (30 mL). The ethereal solution was dried ($MgSO_4$) and evaporated to dryness. The crude product was recrystallized from hexanes to afford **6b** (2.08 g, 59%): mp 108−110 °C; ^1H NMR ($CDCl_3$) δ 7.75−7.82 (m, 2H), 7.87−7.94 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 194.4, 139.7, 134.4 (q, ^2J(CF) = 33 Hz), 130.2, 125.6 (q, ^3J(CF) = 3.7 Hz), 123.5 (q, ^1J(CF) = 272.4 Hz); MS (EI) *m/z* (rel intens) 318 (14), 299 (4), 249 (2), 173 (100), 145 (47), 125 (5), 95 (8), 75 (6). Anal. Calcd for $C_{15}H_8OF_6$: C, 56.62; H, 2.53. Found: C, 56.91; H, 2.53.

Diethyl 2,2-Diphenylethene-1,1-dicarboxylate (7a). Diester **7a** was prepared according to the procedure of Lenhert.[19] To THF (400 mL) at 0 °C and under a nitrogen atmosphere was added a solution of $TiCl_4$ (22 mL, 0.2 mol) in CCl_4 (50 mL), benzophenone (18.2 g, 0.1 mol), and diethyl malonate (16 g, 0.1 mol). After stirring at 0 °C for 40 min, a solution of pyridine (32 mL, 0.4 mol) in THF (70 mL) was added dropwise. The ensuing mixture was stirred for 4 days at room temperature. The reaction mixture was quenched with water (100 mL) and diethyl ether (100 mL). The aqueous phase was separated and washed with diethyl ether (2 × 100 mL). The combined organic phases were then washed with brine (100 mL), saturated $NaHCO_3$ (aq) (2 × 100 mL), and again with brine (100 mL). The ethereal solution was dried ($MgSO_4$) and the solvent evaporated. Unreacted starting materials were removed by distillation (Kugelrohr, up to 150 °C, 1.5 mmHg). The residue was then chromatographed (silica gel, eluent 20% diethyl ether/hexanes) and recrystallized twice from hexanes to afford **7a** (8.29 g, 26%): mp 75−76 °C (lit.[19] mp 74−75 °C).

Diethyl 2,2-Bis[p-(trifluoromethyl)phenyl]ethene-1,1-dicarboxylate (7b). Ketone **6b** (2.0 g, 6.3 mmol) and diethyl malonate (1.0 g, 6.3 mmol) were condensed as described above for the formation of **7a**. After workup, and purification as outlined previously for **7a,b** was obtained (1.19 g, 35%): mp 114−115 °C; ^1H NMR ($CDCl_3$) δ 7.29−7.34 (m, 4H), 7.58−7.64 (m, 4H), 4.15 (q, 4H), 1.10 (t, 6H); ^{13}C NMR ($CDCl_3$) δ 165.3, 143.1, 131.8 (q, ^2J(CF) = 33 Hz); 129.6, 125.8 (q, ^3J(CF) = 3.7 Hz), 124.3 (q, ^1J(CF) = 272.4 Hz), 62.2, 14.0; MS (EI) *m/z* (rel intens) 460 (31) $[M]^+$, 441 (14), 415 (68), 386 (76), 343 (36), 314 (39), 295 (100), 273 (62), 246 (56), 225 (42), 197 (42), 173 (61), 159 (20), 145 (18). Anal. Calcd for $C_{22}H_{18}O_4F_6$: C, 57.40; H, 3.94. Found: C, 57.33; H, 4.03.

Diethyl 2-Cyclopropyl-2-phenylethene-1,1-dicarboxylate (7c). Cyclopropyl phenyl ketone (**6c**) (3.65 g, 25 mmol) and diethyl malonate (4.00 g, 25 mmol) were condensed as described for formation of **7a**. After workup, as described above, the crude product was chromatographed (silica gel, eluent 15% diethyl ether/hexanes) and distilled to afford **7c**, (1.19 g, 17%): bp 135 °C, 0.1 mmHg; ^1H NMR ($CDCl_3$) δ 0.47 (symmetric m, 2H), 0.85 (symmetric m, 2H), 0.89 (t, 3H), 1.31 (t, 3H), 2.75 (symmetric m, 1H), 3.84 (q, 2H), 4.29 (q, 2H), 6.98−7.07 (m, 2H), 7.24−7.34 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 6.7, 11.5, 14.1, 15.0, 60.6, 61.0, 127.4, 127.8, 128.3, 134.7, 161.3, 165.3, 165.4; MS (EI) *m/z* (rel intens) 288 (2) $[M]^+$, 260 (14), 243 (6), 214 (8), 197 (12), 186 (100), 168 (8), 158 (9), 141 (24), 129 (20), 115 (20). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.92; H, 7.02.

1,1-Diphenyl-2,2-bis(diphenylhydroxymethyl)ethene (8a). To a solution of diester **7a** (2.0 g, 6.2 mmol) in diethyl ether (62 mL) at −40 °C and under a nitrogen atmosphere was added a solution of phenyllithium (1.8 M in cyclohexane/ether, 14.4 mL). The resulting dark mixture was slowly allowed to warm to room temperature and was then quenched with saturated NH_4Cl (aq). The ether phase was separated, washed with brine (40 mL), dried ($MgSO_4$), and evaporated to dryness to afford a yellow, highly resinous, oil. Repeated trituration of the crude products with hexanes (6 × 20 mL) afforded **8a** (1.21 g, 36%) sufficiently pure for ionization studies: mp 266−270 °C; ^1H NMR ($CDCl_3$) δ 6.50−6.80 (m, 10H), 6.90−7.50 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 85.5, 124.2, 126.7, 127.3, 127.8, 128.7, 144.3, 144.7, 146.3, 148.0; MS (FAB) *m/z* (rel intens) 543 (1.5) $[M - H]^-$, 361 (4.9), 352 (3.9), 255 (2.3). Anal. Calcd for $C_{40}H_{32}O_2$: C, 88.20; H, 5.92. Found: C, 88.25; H, 6.10.

1,1-Bis[p-trifluoromethyl)phenyl]-2,2-Bis[bis[p-(trifluoromethyl)-phenyl]hydroxymethyl]ethene (8b). To a solution of 4-bromobenzotrifluoride (1.71 g, 7.6 mmol) in diethyl ether (20 mL) under a nitrogen atmosphere was added dropwise at −70 °C *t*-BuLi (1.7 M in pentane, 9.0 mL). The solution was allowed to warm to −40 °C and stirred for 1 h. To the aryllithium was then added dropwise a solution of the diaryl diester **7b** (0.7 g, 1.5 mmol) in diethyl ether (7 mL). The resulting mixture was slowly allowed to warm to room temperature and stirred overnight. The mixture was quenched and worked up as described above for **8a**. The resulting crude orange solid was triturated once with cyclohexane (15 mL) and the insoluble solid recrystallized from *tert*-butyl methyl ether/heptane (2×) to afford **8b** (0.60g, 41%): mp 268−271 °C; ^1H NMR (CD_3COCD_3) δ 6.90−7.90 (m, 24H), 3.11 (s, 1H), 1.18 (s, 1H); ^{13}C NMR (CD_3COCD_3) δ 152.4, 148.4, 146.1, 145.0, 130.4, 129.5 (q, ^2J(CF) = 32 Hz), 128.6, 127.7 (q, ^2J(CF) = 32 Hz), 127.1, 125.3 (q, ^3J(CF) = 3.7 Hz), 123.5, 123, 85.4; MS (FAB) *m/z* (rel intens) 951 (2) $[M - 1]^-$, 789 (2), 634 (33), 633 (100), 616 (25), 615 (53), 488 (5), 471 (10), 459 (10), 335 (10), 318 (10), 303 (17). Anal. Calcd for $C_{46}H_{26}O_2F_{18}$: C, 57.99; H, 2.75. Found: C, 58.07; H, 3.50.

1-Cyclopropyl-1-phenyl-2,2-bis(diphenylhydroxymethyl)ethene (8c). An ether solution of diester **7c** (0.60 g, 2.08 mmol) was treated with phenyllithium and worked up as described above for **8a**. The crude product was recrystallized from ethanol (2 × 20 mL) to afford **8c** (0.40 g, 38%): mp 127−130 °C; ^1H NMR ($CDCl_3$) δ 0.20 (symmetric m, 2H), 0.50 (symmetric m, 2H), 1.84 (symmetric m, 1H), 6.46−6.51 (m, 1H), 6.88−6.94 (m, (2H), 6.96−7.17 (m, 5H), 7.25−7.35 (m, 4H), 7.41−7.49 (m, 2H), 7.63−7.69 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 4.2, 5.6, 14.8, 20.8, 92.8, 94.1, 126.2, 126.5, 126.8, 127.0, 127.2, 127.28, 127.32, 127.5, 127.70, 127.73, 128.1, 128.3, 128.46, 128.51, 129.4, 130.5, 133.1, 137.8, 143.3, 143.6; MS (FAB) *m/z* (rel intens) 507 (21) $[M - H]^-$, 325 (37), 307 (40), 279 (10), 247 (19), 219 (6), 181 (19). Anal. Calcd for $C_{37}H_{32}O_2$: C, 87.37; H, 6.34. Found: C, 87.37; H, 6.34.

1,1-Dimethyl-2,2-bis(diphenylhydroxymethyl)ethene (8d). An ether solution of diethyl isopropylidenemalonate (**7d**) (1.0 g, 5.0 mmol) was treated with phenyllithium and worked up as described above for **8a**. The crude product was triturated with hexanes (3 × 20 mL) to afford **8d** (0.78 g, 37%) sufficiently pure for further work: mp 133−135 °C; ^1H NMR ($CDCl_3$) δ 1.15 (s, 6H), 7.20−7.40 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 26.98, 85.30, 127.1, 127.4, 128.2, 134.8, 143.1, 147.7; MS (FAB) *m/z* (rel intens) 419 (32) $[M - H]^-$, 235 (4), 219 (28), 181 (7). Anal. Calcd for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.77; H, 6.80. Treatment of **8d** with FSO_3H at −80 °C gave a blue solution of what is tentatively assigned on the basis of the following ^{13}C and ^1H NMR data as **14d**: ^1H NMR (SO_2ClF, −20 °C) δ 0.90 (s, 6H), 6.44−7.36 (m, 19H); ^{13}C NMR (SO_2ClF, −20 °C) δ 25.7, 55.2, 123.8, 129.1, 129.2, 129.3, 129.9, 130.0, 131.5, 132.2, 132.6, 134.3, 137.4, 137.8, 138.9, 139.2, 140.5, 140.6, 142.9, 159.8, 164.6, 187.2, 200.6.

---

[37] Prakash, G. K. S.; York, C.; Liao, Q.; Kotian, K.; Olah, G. A. *Heterocycles* **1995**, *40*, 79.

1-Methyl-2,2-bis(diphenylhydroxymethyl)ethene (8e). An ether solution of diethyl ethylidenemalonate (**7e**) (1.0 g, 5.4 mmol) was treated with phenyllithium and worked up as described above for **8a**. The crude product was recrystallized from ethanol (1 × 20 mL, 1 × 10 mL) to afford **8e** (0.76 g, 35%): mp 135−136 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (d, 3H), 5.35 (q, 1H), 7.12−7.42 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 15.70, 83.6, 85.9, 127.1, 127.5, 127.6, 127.9, 128.2, 130.4, 146.3, 147.2, 148.5; MS (FAB) *m/z* (rel intens) 405 (43) $[M - H]^-$, 223 (10), 205 (21), 181 (7), 145 (22). Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.66; H, 6.60. Treatment of **8e** with FSO_3H at −80 °C gave a burgandy solution of what is tentatively assigned on the basis of the following ^{13}C and ^{1}H NMR data as **14e**: ^{1}H NMR (SO_2ClF, −40 °C) δ 0.50 (d, 3H), 4.10 (q, 1H), 6.40−7.50 (m, 19H); ^{13}C NMR (SO_2ClF, −40 °C) δ 13.8, 49.9, 124.8, 128.8, 129.0, 129.1, 129.3, 129.5, 130.0, 130.1, 130.4, 131.2, 131.3, 131.7, 135.0, 136.8, 137.1, 137.2, 137.5, 137.6, 138.5, 139.8, 141.5, 143.3, 153.9, 162.4, 187.4, 193.6.

1-Phenyl-2,2-bis(diphenylhydroxymethyl)ethene (8f). An ether solution of diethyl benzylidenemalonate (**7f**) (2.0 g, 8.1 mmol) was treated with phenyllithium and worked up as described above for **8a**. Trituration of the crude products with hexanes (1 × 60 mL, 3 × 25 mL) afforded **8f** (2.04 g, 54%) sufficiently pure for further work: mp 208−210 °C; ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 1H), 4.30 (s, 1H), 6.46−6.82 (m, 5H), 7.06−7.34 (m, 14H), 7.36−7.44 (M, 3H), 7.52−7.58 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 83.7, 83.8, 85.6, 85.7, 124.4−129.2 (complex), 136.3, 136.5, 136.8, 145.4, 147.1, 148.2; MS (FAB) *m/z* (rel intens) 467 (10) $[M - H]^-$, 285 (14), 267 (12), 179 (6). Anal. Calcd for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 87.03; H, 6.28. Treatment of **8f** with FSO_3H at −80 °C gave a purple solution of what is tentatively assigned on the basis of the following ^{13}C and ^{1}H NMR data as **14f**: ^{1}H NMR (SO_2ClF, −40 °C) δ 5.09 (m, 1H), 5.75−7.62 (m, 24H); ^{13}C NMR (SO_2ClF, −40 °C) δ 60.9, 61.1, 125.4−132.4 (complex), 131.4, 135.7, 139.3−134.8 (complex), 139.3, 141.6, 143.2, 154.2, 161.7, 187.5, 194.8.

1-Phenyl-2,2-dibenzoylethene (9). The title compound was prepared as described by Pratt and Werble.[20] To a solution of benzaldehyde (0.47 g, 4.4 mmol) and dibenzoylmethane (1.00 g, 4.4 mmol) in benzene (10 mL) was added solutions of piperidine (50 mg, 0.6 mmol) and hexanoic acid (130 mg, 1.1 mmol) both in benzene (4 mL). The resulting solution was then azeotroped for 24 h. The benzene solution was washed with a 10% solution of $NaHCO_3$ (aq) (20 mL), brine (20 mL), 5% acetic acid (20 mL), and brine (20 mL), dried ($MgSO_4$), and evaporated. The desired diketone **9** (0.87 g, 63%) was obtained after column chromatography (silica gel, eluent 10% diethyl ether/hexanes) as a pale yellow oil whose spectroscopic data were in agreement with literature data.[20,38]

1-Phenyl-2,2-bis(phenylhydroxymethyl)ethene (10). To a solution of lithium aluminum hydride (0.21 g, 5.5 mmol) in diethyl ether (20 mL) was added a solution of the diketone **9** (0.87 g, 2.8 mmol) in diethyl ether (10 mL). The resulting mixture was stirred overnight, quenched with a saturated solution of $NaHSO_4$ (aq), and filtered. The ether solution was dried ($MgSO_4$) and evaporated and the crude product recrystallized from toluene to afford **10** (0.28 g, 32%): mp 116−117 °C; ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 1H), 5.95 (s, 1H), 7.05 (s, 1H), 7.25−7.45 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 71.2, 74.2, 125.9, 127.08, 127.13, 127.4, 127.9, 128.2, 128.4, 128.6, 128.8, 130.4, 136.3, 142.2, 143.0, 143.7; MS (FAB) *m/z* (rel intens) 315 (22) $[M - H]^-$, 297 (33), 255 (4), 207 (8), 191 (17), 183 (5), 137 (13). Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.52; H, 6.37. Found: C, 83.34; H, 6.61. Treatment of **10** with FSO_3H at −80 °C gave a red solution of what is tentatively assigned on the basis of the following ^{13}C and ^{1}H NMR data as **14g**: ^{1}H NMR (SO_2ClF, −40 °C) δ 4.80 (s) and 5.00 (s) (total 1H), 6.52−7.80 (m, 14H), 8.04 (s) and 8.40 (s) (total 1H), 9.05 (s) and 9.13 (s) (total 1H); ^{13}C NMR (SO_2ClF, −40 °C) δ 54.0, 126.3, 126.9, 128.4, 129.6, 130.3, 131.0, 133.2, 133.7, 134.0, 141.3, 141.7, 144.7, 163.1, 165.5, 172.2, 190.2.

Carbocation Preparation. To a slurry of the appropriate precursor (ca. 50 mg) in SO_2ClF (ca. 0.5 mL) in a 5 mm NMR tube and cooled to −78 °C (dry ice/acetone slurry), or in the case of **8b** at −120 °C (liquid nitrogen/pentane slurry), was added slowly a small quantity of FSO_3H. The ensuing mixture was vigorously stirred (Vortex agitator) with periodic cooling prior to transfer to a precooled NMR instrument. Attempts were made to prepare **17** under various superacid conditions in a similar manner without success.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

JA9522544

---

(38) Tanikaga, R.; Konya, N.; Hamamura, K.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3211.