

Table V. Effect of Phenyl Substitution on Relative Rates

| Number of phenyl substituents | Reaction | |
|-------------------------------|---------------------------------------|---|
| | Phenyl iodine diacetates ^a | <i>tert</i> -Butyl peracetates ^b |
| 0 | [1] | [1] |
| 1 | 1.4 | 1.6×10^4 |
| 2 | 26 | 9×10^6 |
| 3 | 1×10^8 | 4×10^7 |

^a Relative to the rates of phenyl iodine diacetate decomposition calculated for 79.8, 100, and 140° using $\Delta H^\ddagger = 28.9 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -10.2 \text{ cal mol}^{-1} \text{ deg}^{-1}$. ^b Recalculated from the activation parameters given in ref 7-9.

The accelerations produced by phenyl substituents in this reaction series are compared with those for the decomposition of the corresponding *tert*-butyl peracetates⁷⁻⁹ in Table V. At each step in the series the effect is smaller for the phenyl iodine diacetates than for the *tert*-butyl peracetates by a factor of about 10^4 . We interpret this as meaning that the alkyl to carbonyl bond is much less weakened at the transition state in the former series. Because the radical **2** is more stable than a *tert*-butoxy radical, the transition state is reached earlier in the reaction, in accord with the principle that transition states tend to resemble the products more closely when the products are of higher energy.¹⁰

A further consequence of the stability of radical **2** is a marked shift to more ester ROOCR at the expense

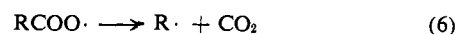
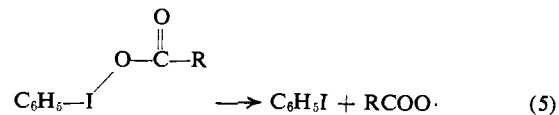
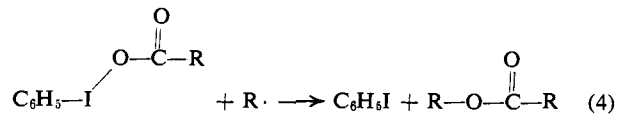
(7) P. D. Bartlett and D. M. Simons, *J. Amer. Chem. Soc.*, **82**, 1753 (1960).

(8) P. D. Bartlett and R. E. Hiatt, *ibid.*, **80**, 1398 (1958).

(9) J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).

(10) (a) J. E. Leffer, *Science*, **117**, 340 (1953); (b) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

of dimer RR in reactions with higher initial concentrations (Tables II and III). The divalent iodine radical persists long enough to give ester by reaction 4 at high steady-state concentrations, but dissociates into iodobenzene and unstable acyloxy radicals at lower concentrations. The latter decarboxylate and combine to give dimer at the expense of ester.



In the decomposition of *tert*-butyl triphenylperacetate,⁹ Lorand and Bartlett found both trityl *tert*-butyl ether and an "abnormal" para coupling product *p*-*tert*-butoxytriphenylmethane among the products. In contrast, we find only the normal trityl triphenylacetate ester. This may reflect a hidden step in eq 4 in which a transient phenyltrityliodonium triphenylacetate is formed before the ester and iodobenzene.

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Stable Carbocations. CXXXV.^{1,2} Protonation of Trihydroxybenzenes and Their Methyl Ethers in Superacids

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Abstract: Protonation of isomeric trihydroxybenzenes and their methyl ethers in four different superacid media (I-IV) was studied. The sites of protonation were found at carbon and/or oxygen. Two different types of diprotonated ions were observed in strongest superacid media (I and II): (i) benzenium ions with a $-\text{OH}_2^+$ or $\text{CH}_3\text{O}(\text{H})^+$ substituent at the meta position and (ii) protonated or alkylated oxocyclohexenyl dication. Isomeric monoprotonated benzenium ions derived from the same precursors were observed in weaker superacid media (III and IV).

In the preceding paper, we discussed the protonation of mono- and dihydroxybenzenes and their derivatives.¹ The behavior of trihydroxybenzenes and their methyl ethers in superacids has not yet been studied systematically. Our major interest in the course of

this study was directed to establish the site of protonation, the possibility of diprotonation, and the formation of isomeric ions through the influence of substituents in the benzenium ions.

On the other hand, diprotonated 2,4,6-trimethylaniline and 2,4-dimethylaniline were observed in HF-SbF_5 solution.³ These benzenium ions (**1** and **2**)

(1) Part CXXXIV: G. A. Olah and Y. K. Mo, *J. Org. Chem.*, submitted for publication.

(2) For a discussion of the general concept of carbocations and differentiation of trivalent carbenium ion from penta- (or tetra-) coordinated carbonium ions, see G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(3) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. 2, 1970, p 845; see reference to unpublished results. Similar results were also obtained in our laboratories.

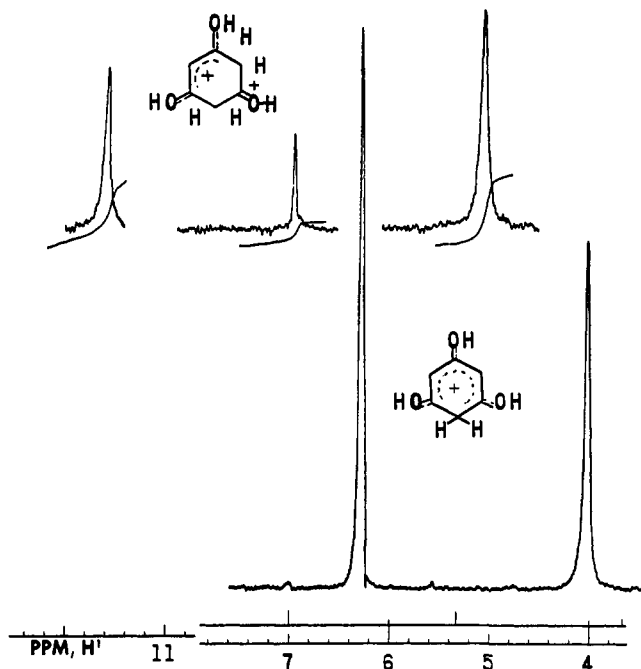
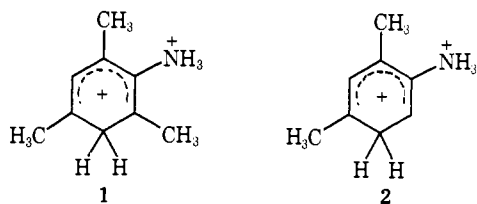


Figure 1. PMR spectra of monoprotonated phloroglucinol (5) (lower) and diprotonated phloroglucinol (6) (upper trace).

have a NH_3^+ group in the meta position (relative to the "aliphatic" methylene group). In the present study, the



structure of benzenium ions or the dication obtained was elucidated from the pmr spectra. In some cases, temperature-dependent pmr spectra were also studied to elucidate the nature of the ions, particularly when more than one benzenium ion (or dication) was formed. The dependence of ion formation and their equilibria upon acidity in various superacid media were also investigated.

Results and Discussion

Isomeric trihydroxybenzenes and their methyl ethers were protonated in four different superacid systems: $\text{SbF}_5\text{-HF}(1:1, M/M)\text{-SO}_2\text{ClF}$ (I), $\text{SbF}_5\text{-HSO}_3\text{F}(1:1, M/M)\text{-SO}_2\text{ClF}$ (II), $\text{SbF}_5\text{-HSO}_3\text{F}(1:4, M/M)\text{-SO}_2\text{ClF}$ (III), and $\text{HSO}_3\text{F-SO}_2\text{ClF}$ (IV). Monoprotection, as well as in a number of cases diprotection, was found. Two different sites of protonation were observed: on carbon or on oxygen. The site of protonation depends on the various superacid systems used. The ions obtained in the four different superacid media, including the ratio of isomeric ions, are summarized in Table I. The pmr parameters of all benzenium ions and dications studied are tabulated in Table II. Representative pmr spectra of benzenium ions and dications are shown in Figures 1-3.

Protonation of Phloroglucinol (3) and 1,3,5-Trimethoxybenzene (4). The protonation of phloroglucinol 3 and its trimethyl ether 4 in strong acids like HSO_3F ,

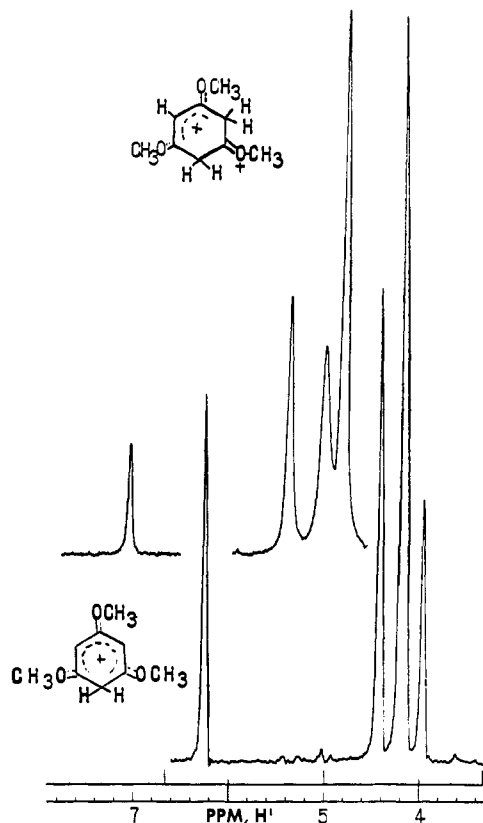


Figure 2. PMR spectra of monoprotonated 1,3,5-trimethoxybenzene (9) (lower) and diprotonated 1,3,5-trimethoxybenzene (10) (upper trace).

Table I. Ions Formed upon the Protonation of Trihydroxybenzenes and Their Methyl Derivatives

| Pre-cursors | Superacids | | | |
|-------------|----------------------|----------------------|----------------------|----------------------|
| | I | II | III | IV |
| 3 | Polymerization | 6 | 5 | 5 |
| 4 | 10 | 10 | 10 | 9 |
| 11 | 14 (83%) 15 (17%) | 14 (83%) 15 (17%) | 14 (83%) 15 (17%) | 13 (33%) 12 (67%) |
| 16 | Polymerization | 19 | 18 | 18 |
| 17 | 21 | 21 | 20 | 20 |
| 22 | Polymerization | 25 (67%) 26 (33%) | 23 (67%) 24 (33%) | 23 (67%) 24 (33%) |
| 27 | 30 (71%) 31 (29%) | 30 (71%) 31 (29%) | 28 (71%) 29 (29%) | 28 (71%) 29 (29%) |
| 32 | Polymerization | 34 | 33 | 33 |
| 35 | 37 | 37 | 37 | 37 |
| 36 | 40 | 39 (80%) 38 (20%) | 38 (70%) 39 (30%) | 38 |

70% HClO_4 , and HF-BF_3 has been studied by uv and pmr spectroscopy.⁴

In the weaker superacids III and IV, phloroglucinol was monoprotated to give the arenium ion 5. The pmr spectrum of ion 5 (Figure 1) in acid IV at -40° has two sharp singlets of equal intensity at δ 4.0 and 6.35. In superacid III, at -40° , the two singlets shifted slightly downfield to δ 4.18 and 6.45, respectively. In both superacid systems III and IV, the hydroxyl

(4) (a) D. M. Brouwer, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas*, **85**, 109, 114 (1966); (b) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Amer. Chem. Soc.*, **84**, 4343 (1962); (c) W. M. Schubert and R. H. Quacchia, *ibid.*, **85**, 1278 (1963); (d) A. J. Kresge, Y. Chiang, and L. E. Hakka, *ibid.*, **93**, 6167 (1971).

Table II. Pmr Data of Monoprotonated and Diprotonated Trihydroxybenzenes and Their Methyl Derivatives^a

| Pre-cursors | Ions | Reaction systems (Temp, °C) | OCH ₃ | CH ₂ | H _a | H _b | OH |
|-------------|------|-----------------------------|--|---------------------------|-------------------------------|---------------------------------------|--------------------------|
| 3 | 5 | IV (-50) | | 4.10 (s) | 6.35 (s) | | |
| 3 | 6 | II (-40) | | 5.26 (s, 4 H) | 7.14 (s, 1 H) | | 12.60 (s, 2 H, allyl OH) |
| 4 | 9 | IV (-40) | 4.20 (s), ortho, 4.40 (s), para | 4.00 (s) | 6.38 (s) | | |
| 4 | 10 | II (-40) | 4.82 (s, 6 H, allyl), 5.40 (s) | 5.06 (s) | 7.04 (s) | | |
| 11 | 12 | IV (-40) | 4.20 (s) | 4.00 (s) | 6.24 (s) | | <i>b</i> |
| | | | 4.20 (s), 4.40 (s) | 4.00 (s) | 6.37 (s) | 6.30 (s) | <i>b</i> |
| 11 | 14 | II (-40) | 4.92 (s, allyl), 5.58 (s) | 5.17 (s) | 7.18 (s) | | 12.65 (s, 1 H, allyl OH) |
| | | | 4.92 (s, allyl) | 5.17 (s) | 7.10 (s) | | <i>b</i> |
| 16 | 18 | IV (-20) | | 4.27 (d, $J_{HH} = 3$ Hz) | 7.18 (d, $J_{HH} = 10$ Hz) | 7.68 (d of t, $J_{HH} = 10$ and 2 Hz) | <i>b</i> |
| 16 | 19 | II (-60) | | 4.60 (s br) | 7.3 (d br, $J_{HH} = 10$ Hz) | 8.0 (d br, $J_{HH} = 10$ Hz) | <i>b</i> |
| 17 | 20 | IV (-40) | 4.31 (s, m), 4.50 (s, o), 4.64 (s, p) | 4.38 (d, $J_{HH} = 2$ Hz) | 7.53 (d, $J_{HH} = 10$ Hz) | 8.03 (d of t, $J_{HH} = 10$ and 2 Hz) | |
| 17 | 21 | II (-40) | 4.71 (s, o), 4.90 (s, p), 5.14 (s, m) | 4.63 (s, br) | 7.68 (d, $J_{HH} = 10$ Hz) | 8.33 (d br, $J_{HH} = 10$ Hz) | |
| 22 | 23 | IV (-40) | 4.50 (s) | 4.30 (s, br) | 7.23 (d, $J_{HH} = 10$ Hz) | 7.7 (m) ^c | <i>b</i> |
| | | | 4.63 (s) | 4.3 (s, br) | 7.42 (d, $J_{HH} = 10$ Hz) | 7.7 (m) ^c | <i>b</i> |
| | | | 4.70 (s) | 4.5 (s, br) | 7.6 (d br, $J_{HH} = 10$ Hz) | 7.1 (m) ^c | <i>b</i> |
| 22 | 26 | II (-40) | 4.90 (s) | 4.5 (s, br) | 7.6 (d br, $J_{HH} = 10$ Hz) | 8.1 (m) ^c | <i>b</i> |
| | | | 4.54 (s, o), 4.23 (s, m) | 4.40 (s, br) | 7.28 (d, $J_{HH} = 10$ Hz) | 7.82 (d of t, $J_{HH} = 10$ and 2 Hz) | <i>b</i> |
| 27 | 29 | IV (-40) | 4.23 (s, m), 4.70 (s, p) | 4.40 (s, br) | 7.43 (d, $J_{HH} = 10$ Hz) | 7.8 (d, br, $J_{HH} = 10$ Hz) | <i>b</i> |
| | | | 4.80 (s, o), 5.20 (s, m) | 4.6 (s, br) | 7.4 (d, br, $J_{HH} = 10$ Hz) | 8.1 (br) | 11.0 (br) |
| | | | 4.98 (s, o), 5.22 (s, m) | 4.6 (s, br) | 7.6 (d, br, $J_{HH} = 10$ Hz) | 8.1 (br) | 11.0 (br) |
| 32 | 33 | IV (-40) | 4.50 (s, o), 4.63 (s, p) | 4.40 (d, $J_{HH} = 2$ Hz) | 7.50 (d, $J_{HH} = 10$ Hz) | 7.94 (d of t, $J_{HH} = 2$ and 10 Hz) | <i>b</i> |
| 32 | 34 | II (-30) | 4.8 (s, br), 5.0 (s, br) | 4.7 (s, br) | 7.9 (br) | 8.0 (br) | <i>b</i> |
| 35 | 37 | I (-40) | | 4.4 (d, $J_{HH} = 4$ Hz) | 6.7 (s) | 6.8 (t, $J_{HH} = 4$ Hz) | <i>b</i> |
| 36 | 38 | IV (-45) | 4.20 (s, m), 4.47 (s, o), 4.60 (s, p) | 4.26 (d, $J_{HH} = 2$ Hz) | 6.78 (s) | 6.83 (t, $J_{HH} = 2$ Hz) | |
| 36 | 39 | II (-38) | 4.73 (s, allyl), 5.17 (s, allyl), 5.60 (s) | 4.9 (s, br) | 7.8 (s, br) | | |
| 36 | 40 | I (-40) | 4.93 (s), 5.08 (s), 5.44 (s) | 5.0-5.4 (s, br) | 7.2 (s, br) | 8.2 (s, br) | <i>b</i> |

^a Proton chemical shifts are referred to external TMS. ^b Hydroxy protons are not observable (due to exchange with acid). ^c Two sets of overlapping doublet of triplets.

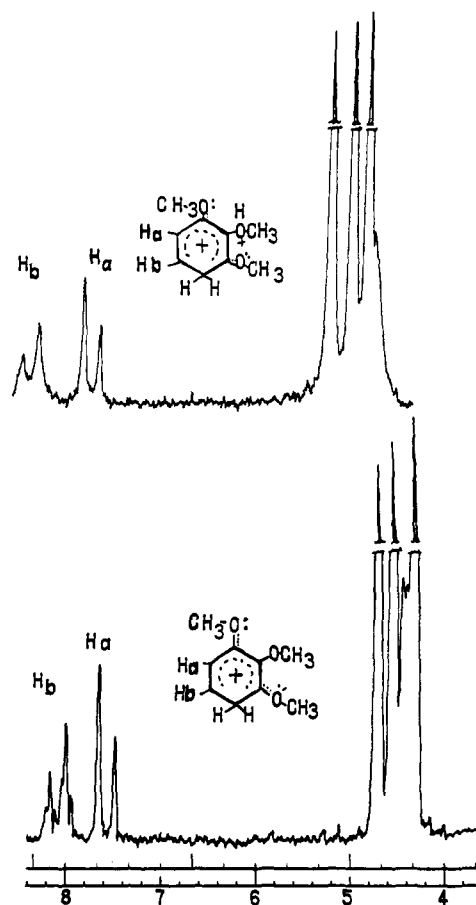
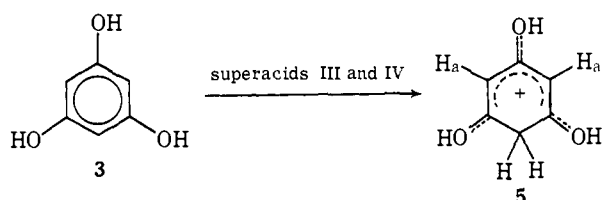


Figure 3. Pmr spectra of monoprotonated 1,2,3-trimethoxybenzene (**24**) (lower) and diprotonated 1,2,3-trimethoxybenzene (**25**) (upper trace).

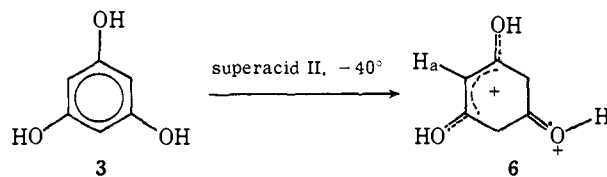


protons were not observed because of rapid exchange with solvent.

When **3** was dissolved in superacid II, the pmr spectrum (Figure 1) of the resulting solution showed two singlets at δ 5.26 (4 H) and 7.14 (1 H). The relative ratio of the two peaks is 4:1. In addition, a two-proton deshielded singlet resonance was observed at δ 12.60. These observations are consistent with diprotonated phloroglucinol **6**. The proton attached to the carbonyl oxygen was not observed, presumably due to exchange with the solvent system. The relative stability of ion **6** is not surprising since, in our previous work, the diprotonation of β -diketones³ and of α -hydroxy ketones⁶ was found in superacid II. Considering the stepwise protonation of **3** to ion **5** and then to dication **6**, due to low charge density at the meta carbon atoms in ion **5**, further protonation at these positions is not unlikely. A carbon-13 nmr study of ion **5** showed that the meta carbons have a cmr shift

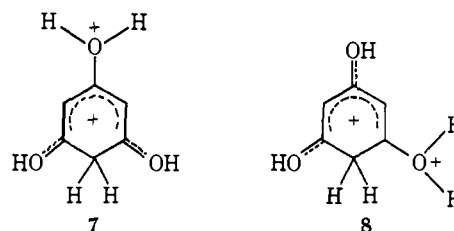
(5) G. A. Olah and M. Calin, *J. Amer. Chem. Soc.*, **90**, 4672 (1968).

(6) G. A. Olah and A. T. Ku, *J. Org. Chem.*, **35**, 3922 (1970).



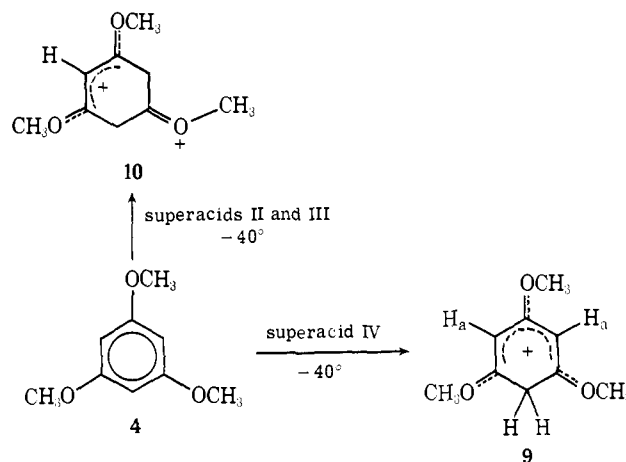
of δ_{13C} 66.0 strongly supporting this assumption. The ortho and para carbons have cmr shifts of δ_{13C} 9.7 and 4.4, respectively.

Further protonation of ion **5** at oxygen is also possible (the oxygen atoms have available lone-pair electrons). The resulting dication **7** and **8** would be expected to be less stable than dication **6** because a hydroxonium group ($-\text{OH}_2^+$) is attached to a highly charged ortho or para carbon atom (in respect to the methylene group).



Dissolving **3** in superacid I gave no identifiable ions; only polycondensed polymeric products were obtained. Similar polycondensations were found to take place in the case of dihydroxybenzenes.¹

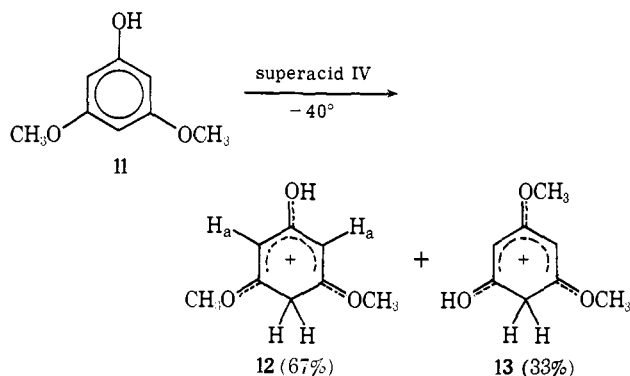
Phloroglucinol trimethyl ether (1,3,5-trimethoxybenzene (**4**)) was also protonated and studied in the four superacid systems (I-IV). In superacid IV, **2** was monoprotonated to give arenium ion **9**. The pmr spectrum of ion **9** (Figure 2) showed four well-



resolved singlets at δ 4.00 (CH_2 , 2 H), 4.20 (ortho OCH_3 , 6 H), 4.40 (para OCH_3 , 3 H), and 6.38 (vinyl protons, 2 H). In superacid III at -40° , unlike phloroglucinol, **2** was diprotonated to ion **10**. In superacid II, **2**, as expected, was also diprotonated to give ion **10**. The pmr spectrum of ion **10** at -40° (Figure 2) showed four well-resolved singlets with area ratios 6:2:3:1 at δ 4.82 (allyl OCH_3), 5.06 (CH_2), 5.40 (ketonic methyl), and 7.04 (vinylic H), respectively. Throughout the temperature range from -20 to -80° , we were unable to observe the geometrical isomer pair (syn and anti) of both ions **9** and **10**, indicating either ions **9** and **10** are present as rapidly equilibrating ions (of syn and

anti forms) or only one stable form (syn or anti) is present in the superacid solutions.

Protonation of 3,5-Dimethoxyphenol (11). Protonation of **11** in $\text{FSO}_3\text{H-SO}_2\text{ClF}$ (IV) gave two isomeric ions **12** and **13** in the ratio of 2:1. Similar results were found when **11** was protonated in 70% perchloric



acid.^{4d} The pmr spectrum shows the methylene protons of both ions **12** and **13** coinciding at δ 4.00 (2 H). There are two sharp singlets (a total of six protons) at δ 4.20 and 4.40 with a peak area ratio 6:1. Thus, we can assume that these two singlets are those of the methoxy groups of both ions **12** and **13**. The more deshielded and less intense singlet is that of the para methoxy group of ion **13** (as a similar absorption is found in ion **9**) due to the fact that more deshielding of the para positions than of the ortho positions has been found experimentally⁷ and theoretically.⁸ Thus the singlet at δ 4.20 is partially attributed to ortho methoxy protons of unsymmetrical ion **13** and partially attributed to the two ortho methoxy protons of symmetrical ion **12**. Then the ratio of ion **12** to ion **13** is calculated as 3:1. In addition, the two identical vinyl protons of ion **12** show a sharp singlet at δ 6.24, while the two nonidentical vinyl protons of ion **13** show two singlets at δ 6.30 and 6.37.

The fact that the formation of ion **12** is preferred over **13** (by 2:1) indicates that the site of protonation is four times more favorable at the carbon atom para to the hydroxyl than para to the methoxyl groups (ion **11** has two available protonation sites para to the OCH_3 and only one site para to the OH). The higher selectivity of protonation at the carbon para to the OH than to the OCH_3 group and the observation of higher charge density at the para position than at the ortho position indicates that OH is a better stabilizing group than OCH_3 in a benzenium ion system. This result does not agree with the order of inductive electron release, $\text{R} > \text{H}$, but it is consistent with the cmr study of C-protonated phenol and anisole, e.g., the carbon-13 shift of para carbon in C-protonated phenol ($\delta_{13\text{C}}$ 12.1) is less deshielded than that of C-protonated anisole ($\delta_{13\text{C}}$ 0.8).¹ Furthermore, it also agrees with the fact that acid-catalyzed hydrogen exchange occurs more rapidly in phenols than in the corresponding ethers⁹ and that σ^+ for OH is more negative than for OCH_3 .¹⁰

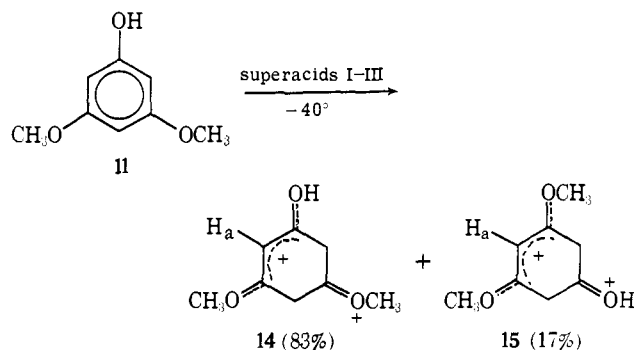
(7) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *J. Org. Chem.*, **37**, 2034 (1972).

(8) Reference 3, p 856.

(9) A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Amer. Chem. Soc.*, **93**, 6181 (1971).

(10) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

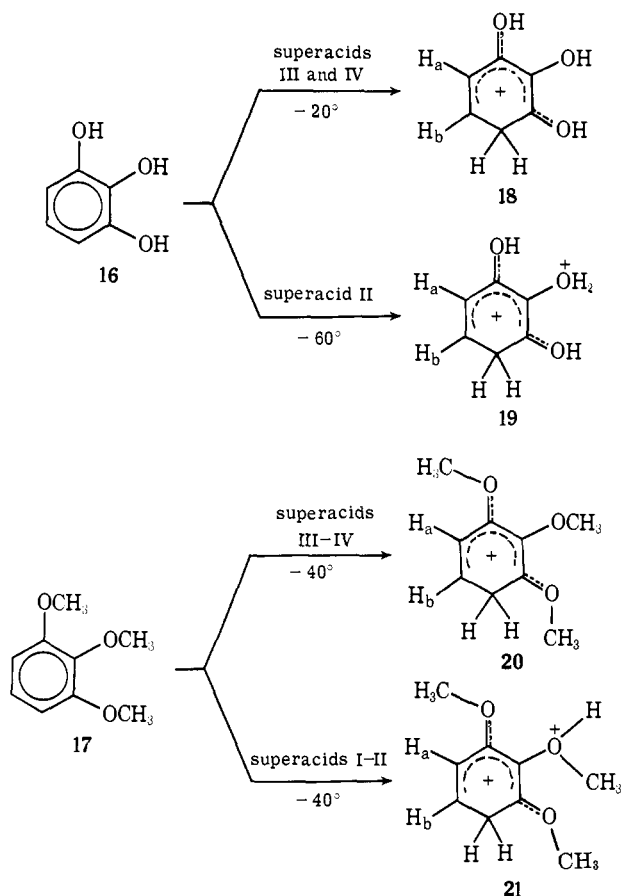
Protonation of **11** in superacids I, II, and III at -40° gave identical species whose pmr spectra are consistent with the formation of two isomeric diprotonated ions



14 and **15**. The ratio of ion **14** to ion **15** was determined from the peak areas of their OCH_3 absorptions (two singlets at δ 4.92 and 5.58) and was found to be 6:1. Since the ratio of ion **12** to ion **13** is 2:1 and ion **12** is symmetrical and only gives single diprotonated ion **14**, but ion **13** could either give ion **14** or ion **15**, the ratio of 6:1 for **14**:**15** indicates the ease of additional protonation at the meta carbons of **13** is equal. The structures of ions **14** and **15** are based on their pmr spectra. A slightly broadened singlet absorption (four protons) at δ 5.17 is assigned to the methylene protons of both ions **14** and **15**. The less intense deshielded singlet (δ 5.58) is known to be the $\text{CH}_3\text{O}^+=\text{C}<$ which is contributed solely by ion **14**. The shielded vinylic methoxyl singlet (δ 4.92) arises from both ions **14** and **15**. The vinyl protons of ion **14** show a singlet at δ 7.18, and of ion **15** a shoulder on that singlet. The hydroxylic proton of ion **14** is observed as a singlet at δ 12.65, but that of ion **15** is not observable.

Protonation of Pyrogallol (16) and 1,2,3-Trimethoxybenzene (17). Protonation of **16** in superacids III and IV at -20° gave the 2,3,4-trihydroxybenzenium ion **18**. The pmr spectrum of ion **18** is similar to that of C-protonated phenol.¹ The methylene protons show a doublet at δ 4.27 ($J_{\text{HH}} = 3$ Hz). In the vinyl region, a doublet of triplets at δ 7.68 ($J_{\text{HH}} = 10$ and 3 Hz, ortho proton) and a doublet at 7.18 ($J_{\text{HH}} = 10$ Hz, meta proton) are found. The hydroxyl protons were not observable even at -90° . When **16** was protonated in superacid II, the pmr spectrum was similar to that of ion **18** but all the three absorptions were deshielded. For example, the methylene protons are deshielded to δ 4.6 (slightly broadened). Similarly, the ortho and meta protons are now deshielded at δ 8.0 (broadened doublet) and 7.4 (slightly broadened doublet), respectively. Again, no hydroxyl proton absorption was found in the pmr spectrum, presumably due to rapid proton exchange with the acid. These data suggest **16** was monoprotated in superacids III and IV and diprotonated in superacid II to form ion **19**.

In superacid I, **16** polycondensed to unidentified products. Protonation of **17** in superacids III and IV gave the expected benzenium ion **20**. In superacids I and II **17** was diprotonated to yield ion **21**. The assignment of ion **20** is based on its pmr spectrum (Figure 3). Three singlet absorptions (each of three protons) at δ 4.31, 4.50, and 4.64 are assigned to the meta, ortho, and para methoxy groups, respectively. The more deshielded nature of the para methoxy group

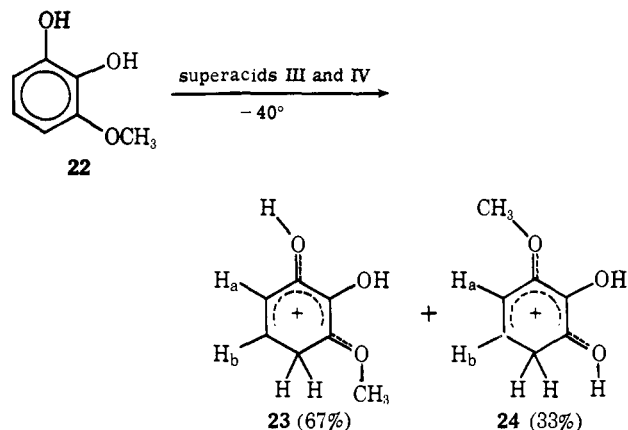


than of the ortho and meta methoxy groups has been discussed previously. The methylene protons show a doublet at δ 4.38 ($J_{\text{HH}} = 2$ Hz) since they are coupled to the ortho vinylic proton. This ortho vinylic proton shows a doublet of triplets at δ 8.33 ($J_{\text{HH}} = 2$ and 10 Hz). The meta vinylic proton is a doublet at δ 7.35.

The pmr spectrum of ion **21** (Figure 3) is similar to the pmr spectrum of ion **20**. The important feature of the pmr spectrum of ion **21** is the substantial deshielding of the meta OCH_3 protons (0.73 ppm). The other resonance lines are only slightly deshielded (see Table II). In superacid II, the hydroxyl proton of ion **21** was not observable but in superacid I, a broadened absorption was found at δ 12.4. However, the resolution of the spectrum of ion **21** is poorer in this medium.

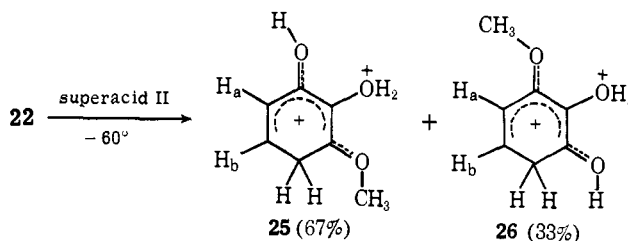
No syn-anti isomers are observed for either ion **20** or **21**. Previous studies¹ have shown that both ortho and para OCH_3 groups in benzenium ions have partial double bond character with the ring. Sterically, both ortho and para OCH_3 groups will prefer to be in anti forms (farther apart from the meta OCH_3). Since the meta OCH_3 has no partial double bond character with the ring, it should be freely rotating.

Protonation of 3-methoxycatechol (22) in the four superacids is similar to protonation of **16** and **17**. In superacids III and IV, **22** was monoprotated to give isomeric benzenium ions **23** (67%) and **24** (33%). The ratio of **23**:**24** is independent of temperature and acidity (within the range studied). The pmr spectrum of the solution containing the mixture of **23** and **24** shows two different, sharp methoxy singlets at δ 4.50 (**23**) and 4.63 (**24**). We have previously discussed that the para methoxy group is more deshielded than the ortho. The more predominant formation of ion **23** to ion **24**



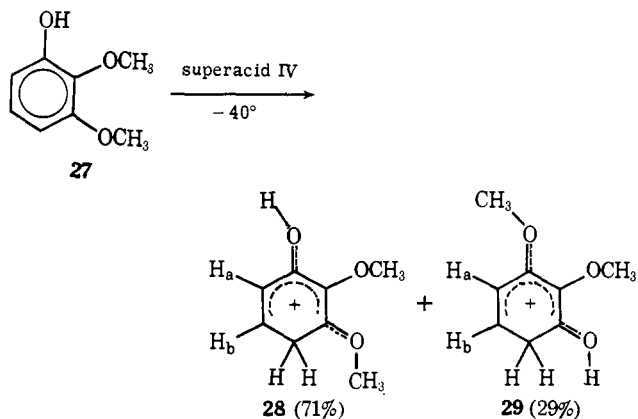
(2:1) indicates that hydroxyl is a better stabilizing group than methoxyl. Such behavior has been discussed previously. The methylene protons of ions **23** and **24** have identical proton shifts at δ 4.3, showing a slightly broadened singlet (Table II).

In superacid II, **22** was diprotated to give isomeric ions **25** (67%) and **26** (33%). The pmr spectrum of ions **25** and **26** has similar features but is deshielded



compared to that of ions **23** and **24**, respectively. The methoxy protons of ions **25** and **26** are deshielded from δ 4.50 (**23**) and 4.63 (**24**) to 4.70 (**25**) and 4.90 (**26**), respectively. Other proton absorptions are also deshielded to a similar extent (Table II). In superacid I, **22** gives only an indication of polycondensed, unidentified products.

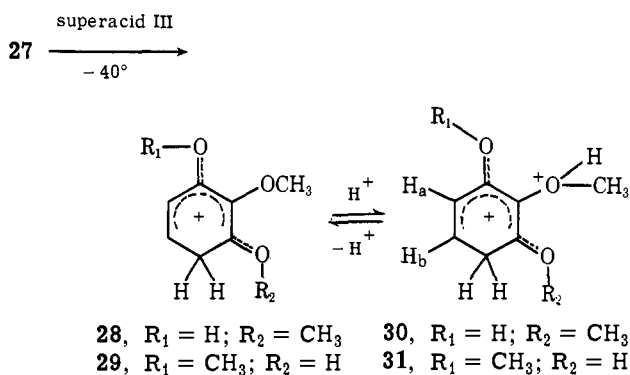
Protonation of 2,3-Dimethoxyphenol (27). C-Protonation of **27** in superacid IV gave the expected isomeric ions **28** and **29** in the ratio of 7:3. Again, the benzenium ion with a para OH (**28**) is formed preferentially



over the benzenium ion with a para OCH_3 . It is fortunate that the proton shifts of the ortho OCH_3 and para OCH_3 are distinguishable and make it possible to determine the ratio of isomeric ions **28** and **29**. In the pmr spectrum, two sharp singlet absorptions in the

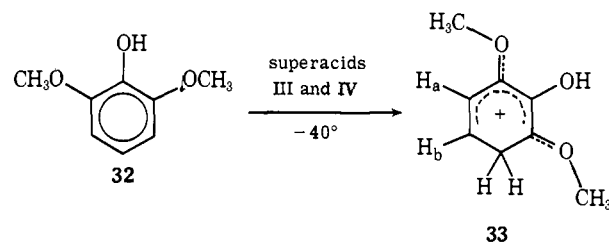
ratio of 7:3 (at δ 4.54 and 4.70, respectively) are assigned to the methoxyl protons of both ions **28** and **29**, respectively. The methylene protons of ions **28** and **29** give an overlapping slightly broadened singlet at δ 4.40. The broadening can also be accounted for by coupling to the ortho vinylic proton. The meta OCH_3 of both ions **28** and **29** again overlaps to give a singlet absorption at δ 4.23. The vinyl protons of ion **28** can be readily recognized as a doublet at δ 7.28 ($J_{\text{HH}} = 10$ Hz) for the meta proton and a doublet of triplets at 7.82 ($J_{\text{HH}} = 10$ and 2 Hz) for the ortho proton. In ion **29**, the meta proton shows a less intense doublet at δ 7.43 ($J_{\text{HH}} = 10$ Hz) and the ortho proton resonance lines overlap with the triplet of doublets of ion **28**.

In superacid III, **27** is also C-protonated. The pmr spectrum shows only slight differences from the previously discussed spectra. Particularly, the proton shifts of meta OCH_3 of ions **28** and **29** are now shifted further downfield (almost coinciding with the ortho OCH_3 of ion **28**). The result indicates a rapid equilibration of ions **30** with the diprotonated ions **31**.

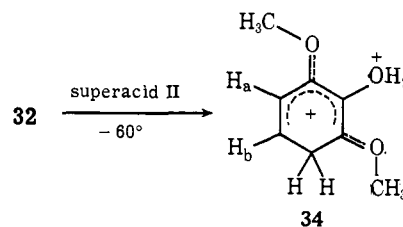


In superacids I and II, **27** was completely diprotonated to give the isomeric ions **30** (71%) and **31** (29%). The pmr spectrum shows a slightly broadened singlet absorption at δ 4.60 for the methylene protons and two distinguishable singlets at δ 4.80 and 4.98 for the ortho OCH_3 of ions **30** and **31**, respectively. In addition, the meta OCH_3 of ions **30** and **31** shows two (almost identical) absorption lines at δ 5.20 and 5.22, respectively. The chemical shifts of meta OCH_3 (in ions **30** and **31**) are significant since they are deshielded by about 1 ppm from the meta OCH_3 of the monoprotinated ions **28** and **29**. Furthermore, a rather broadened singlet absorption at δ 11.0 clearly indicates the formation of $-\text{O}(\text{H})\text{CH}_3^+$ in ions **30** and **31**.

Protonation of 2,6-Dimethoxyphenol (32). Protonation of **32** in superacids III and IV yielded the benzenium ion **33**. The pmr spectrum of ion **33** is well resolved, particularly in superacid IV. It shows two sharp singlet absorptions at δ 4.5 and 4.63 (ortho and para OCH_3 , respectively), a shielded doublet absorption at δ 4.40 (methylene, $J_{\text{HH}} = 2$ Hz), a deshielded doublet at 7.50 (meta CH, $J_{\text{HH}} = 10$ Hz), and a doublet of triplets at 7.94 (ortho CH_3 , $J_{\text{HH}} = 2$ and 10 Hz). In contrast to the study of protonation of **27**, we found no indication of diprotonation of **32** in superacid III. Obviously, further protonation at the meta OH in ion **33** will result in rapid exchange with the original OH proton in weaker acid III. However, in the stronger superacid II, **32** was diprotonated to give ion **34**. The pmr spectrum of ion

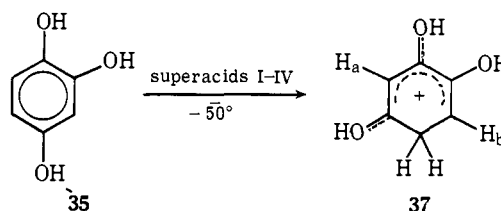


34 is similar to that of ion **33** but all proton absorption lines are further deshielded (Table II). In superacid I,



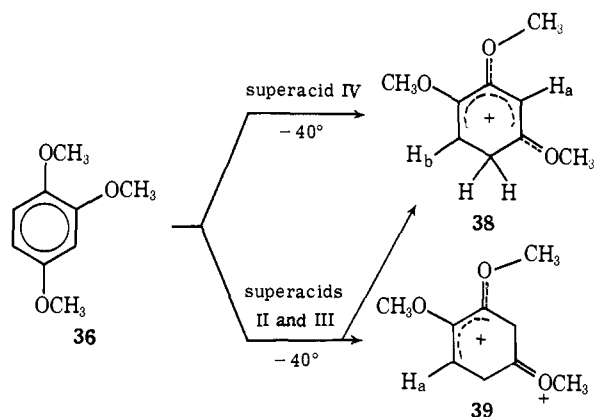
32 gives only unidentifiable polycondensed products. Similar behavior has been observed in the case of the other trihydroxybenzenes.

Protonation of Hydroxyquinol (35) and 1,2,4-Tri-methoxybenzene (36). Protonation of **35** in all four superacids gave the identical monoprotinated benzenium ion **37**. This observation is rather surprising be-



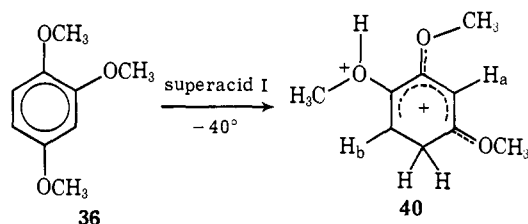
cause **35** is the only trihydroxybenzene which does not diprotonate in any of the superacid media. The pmr spectrum of **37** is rather simple. The methylene protons show a doublet at δ 4.14 ($J_{\text{HH}} = 4$ Hz), the ortho proton has a triplet at δ 6.8 ($J_{\text{HH}} = 4$ Hz) since it couples to the methylene protons, and the meta proton displays a sharp singlet at δ 6.70. The hydroxyl proton shows a very broad, variable position peak between δ 9 and 12 indicating proton exchange with the acid. The protonation of **36** in superacid IV at -40° gives the only C-protonated benzenium ion **38**. In stronger superacid systems II and III, monoprotinated ion **38** as well as diprotonated ion **39** were observed.¹¹ The pmr spectrum of ion **38** shows three sharp singlet absorptions at δ 4.20 (meta OCH_3), 4.47 (ortho OCH_3), and 4.60 (para OCH_3). The methylene protons of ion **38** show a doublet at δ 4.26 ($J_{\text{HH}} = 2$ Hz) since they are coupled to the ortho vinylic proton, which is a triplet at δ 6.83 ($J_{\text{HH}} = 2$ Hz). The meta vinylic proton is a singlet at δ 6.78. All the resonance lines of ion **39** are deshielded from those of ion **38**. There are three singlet absorptions (each of three protons) at δ 4.73, 5.17, and 5.60, assigned to the methoxyl protons. The most shielded singlet is assigned to the methoxy group attached to the center carbon atom in the allyl system,

(11) One of the referees pointed out that it is difficult to understand why **36** can be diprotonated but not **35**. The most likely explanation is that the monoprotinated ion **37** is rapidly proton exchanging with the acid solvent system, while the rate of proton exchange of ion **38** is relatively slow. This may also explain why O-protonation of anisole is more readily achieved than that of phenol.¹



since this is the least deshielded position.¹² The singlet absorption at δ 5.17 is assigned to the terminal methoxy group in the allyl system of ion 39. The most deshielded methoxy group is assigned $>C=OCH_3^+$.

Protonation of 36 in the strongest superacid I gave a pmr spectrum which does not indicate formation of either ion 38 or ion 39. However, there are three distinguishable singlet absorptions at δ 4.93, 5.08, and 5.44. These proton resonances can be assigned to the three methoxy groups. Overlapping with the three absorption peaks, there is a broadened resonance from δ 5.0 to 5.4 indicative of the methylene protons. In the vinyl region, two rather broadened singlet absorptions at δ 7.2 and 8.2 were observed. Overall, the pmr spectrum is similar to that of ion 38 except the whole spectrum is deshielded. These results suggest the formation of a diprotonated ion 40. Intercon-



version of dication 39 to dication 40 or *vice versa* was not observed in the temperature range from -80 to -20° , although both dications were presumably formed by further protonation of ion 38.

Conclusion

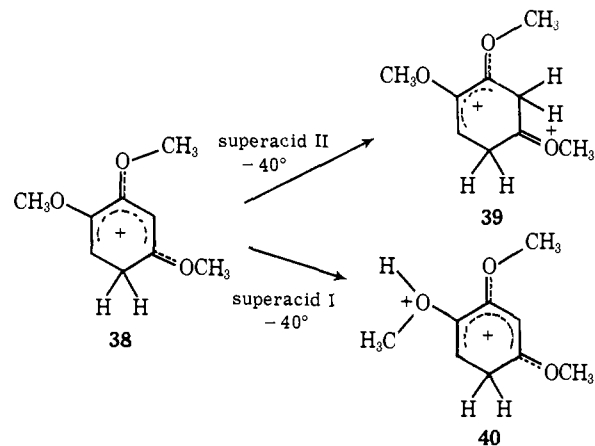
The course of protonation of trihydroxybenzenes and their methyl ethers in superacids is more complicated than those of mono- and dihydroxybenzenes.¹ In most cases, diprotonation was observed in the strongest superacid system I, particularly with trihydroxy- and trialkoxybenzenes, except hydroxyquinol 35. Two different types of diprotonation were found. They are (i) the formation of a protonated or alkylated oxocyclohexenyl dication system (*e.g.*, ion 6) and (ii) a benzenium ion with a $CH_3O(H)^+$ or OH_2^+ group at the meta position (*e.g.*, ion 10). The general feature of the first type of dication is that the allylic system has two hydroxyl or alkoxy groups attached to it. The two hydroxyl or alkoxy groups contribute to better stabilization of the dication if they are both located at the terminal carbons of the allyl system. This can be

(12) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *J. Amer. Chem. Soc.*, **94**, 3554 (1972).

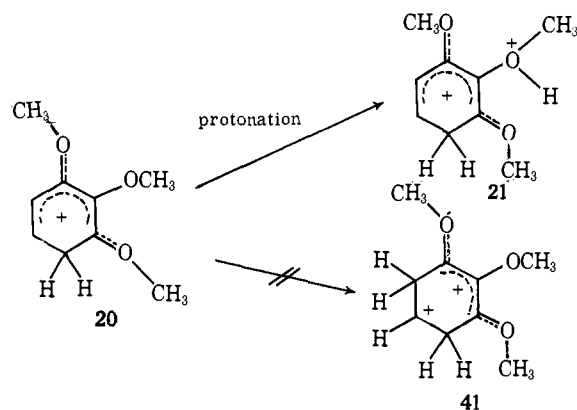
demonstrated by a comparison with the protonation of 1,3,5- and 1,2,4-trimethoxybenzenes (2 and 37, respectively). In superacid III, 2 was completely diprotonated to dication 10 while 37 was partially (30%) diprotonated to dication 39. Hydroxy and alkoxy groups can mesomerically stabilize highly charged carbon centers, as, for example, in C-protonated anisole and phenol. In allyl cation, the terminal carbon atoms carry essentially most of the charge and thus OH or OR at these positions will stabilize them better.¹²

The general characteristics of the second type of diprotonation are that the benzenium ion itself has two stabilizing groups (methoxy or hydroxy) attached at the ortho and para positions and an alkoxy or hydroxy group at the meta position, allowing a second protolytic attack at the oxygen atom lone pairs.

The site of protonation is of interest in the trihydroxybenzenes and their methyl ethers. Naturally, a proton (or any electrophile) will attack the most electron-rich site in a molecule. Due to the high degree of charge delocalization in these polyhydroxy- and polyalkoxybenzenium ions, the meta carbons are still nucleophilic enough for an additional electrophilic attack to take place to yield the dications. However, in the case when two different sites (both carbon and oxygen) were available for electrophilic attack, as in 38, two type of dications were observed in two different superacid systems. In contrast, ion 20



also has two different available sites for electrophilic attack, but only O-protonated ion 21 was observed. The C-protonated dication 41 is not formed.



Furthermore, we also found that protonation occurs at a position para to the hydroxy group more favorably

then to the alkoxy group. This observation has been discussed previously in connection with the formation of ion **12** which is preferred over ion **13** by a factor of three.

Experimental Section

Materials. All the trihydroxybenzenes and their methyl ethers were commercially available materials and were used without further purification. Antimony pentafluoride and fluorosulfuric acid were purified as previously described.¹³

Preparation of the Ions. Samples of protonated aromatic compounds were prepared by dissolving approximately 1.5 ml of each of the four superacids in an equal volume of sulfuric chloride fluo-

ride and cooling the solution to -78° . Then to this solution was added with vigorous stirring the trihydroxy(alkoxy)benzenes (approximately 0.2 ml or 0.2 g) at -78° . The resulting clear solution was transferred to an nmr tube for spectral studies.

Nmr Spectra. A Varian Associates Model A56/60A nmr spectrometer equipped with a variable-temperature probe was used to obtain pmr spectra. Proton chemical shifts are referred to external (capillary) TMS. Carbon-13 indor spectra were obtained on a Varian Associate Model HA 100 nmr spectrometer with experimental details described previously.¹⁴

Acknowledgment. Support of our work by the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

(13) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967).

(14) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

Nature of the Carbonium Ion. X. The 2-Protoadamantyl Cation¹

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Contribution from the Metcalf Research Laboratories, Brown University, Providence, Rhode Island 02912. Received September 13, 1971

Abstract: The syntheses of 2-(endo-bicyclo[3.2.1]oct-6-en-3-yl)ethyl *p*-bromobenzenesulfonate (**5b**) and its saturated analog, **7**, are described. Product studies for the acetolysis, ethanolysis, formolysis, and trifluoroethanolysis of **5b** were conducted. The acetolysis derived products were 2-adamantyl acetate (**14b**), *exo*-2-protoadamantyl acetate (**13c**), *exo*-2-isotwistyl acetate (**25c**), *exo*-10-protoadamantyl acetate (**26c**), *exo*-2-isoprotoadamantyl acetate (**24c**), and unsaturated acetate (**5c**). Only unrearranged acetate was obtained from acetolysis of **7**. Rate measurements of the acetolyses of **5b** and **7** revealed substantial π -orbital participation in ionization of the unsaturated compound. Product compositions suggested a facile hydride shift route, subsequent to ionization, leading to the major 2-adamantyl product. Also described are the syntheses of 2-endo- (**12b**) and 2-exo- (**13b**) protoadamantyl *p*-bromobenzenesulfonates. Solvolysis product studies were conducted in the manner utilized for **5b**. Acetolysis products of **12b** and **13b** were nearly identical in proportion. These products included all the tricyclic acetates detected from **5b** with the addition of 4-twistyl acetate (**23b**). Unlike the **5b** acetolyses, 2-adamantyl acetate was not the major product. A substantial *exo*:*endo* rate ratio (**13b**:**12b** = 10^3) was detected by kinetic measurements of the acetolyses. Formolyses and trifluoroacetolyses of **12b** and **13b** showed considerable variations in product proportions between the epimers. A consolidated interpretation of the cationic pathways for the π -route and σ -route 2-protoadamantyl cations is presented.

Much attention has been given to ten carbon tricyclic derivatives since the discovery by Schleyer and Donaldson of an efficient synthetic route to the adamantyl ring system,³ and the subsequent observations of the biological activities of many compounds with this ring structure.⁴ The majority of the compounds synthesized and studied have been the bridgehead substituted, 1-adamantyl derivatives despite the logic that derivatives with other tricyclic skeleta, isomeric with adamantane (and even bridge-substituted adamantanes), should be of similar interest. This has been primarily due to the nature of the synthetic tech-

niques which take advantage of the extreme stabilities of 1-adamantyl cations and radicals.

We have, by consequence, chosen to investigate alternate routes to these tricyclic derivatives which utilize the carbonium ion rearrangements leading toward adamantanes, but involve solvolytic reactions rather than the stringent Lewis acid conditions of "adamantization." It was felt that the milder conditions of solvolyses would allow isolation of the isomeric skeleta and the 2-adamantyl products. In a previous report,⁵ we described the preliminary results from a solvolytically initiated π -route ring closure which led predominantly to a 2-adamantyl product. We now wish to describe this study in more detail, along with its continuation in which the π -route behavior of the protoadamantyl ion was examined with respect to solvent effects and compared directly with a similar study of the σ -route 2-protoadamantyl ions.

(1) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstracts, ORGN 134.

(2) National Defense Education Act Fellow, 1966-1969.

(3) For a review see: R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); V. V. Sevost'yanova, M. M. Krayushlein, and A. G. Yurchenko, *Usp. Khim.*, **39**, 1721 (1970); and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971).

(4) See, for example, E. W. Davies, *et al.*, *Science*, **144**, 862 (1964); H. Wendel, *Fed. Proc., Fed. Am. Soc. Exp. Biol.*, **23**, 387 (1964); Grunert, *et al.*, *Virology*, **26**, 262 (1965).

(5) L. A. Spurlock and K. P. Clark, *J. Amer. Chem. Soc.*, **92**, 3829 (1970).