

tities of d_2 , d_3 , . . . , d_9 trimethylbutanes were found. Such extensive exchange was also obtained with isobutylene and the methylbutenes and suggests that after a D_2^- transfer occurs in solution the products are able to react several more times before separating. Thus the reactants and product participating in the radical cation exchange appear to undergo reaction while in a solvent cage.

In the trimethylbutene experiment some triptane- d_0 was also formed. This was probably formed by allylic hydride transfer from triptene to the triptyl ion. The relative intensity of the d_0 through d_9 isomers is shown in Figure 1.

Assuming that the reactions observed involve radical cations, it is likely that they are examples of eq 4 and hence an H_2 transfer. This may be inferred from the ionization potential or appearance potential of the respective radical cations. In Table IV it may be seen that saturated compounds generally are more difficult to oxidize than olefins although the difference between propylene and methylcyclopentane or methylcyclohexane is not large. This question ought to be the subject of future research.

In summary, a dual approach to the reaction of olefins in the SbF_5-HSO_3F system has shown that in addition to normal carbonium formation and reactivity much of the olefin reacts *via* an unexpected route.

TABLE IV
APPEARANCE POTENTIALS OF REPRESENTATIVE
RADICAL CATIONS

Ion	AP or IP, eV ^a
$C_3H_8^+$	9.74
$i-C_4H_9^+$	9.23
$(CH_3)_2C=CHCH_3^+$	8.8
$CH_3-c-C_6H_{11}^+$	9.9
$CH_3-c-C_6H_9^+$	9.9
$i-C_4H_{10}^+$	10.57

^a J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, NSRDS-NBS (26), June 1969.

Several possible routes exist. One involves an interfacial chain reaction in which the olefin is protonated and extracts a hydride from the donor forming a cation which then protonates another olefin, etc. An alternative involves the formation of radical cationic intermediates. In any event, the addition of olefins like propylene or isobutylene to SbF_5-HSO_3F solutions in the presence of hydride donor does not proceed to paraffin products exclusively by a normal path where one proton is transferred by the acid and the other from the hydride donor.

Registry No.—Antimony pentafluoride, 7783-70-2; fluorosulfonic acid, 7789-21-1.

Stable Carbocations. CXXXIV.¹ Protonation of Mono- and Dihydroxybenzenes and Their Methyl Ethers in Superacids

GEORGE A. OLAH* AND Y. K. MO

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received June 12, 1972

The protonation of mono- and dihydroxybenzenes and their methyl ethers was studied in four different superacid media, $HF-SbF_5$ (1:1 M:M)- SO_2ClF (I), HSO_3F-SbF_5 (1:1 M:M)- SO_2ClF (II), HSO_3F-SbF_5 (4:1 M:M)- SO_2ClF (III), and HSO_3F-SO_2ClF (IV) by low-temperature nmr spectroscopy. The sites of protonation (O- vs. C-) were dependent upon the acid media used. The structures of the formed ions were assigned based on their nmr (1H and ^{13}C) spectra. Isomeric ions derived from the same precursor were also observed. Stability of hydroxy(alkoxy)benzenium ions, including isomeric ion forms derived from the same precursors and the relative ease of protonation is discussed in terms of steric, resonance, and inductive effects. Phenylxonium ion (O-protonated phenol) formation was generally observed in HF containing small amounts of antimony pentafluoride at low temperature ($-105 \sim -80^\circ$) while C-protonated phenols were found in acids of higher strength and at higher temperature.

Hydroxy- and alkoxy-substituted benzenium ions have been studied by a number of investigators.² The site of protonation seemed to depend on the acid-solvent system and temperature. However, no systematic study of protonation of hydroxy(alkoxy)benzenes in different acid systems was so far attempted. Furthermore, the sites of protonation are not yet well understood. The effect of substituents on benzenium ions were also not yet extensively studied. Isomeric ions derived from the same precursor are known (*e.g.*, C- and O-protonated anisole),^{2b} but the factors (electronic and steric, as well as those of media) that control the

relative amounts of isomeric ions formed were not known.

We now report a systematic study of these questions by pmr spectroscopy of ions obtained from mono- and dihydroxybenzenes and their methyl ethers. Four superacid systems were used: I, $HF-SbF_5$ (1:1 M:M)- SO_2ClF ; II, HSO_3F-SbF_5 (1:1 M:M)- SO_2ClF ; III, HSO_3F-SbF_5 (4:1 M:M)- SO_2ClF ; and IV, HSO_3F-SO_2ClF . In addition, protonation of phenol was carried out in weaker acids, like HF containing traces of SbF_5 , in order to study both substituent and solvent effects. The nature of the extensive charge delocalization in the *p*-hydroxy- and methoxybenzenium ions was also studied by carbon-13 nmr spectroscopy.

Results and Discussion

The hydroxybenzene derivatives were protonated in the four different superacid systems (I-IV). Ions

(1) Part CXXXIII: G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *J. Amer. Chem. Soc.*, **94**, 4729 (1972).

(2) (a) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964); (b) D. H. Brouwer, E. L. Mackor, and C. MacLean, *Recl. Trav. Chim. Pays-Bas*, **85**, 109, 114 (1966); (c) R. W. Alder and F. J. Tayler, *J. Chem. Soc. B*, 845 (1970); (d) M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *ibid.*, 1624 (1971).

TABLE I
 ION FORMATION UPON PROTONATION OF MONO- AND DIHYDROXYBENZENES AND THEIR SUBSTITUTED DERIVATIVES^a

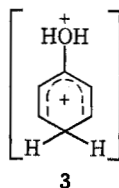
Aromatic precursor	Ions formed in superacid systems			
	I	II	III	IV
1	2	2	2	2
5	6	6	6	6
9a	10a	10a	10a, 9a ⇌ 11	9a ⇌ 11
9b	10b (syn) ⇌ 10b (anti)	10b (syn) ⇌ 10b (anti) (35%) (35%) 9b ⇌ 12 (30%)	10b (syn) ⇌ 10b (anti) (12.5%) (12.5%) 9b ⇌ 12 (75%)	9b ⇌ 12
13	14a	14a	14a	14a
15	16a	16a	16a	16a
17	18a (80%) ⇌ 18b (20%)	18a (80%) ⇌ 18b (20%)	18a (8%) ⇌ 18b (20%)	18a (80%) ⇌ 18b (20%)
19	20	20	20	20 (75%), 19 ⇌ 20a (25%)
21	22	22	22	22
23	24 (40%) 26 (60%)	24 (87%) 25 (13%)	24 (80%) 25 (20%)	24 (65%) 25 (35%)
27	28	28	28	28
29	31	30	30	29 ⇌ 30
33	Polymerization	34	34	34
35	36 (98%) 37 (2%)	36 (98%) 37 (2%)	36 (98%) 37 (2%)	36 (98%) 37 (2%)
38	39 40	39	39	39
41	Polymerization	42	42	42 ⇌ 45
46	Polymerization	47	47	47
48	Polymerization	48 ⇌ 50	48 ⇌ 50	48 ⇌ 50
52	55	53	53	53, 52 ⇌ 54
56	57a	57	57	57
58	60	58 ⇌ 59 ⇌ 60	58 ⇌ 59 ⇌ 60	58 ⇌ 59 ⇌ 60

^a For actual experimental conditions (*e.g.*, temperature), see text.

formed are summarized in Table I. The pmr data of the hydroxy- and methoxybenzenium ions as well as the related oxonium ions obtained under varied conditions are tabulated in Tables II and III, respectively.

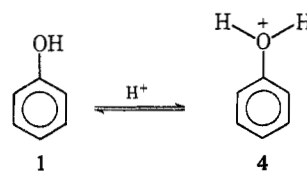
Phenol and Anisole. C-Protonation vs. O-Protonation. A. Phenol (1).—The chemical behavior of phenol in strong acid systems, like fluorosulfuric acid^{2a} and HF-BF₃-sulfolane,^{2c} has been studied by Gillespie and Adler, respectively. Our interests in the protonation of phenol are to investigate the behavior of phenol in various superacid media and hopefully to find the conditions for O-protonation as well as C-protonation. Furthermore, the extensive charge delocalization of ion 2 was studied by carbon-13 nmr spectroscopy (INDOR method).

In all superacid systems I-IV, 1 was completely C-protonated to give ion 2. The nmr spectra (Figure 1, bottom trace) of these solutions were identical except that the hydroxylic proton was not observable in superacid system IV. The hydroxylic proton absorption of 2 in superacids I-III is temperature dependent. At -30°, it becomes a broadened line at δ 11.3 indicating rapid proton exchange with the superacid. The exchange reaction may involve diprotonation on the oxygen atom and thus involvement of dipositive transition state 3.



When 1 was dissolved in liquid HF containing 5% of SbF₅, the pmr spectrum (Figure 1) of the solution at

-40° showed a multiplet centered at δ 6.8 and the acid peak at δ 8.8. When the solution was cooled to -90°, the multiplet became a broadened absorption line remaining at δ 6.8 but a new, very broad absorption appeared at δ 9.4. Upon further cooling down to -105°, the new very broad absorption line sharpened and remained at δ 9.4 (Figure 1). The intense acid peak forms a shoulder at ~δ 9.0. These results indicate the formation of O-protonated phenol, 4. As expected, the aromatic protons of 4 show a multiplet

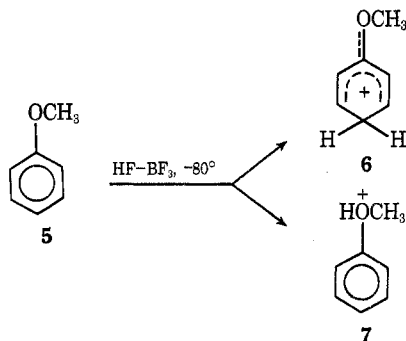


and the -OH₂⁺ shift is similar to those of -OH₂⁺ of protonated aliphatic alcohols, ⁺ROH₂.³ In relatively weak acids it is always difficult to observe nonexchanging protonated heteroorganic compounds. In order to slow down the rate of proton exchange, O-protonated phenol must be observed at very low temperature.

The multiplet of the aromatic protons of ion 4 is shielded from the ring protons of ion 2, indicating that O-protonation of phenol leads to a charge-localized ion. On the other hand, C-protonation of phenol involves π electrons and leads to a charge-delocalized benzenium ion 2 (see subsequent discussion of carbon-13 nmr studies of ions 2 and 6).

(3) (a) G. A. Olah and E. Namanworth, *J. Amer. Chem. Soc.*, **88**, 5327 (1966); (b) G. A. Olah, J. Sommer, and E. Namanworth, *ibid.*, **89**, 3576 (1967).

B. Anisole (5) has been protonated in various acid media by Gillespie,^{2a,4} Brouwer,^{2b} Olah,⁵ and their coworkers. In fluorosulfuric acid with or without antimony pentafluoride, *p*-methoxybenzenium ion (6) is generated. In HF-BF₃ solution at -60°, 5 was both C- and O-protonated to ions 6 and 7.^{2b} As the



temperature was raised to -10°, only ion 6 was observed. In the four superacid systems I-IV, 5 was found to be C-protonated to give ion 6. The pmr spectrum of ion 6 was temperature dependent because of the inhibition of rotation about the partial C=O double bond.

C. Carbon-13 Nmr Studies of Ions 2 and 6.—In order to study the trend of charge distribution of ions 2 and 6, we undertook a carbon-13 nmr study, which is an excellent tool for the investigation of carbocations. The carbon-13 data provide important new information about the nature of ions 2 and 6. Table IV summarizes the carbon-13 nmr data of protonated and parent phenol and anisole and, for comparison, we also list the carbon-13 shifts of protonated toluene.⁶

The sp³ methylene carbon has almost identical carbon shifts in both ion 2 and 6. These data further prove that protonation is indeed occurring at the aromatic ring. The sp³ carbon of *p*-toluenium ion 8 has a carbon shift deshielded by 6 ppm from those of ions 2 and 6, indicating partial charge delocalization to the oxygen atoms. The sp² carbon shifts of all the three ions 2, 6, and 8 clearly show that the deshielding effects follow the order para < ortho < meta. In other words, charge is mainly delocalized into the ortho,para carbons and the oxygen atom. These results are consistent with theoretical calculation.⁷

Owing to the anisotropy effect of the oxygen atom in ion 6, carbons 5 and 6 are more deshielded than carbons 3 and 2, respectively. Long-range proton-proton coupling between *p*-CH₃ and CH₂ protons in *p*-toluenium ion⁷ and proton-fluorine coupling between CH₂ and *p*-F in *p*-fluorobenzenium ion⁸ are known. In ion 6, we also observe long-range proton-carbon coupling ($T_{\text{CH}} = 143.8$ Hz) between CH₃O carbon and CH₂ protons through six bonds. The proton-carbon coupling was evidenced from the CH₂ proton main peak enhanced INDOE spectrum. The INDOE spectrum showed a quartet at δ 129.3 ppm (from CS₂) when the CH₂ protons were doubly irradiated.

(4) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964).

(5) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *J. Amer. Chem. Soc.*, **89**, 5259 (1967).

(6) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelley, and G. D. Mateescu, *ibid.*, **94**, 2034 (1972).

(7) D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," G. A. Olah and P. V. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 865.

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

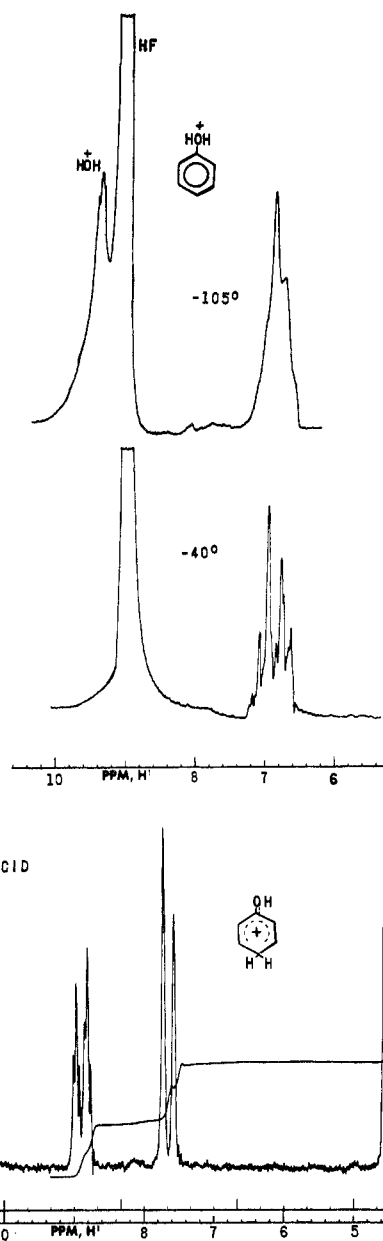
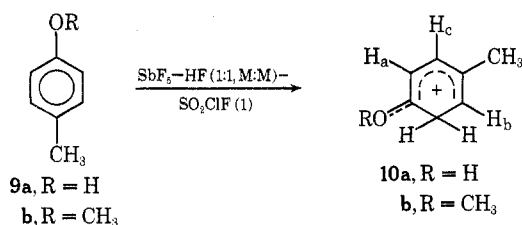


Figure 1.—Pmr spectra (60 MHz) of C-protonated phenol 2 (bottom trace) and O-protonated phenol at -40° and -105° (middle and upper traces).

Finally, it should be mentioned that the carbon-13 shifts of ions 2 and 6 show a close relationship to those of protonated α,β -unsaturated carbonyl compounds.⁹

Protonation of Isomeric Cresols and Their Methyl Ethers. A. *p*-Cresol and *p*-Methylanisole.—Protonation of *p*-methylanisole (9b) in HF-BF₃ at -85° has been reported by Brouwer and coworkers.^{2b} They found that the site of protonation was at the ethereal oxygen atom and not at the aromatic ring. In super-



(9) G. A. Olah, Y. Halpern, Y. K. Mo, and G. Liang, *ibid.*, **94**, 3554 (1972).

TABLE II
¹H MAGNETIC RESONANCE DATA OF MONO- AND DIHYDROXY(METHOXY)BENZENIUM IONS^a


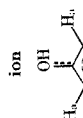

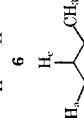

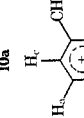

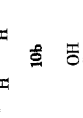

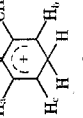

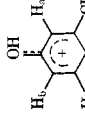

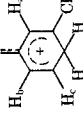

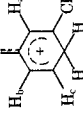
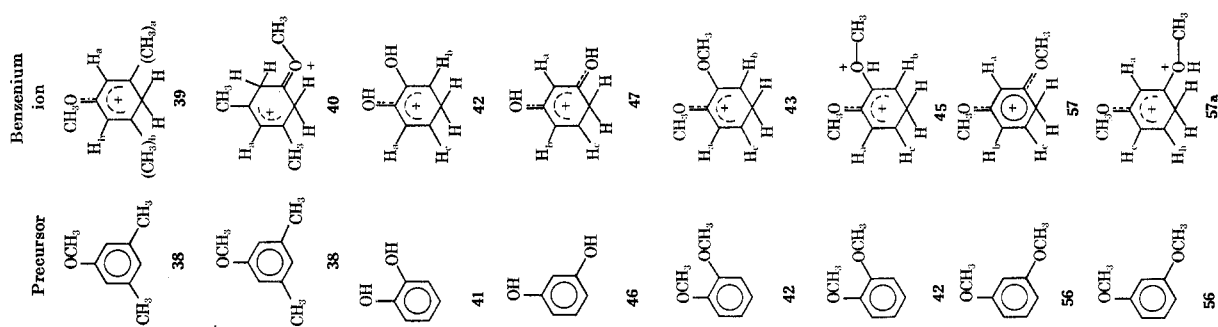
Precursor	Benzenium ion	Superaacid system, temp in °C	CH ₃	OCH ₃	CH ₂	H _a	H _b	H _c	OH
		II, -15			4.50 (t) <i>J</i> _{HH} = 2.5 Hz	7.68 (d) <i>J</i> _{HH} = 10 Hz	8.91 (d t) <i>J</i> _{HH} = 10 and 2.5 Hz		11.3 (br)
		II, -50		4.80 (s)	4.50 (br s)	7.5 (br d) <i>J</i> _{HH} = 10 Hz 7.8 (br d) <i>J</i> _{HH} = 10 Hz	8.6 (br d) <i>J</i> _{HH} = 10 Hz 9.0 (br d) <i>J</i> _{HH} = 10 Hz		
		I, -60	2.60 (s)		4.6 (br s)	7.40 (d) <i>J</i> _{HH} = 10 Hz	7.6 (br s)	8.86 (d) <i>J</i> _{HH} = 10 Hz	c
		I, -48	2.68 (s)	4.79 (s)	4.6 (br s)	7.57 (d) <i>J</i> _{HH} = 10 Hz	7.7 (br s)	8.88 (d) <i>J</i> _{HH} = 10 Hz	
		IV, -16	2.51 (s)		4.4 (m)	-7.54 (d) <i>J</i> _{HH} = 9 Hz	8.55 (q) <i>J</i> _{HH} = 1.8 Hz	8.73 (d q) <i>J</i> _{HH} = 2.5 and 9 Hz	-12.2 (br)
		IV, -16	2.40 (s)	4.68 (s)	4.3 (br s)	7.67 (d) <i>J</i> _{HH} = 10 Hz	8.3 (br s)	8.77 (d q) <i>J</i> _{HH} = 10 and 1.5 Hz	
		I, -60	2.97 (s)		4.5 (br s)	7.50 (s)	7.57 (d) <i>J</i> _{HH} = 10 Hz	8.74 (d) <i>J</i> _{HH} = 10 Hz	c
		I, -16	2.83 (s)	4.69 (s)	4.3 (br s)	7.50 (s)	7.42 (d) <i>J</i> _{HH} = 10 Hz	8.5 (br d) <i>J</i> _{HH} = 10 Hz	


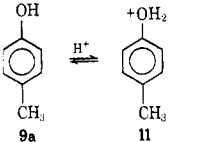
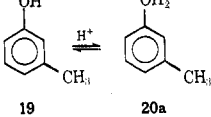
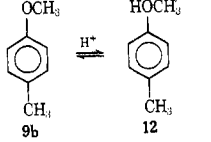
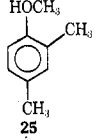
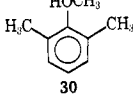
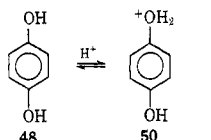
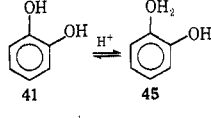
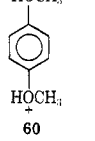
TABLE II (Continued)

Superaacid system, temp in °C	CH ₃	OCH ₃	CH ₂	H _a	H _b	H _c	OH
III, -60	2.70 (s) (a) 2.83 (s) (b)	4.64 (s)	4.23 (s)	7.23 (s)	7.50 (s)		
I, -40	3.62 (s)	5.60 (s)	5.5 (br s)	8.66 (s)			
II, -40		4.6 (br s)		7.74 (d) $J_{HH} = 9$ Hz	8.03 (t) $J_{HH} = 2$ Hz	8.90 (d t) $J_{HH} = 9$ and 2 Hz	c
II, -40		4.73 (d) $J_{HH} = 3.5$ Hz		6.82 (s)	7.31 (d) $J_{HH} = 10$ Hz	8.10 (d t) $J_{HH} = 10$ and 3.5 Hz	e
III, -40		4.70 (s, meta) 4.93 (s, para)	4.8 (s, br)	7.90 (d) $J_{HH} = 10$ Hz	7.96 (s)	9.16 (d) $J_{HH} = 10$ Hz	
I, -60		3.34 (s, para) 5.6 (br s, meta)	5.3 (br s)	-8.32 (d) $J_{HH} = 10$ Hz	9.2 (br s)	9.6 (br d) $J_{HH} = 10$ Hz	c
II, -40		4.52 (s, ortho) 4.63 (s, para)	4.24 (d) $J_{HH} = 3$ Hz	6.8 (d) $J_{HH} = 0.5$ Hz	7.20 (d d) $J_{HH} = 10$ and 0.5 Hz	7.84 (d t) $J_{HH} = 10$ and 3 Hz	
I, -60		5.5 (br s, para) 5.6 (br s, ortho)	5.2 (br s)	8.2 (d) $J_{HH} = 10$ Hz	8.3 (br s)	9.2 (br d) $J_{HH} = 10$ Hz	c



^a Proton chemical shifts are referred to external capillary TMS in parts per million. ^b Rapid interconversion of two isomeric ions. ^c OH proton is not observable owing to rapid exchange.

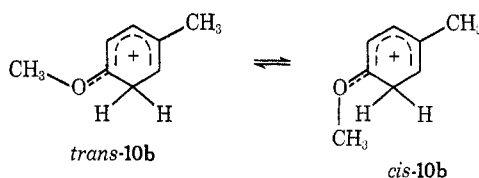
TABLE III
¹H MAGNETIC RESONANCE DATA OF ARYLOXONIUM IONS

Oxonium ion	Superacid system, temp in °C	Chemical shifts ^a				Remarks
		CH ₃	OCH ₃	Ring	OH	
 4	See text			6.8 (m)	9.4 (br)	
 9a ⇌ 11	IV, -40 III, -60	2.43 (s) 2.52 (s)		7.33 (s) 7.50 (s)	b b	100% 35% with 65% C-protonation
 19 ⇌ 20a	IV, -80	2.43 (s)		7.09 (s)	b	25% with 75% C-protonation
 9b ⇌ 12	II, -40 III, -40 IV, -90	2.66 (s) 2.50 (s) 2.48 (s)	5.04 (s) 4.98 (s) 4.67 (s)	7.68 (s) 7.65 (s) 7.50 (s)	b b b	30% with 70% C-protonation 75% with 25% C-protonation 100%
 25	III, -60	2.63 (s)	5.01 (d) <i>J</i> _{HH} = 2.5 Hz	7.62 (s)	11.8 (br) ^c	
 30	II, -60	2.70 (s)	5.07 (d) <i>J</i> _{HH} = 2 Hz	7.4 (s)	11.6 (br) ^c	
 48 ⇌ 50	III, -40 IV, -40			7.93 (s) 7.50 (s)	b b	
 41 ⇌ 45	IV, -40			7.44 (s)	b	
 60	I, -40		5.48 (d) <i>J</i> _{HH} = 3 Hz	8.24 (s)	11.92 (q) <i>J</i> _{HH} = 3 Hz	

^a Chemical shifts are referred to external TMS: s = singlet; b = broad; d = doublet. ^b The OH peak is not observable since it exchanges with acid systems. ^c The broad peak should be a quartet.







acid I both **9a** and **9b** were C-protonated to give the stable benzenium ions, **10a** and **10b**, at -48 and -60°, respectively. The structure of ion **10a** is based on its pmr spectrum (Table II). The hydroxylic proton cannot be observed in the spectrum, presumably because it exchanges rapidly with the superacid.

The pmr spectrum of ion **10b** is similar to that of **10a**, except for an additional three-proton singlet is found at δ 4.79 (see Table II). The two isomeric ions (*cis*-**10b** and *trans*-**10b**) were not observed in superacid I, presumably because interconversion of



the *cis*-*trans* isomers is rapid. We were so far unable to freeze out the relatively low energy process in this particular medium even at -80°. However, the *cis*-*trans* isomers of **10b** can be observed in superacid media II-IV.

TABLE IV
COMPARISON OF CARBON-13 NMR SHIFTS OF PROTONATED AND PARENT PHENOL, ANISOLE, AND TOLUENE^a

	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	Ref
	+37.4	+76.8	+62.4	+71.7				5b
	+12.1 (-25.3)	+66.9 (-9.9)	+17.3 (-45.1)	+151.6 (+80.5)				This work
	+32.7	+79.0	+63.0	+72.0	+63.0	+79.0	+138.4	5b
	+0.8 (-31.9)	+71.4 (-7.6)	+25.0 (-38.0)	+151.8 (+79.8)	+18.2 (-44.8)	+65.2 (-13.8)	+129.3 (-91.0)	This work
	+56.5	+65.3	+68.4	+171.8				2
	-7.3 (-49.2)	+55.2 (-10.1)	+13.4 (-41.9)	+145.1 (+76.7)				6a

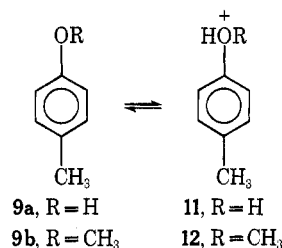
^a Carbon-13 shifts are referred to CS₂.

In superacid II at -10° , **9a** was found to be completely C-protonated, giving ion **10a**. In the same superacid (II) **9b** showed a more complicated pmr spectrum, indicating that two or three isomeric ions were formed. The pmr spectrum of this mixture is temperature dependent. At -80° , the two isomeric ions (*cis*-**10b** and *trans*-**10b**) are present in about equal portions (35% each) with 30% of O-protonated *p*-methylanisole (**11**) (based on comparison with pmr spectra of individual ions). As the temperature was raised to -40° , the intensities of the pmr resonances corresponding to ions *cis*-**10b** and *trans*-**10b** became identical with those observed when **9b** was protonated in superacid system I. The remaining portions of the spectrum are consistent with formation of ion **11**, since they are identical with the spectrum observed when **9b** was completely O-protonated in superacid IV. Thus, the complicated pmr spectrum of this reaction mixture (**9b** in superacid system II) indicates the equilibria $\mathbf{11} \rightleftharpoons \mathbf{9b} \rightleftharpoons \textit{cis}\text{-}\mathbf{10b} \rightleftharpoons \textit{trans}\text{-}\mathbf{10b}$.

It is of interest to note that **9a** is completely C-protonated in superacid II while **9b** is partially C-protonated under identical conditions. The only difference between ions **10a** and **10b** is the nature of the stabilizing groups, OH and OCH₃, respectively. That a hydroxy group is a better substituent in stabilizing arenium ions than an alkoxy group, as has been observed in other systems.¹⁰

In superacid III, **9a** is 25% C-protonated to give **10a** and 75% O-protonated to give ion **11**. The pmr spectrum of the solution also shows two additional singlets at δ 2.52 and 7.50, besides the resonance absorption of ions **10a**. These two singlets were also observed when **9a** was completely O-protonated in superacid IV, except that the proton shifts are slightly changed owing to different media (see Table III). Similarly, **9b** is also 35% C-protonated to give

10b and 65% O-protonated to ion **12** in superacid III. The ratio of C-protonation to O-protonation decreased with the decreasing molar ratio of HSO₃F/SbF₅, *i.e.*, the acidity of the medium.

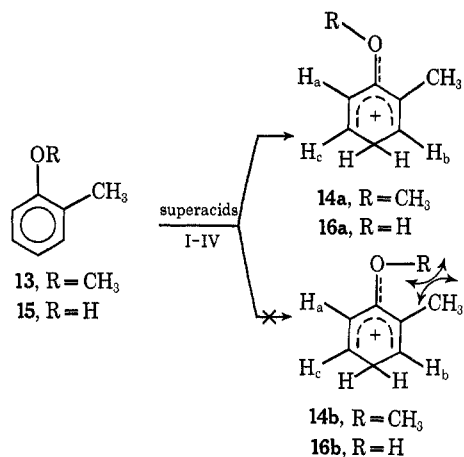


The hydroxylic protons were not observable in both cases. However, the pmr spectrum of ion **12** was consistent with that reported by Brouwer^{2b} except for the methoxy protons. The methoxy protons show a singlet at δ 4.67 instead of a doublet, indicating that rapid equilibration (*i.e.*, protonation-deprotonation) occurs. Table III also shows the influence of medium toward the proton shifts of both ions **11** and **12**. In stronger acid systems, more deshielding is observed and the individual aryloxocarbenium ions also have longer lifetimes.

B. *o*-Cresol and *o*-Methylanisole.—*o*-Methylanisole (**13**) is C-protonated in all the four superacid systems at low temperature to give the transoid benzenium ion (**14a**). The cisoid ion (**14b**) was not observed in the temperature range -80 to -28° , owing probably to the fact that ion **14b** is sterically less favorable than ion **14a**.

The methoxy protons show a sharp singlet at δ 4.68, indicating that only the more stable transoid ion **14a** is formed and no cisoid ion **14b** is present. The meta proton, H_a of ion **14a**, is a doublet at δ 7.67 ($J_{\text{HH}} = 10$ Hz) and is coupled to the ortho proton, H_c, which shows a doublet of quartets at δ 7.77 ($J_{\text{HH}} = 10$ and 1.5 Hz). The doublet of quartets of the

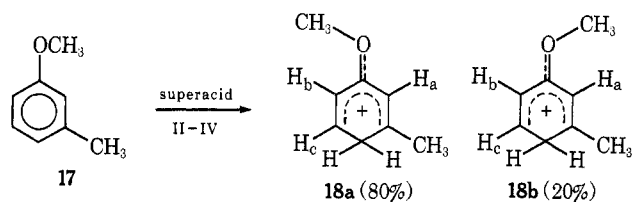
(10) (a) A. J. Kresge, Y. Chiang, and L. E. Hakka, *J. Amer. Chem. Soc.*, **93**, 6167 (1971); (b) G. A. Olah and Y. K. Mo, *ibid.*, **94**, 5341 (1972).



H_c proton arises from coupling between H_c and the CH₂ protons and also the long-range coupling to the H_b proton. Owing to the almost identical magnitude of coupling constant between H_c and CH₂, and H_c and H_b, a quartet is observed. Furthermore, the large coupling is due to coupling between H_a and H_c. All these couplings have been proven by double irradiation experiments.

Similarly, *o*-cresol (**15**) is also C-protonated in the four superacid systems at low temperature. In all cases, the site of protonation is on the ring carbon para to the hydroxy group and thus all give the same transoid benzenium ion (**16a**). The cisoid ion (**16b**) was again not observed and variable-temperature pmr studies indicated no interconversion of **16a** and **16b** between -80 and -20° . Rapid proton exchange between the hydroxylic proton and solvent system can be ruled out because of the observed pmr singlet for the OH proton absorption at δ 12.2. Thus, as in the previously discussed case, ion **16a** is sterically more favored than ion **16b**. The pmr spectrum of ion **16a** is similar to that of ion **14a**, except that a deshielded singlet at δ 12.2 (OH) is present instead of the methoxy absorption (Figure 2). The long-range coupling between the H_b and H_c protons is again observed.

C. *m*-Cresol and *m*-Methylanisole.—Protonation of *m*-methylanisole (**17**) in superacids II, III, and IV at -80° all give the isomeric benzenium ions **18a** and **18b**



in a ratio of 4:1. The clearest evidence for the formation of two isomeric ions **18a** and **18b** arises from the temperature-dependent pmr studies. The solution at -64° shows in its pmr spectrum two sharp singlets for the methyl protons in a ratio of 4:1, at δ 2.90 and 2.78. In addition, two sets of slightly broadened doublets (both have $J_{\text{HH}} = 10$ Hz) for the ortho proton are observed at δ 8.4 and 8.7 (also in a ratio of 4:1). When the temperature of the solution was raised to -16° , the two methyl singlets became a sharp singlet at δ 2.83 and the two sets of doublets (ortho proton) showed a doublet at δ 8.5 ($J_{\text{HH}} = 10$ Hz). These results indicate that interconversion of ions **18a** and **18b**

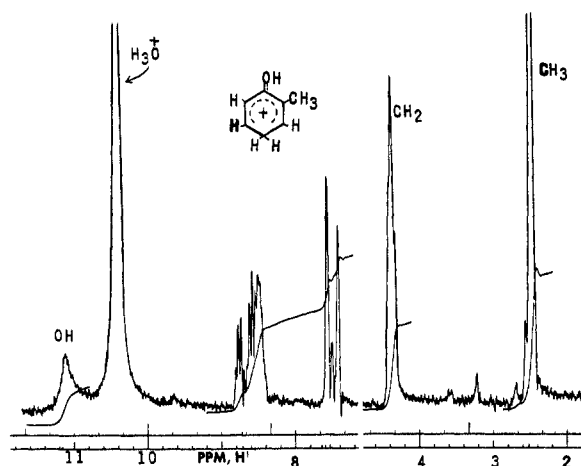
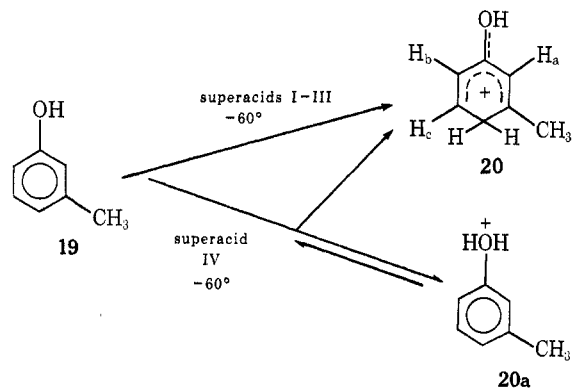


Figure 2.—Pmr spectrum of C-protonated *o*-cresol (3-methyl-4-hydroxybenzenium ion).

occurs at higher temperature. It should be noted that the methoxy protons and the two meta protons (H_a and H_b) have coincidental chemical shifts in ions **18a** and **18b**.

Protonation of **17** in superacid I gave the rapidly equilibrating ions **18a** \rightleftharpoons **18b** even at -80° . The pmr spectra of equilibrating ions **18a** \rightleftharpoons **18b** are almost identical in all four superacid systems at -10° .

m-Cresol (**19**) is completely C-protonated in the superacids I, II, and III, giving ion **20**. Since the

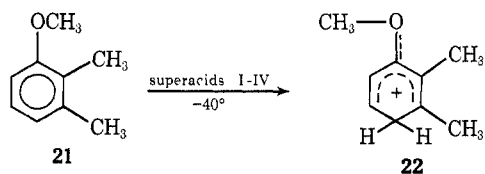


hydroxyl proton is not observable, isomeric ions cannot be observed even at -90° , indicating that rapid proton exchange occurs between ion **20** and the superacid system.

In superacid system IV, both C- and O-protonation of **19** was found. The pmr spectrum shows a singlet at δ 7.10 for the aromatic protons and the CH₃ singlet at δ 2.43 in addition to the pmr resonance lines of ion **20**.

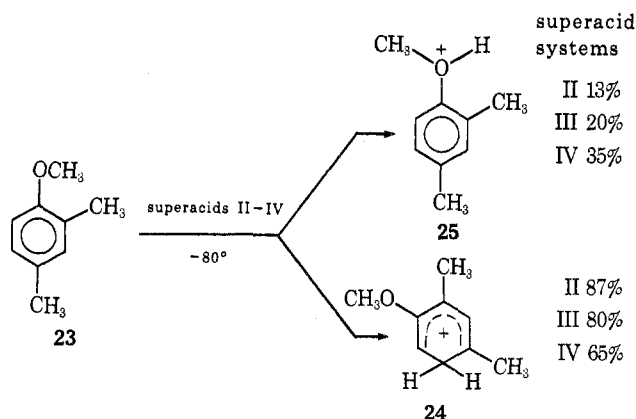
Protonation of Isomeric Dimethylanisoles.—Four isomeric dimethylanisoles (2,3-, 2,4-, 2,5-, and 2,6-) were protonated in all the four superacids.

A.—2,3-Dimethylanisole (**21**) is monoprotated in all the four superacid systems to give the benzenium ion **22**. Owing to the steric effect of the *o*-CH₃ group, only



a single isomeric ion was observed. It is suggested that the methoxy group is preferentially trans to the methyl group.

B.—Two different monoprotonated ions (C-protonated ion 24 and O-protonated ion 25) are formed in various ratios when 2,4-dimethylanisole (23) was



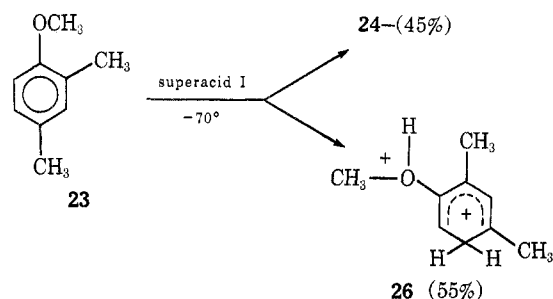
treated in the superacids II, III, and IV. The ratio of 24:25 increases as the acidity is increased (*i.e.*, the ratio of $\text{SbF}_5\text{-HSO}_3\text{F}$ is increased). The relative amount of each ion was determined by the peak areas of a specific resonances in the pmr spectra.

The site of protonation in 23 is of interest. Usually, a methoxy group is the most powerful orienting substituent. As the para position (with respect to OCH_3) of 23 is blocked, the proton attacks the C_5 carbon to give ion 24. Inductively, ion 24 is stabilized by the two methyl groups (ortho and para) and the methoxy group is freely rotating (no partial double bond character) and has almost no influence on the stabilization of ion 24. The ratio of 24:25 was found temperature independent, ranging from -80 to -30° in superacids II and III. It decreases, however, with increasing temperature in superacid IV. For example, the ratio is 3.5:6.5 at -80° and is decreased to 1.3:8.7 at -20° .

The pmr spectrum of ion 24 (mixed with ion 25) shows a slightly broadened methylene singlet absorption at δ 4.43. The two methyl groups, coincide at δ 2.50 (sharp singlet), and the methoxy group show a singlet at δ 4.70. The ortho-vinyl proton shows a slightly broadened singlet absorption at δ 8.5, since it couples to the methylene protons. The meta-vinyl proton also is a singlet at δ 7.5.

The pmr spectrum of ion 25 shows the methoxy doublet at δ 5.01 ($J_{\text{HH}} = 2.5$ Hz) indicative of O-protonation. The hydroxylic proton is a rather broad quartet at δ 11.8 in the characteristic region of O-protonated ethers.¹¹ The two methyl groups show a coincidental singlet at δ 2.63 and the three aromatic protons as a singlet at δ 7.62.

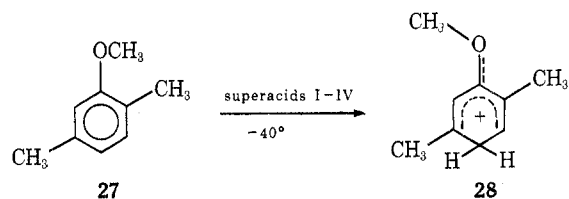
In superacid I, 23 is both monoprotonated and diprotonated to give ions 24 and 26, respectively. The evidence for the formation of dication 26 comes from the pmr spectrum of the reaction mixture. In the pmr spectrum, nothing corresponding to O-protonated ion 25 was observable. However, there are five absorption lines identical with those of ion 24 in every respect. The remaining five absorption lines show similar features to those of ion 24 but deshielded by



about 0.8 ppm. This indicates that a diprotonated species with a structure resembling ion 24 is formed. Ion 26 seems best to fit spectral data (Table II). The unusual behavior of superacid system I toward 23 is rather surprising. However, as previously mentioned, the methoxy group in ion 24 has almost no conjugative effect and additional protonation in superacid I could take place on the oxygen lone pair to yield ion 26.

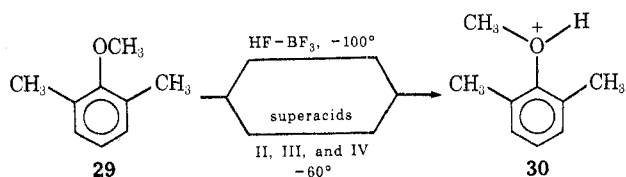
The pmr spectra of the mixture of ions 24 and 26 is slightly temperature dependent. The ratio of 26:24 decreased from 5:4 at -70° to 4:5 at -10° and the change was found to be reversible. Ion 26 is the first directly observed diprotonated long-lived benzenium type ion derived from a monoalkoxybenzene (diprotonation also was observed in the case of 2,6-dimethylanisole, *vide infra*).

C.—Protonation of 2,5-dimethylanisole (27) in all four superacids gave the identical benzenium ion 28. The pmr spectrum of ion 28 is well resolved and can be



readily assigned. The meta- and ortho-methyl proton absorptions show two singlets at δ 2.42 and 2.85, respectively. Owing to the steric effect of the ortho CH_3 group, we only observed the isomeric trans ion. Thus, a sharp singlet at δ 4.73 was assigned to the methoxy protons. The methylene protons show a slightly broadened singlet at δ 4.2, since they are coupled to the ortho-vinyl proton. The ortho proton appears as a triplet at δ 8.22 ($J = 1.5$ Hz).

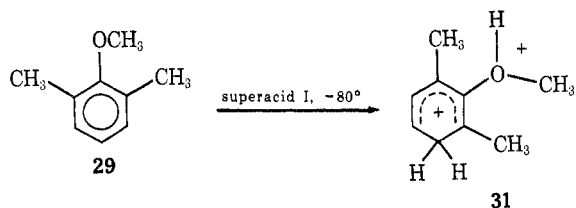
D.—Protonation of 2,6-dimethylanisole (29) in HF-BF_3 at -100° has been studied by Brouwer, Mackor, and MacLean.^{2b} They found that only the O-protonated oxonium ion 30 was obtained under their



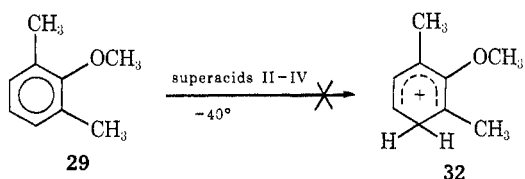
experimental conditions. We extended this study to the behavior of 29 in the four superacids. Indeed, 29 was O-protonated in superacids II, III, and IV at -60° . The best medium is superacid III, in which a well-resolved pmr spectrum is observed (Figure 3, upper trace). In superacid IV, no hydroxylic proton

was observed, indicating rapid equilibration with the solvent acid. The pmr spectrum of ion **30** is similar (with slight differences) to the reported data (Table II).

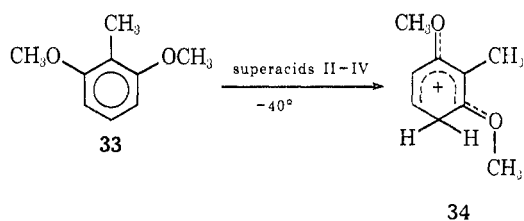
It is, however, interesting to observe the different behavior of **29** in superacid I. The pmr spectrum (Figure 3, lower trace) shows no indication of ion **30**. The aromatic protons are split into two equal intensity broadened peaks at δ 8.5 and 9.6. In the $-\text{OH}_2^+$ region, a relatively broadened absorption is observed at δ 13.8. There are three slightly broadened singlets at δ 3.5 (6 H, CH_3), 5.4 (3 H, OCH_3), and 5.8 (2 H, CH_2). Based on these data, we conclude that **29** is diprotonated in superacid I to give ion **31**. In comparison,



ion **31** is sterically less favored than ion **26**, even though they both formed in the same superacid medium. However, it is rather surprising that in superacids II-IV **29** does not undergo C-protonation to give the monoprotonated benzenium ion **32**, and only O-pro-



tonation is observed to give ion **30**. In contrast, 2,6-dimethoxytoluene (**33**) is C-protonated in superacids II-IV to give 2,4-dimethoxy-3-methylbenzenium ion (**34**). The structure of ion **34** was confirmed by its



pmr spectrum (see Table II). In superacid I, **33** was polymerized to unidentified products.

E.—Protonation of 3,4-Dimethylanisole (**35**) in HSO_3F solution has been studied by Vaughan and co-workers.^{2d} They found two different C-protonated ions, **36** (98%) and **37** (2%). Similar results were

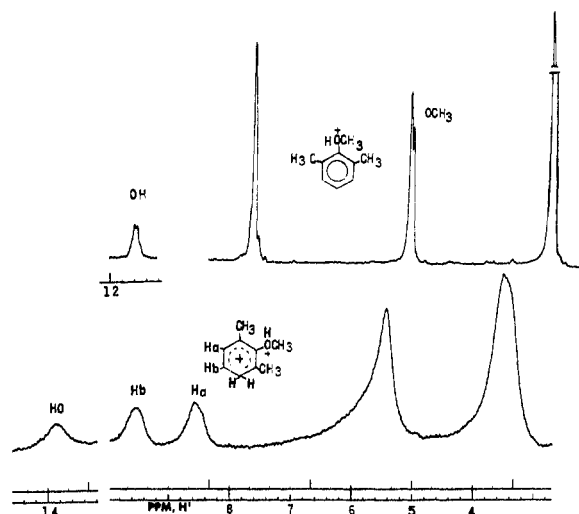
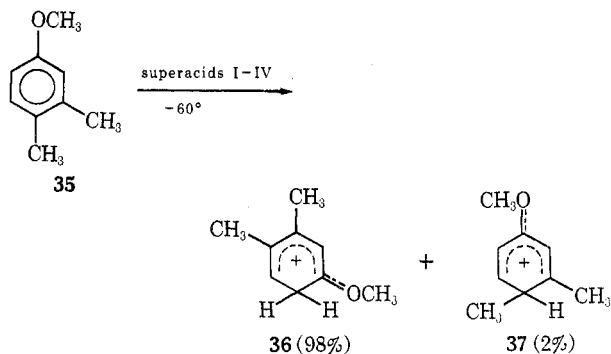
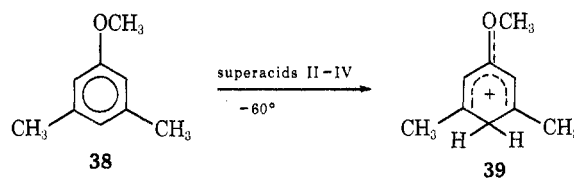


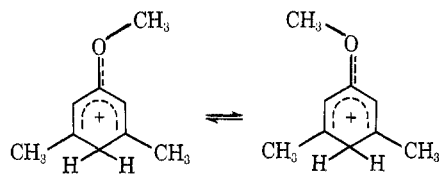
Figure 3.—Pmr spectra of O-protonated 2,6-dimethylanisole (upper trace) and diprotonated 2,6-dimethylanisole (bottom trace).

obtained in the protonation of **35** in the four superacids. The pmr spectrum of ion **36** is in accordance with its structure (Table II). Formation of ion **37** is based on the presence of a low-intensity (*ca.* 2%) shielded doublet at δ 1.8 ($J_{\text{CH}_3, \text{H}} = 7$ Hz) corresponding to the methyl proton attached to the methylene carbon atom.

F.—Protonation of 3,5-dimethylanisole (**38**) in HF solution was examined by Brouwer and coworkers.^{2b} They found only a single benzenium ion **39**. In super-

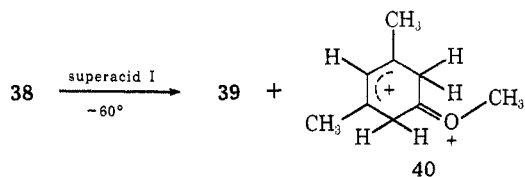


acids II-IV, ion **39** is obtained and the pmr spectrum is similar to that reported.^{2b} The pmr spectrum of ion **39** is found, however, to be temperature dependent, owing in all probability to the hindered rotation of the methoxy group. At low temperature (-80°),



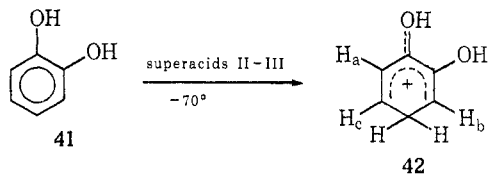
the rotation is slow or does not occur at all, as different methyl groups and vinylic methine protons are observed. (Table II). At higher temperatures (*e.g.*, -20°), each set of the two singlets collapsed and finally became a singlet. The rotation of the OCH_3 group at -20° is rapid, causing two methyl groups and also the two ring methine protons to become equivalent.

In superacid I, **38** is both mono- and diprotonated to give ions **39** and **40**, respectively. The ratio of ions

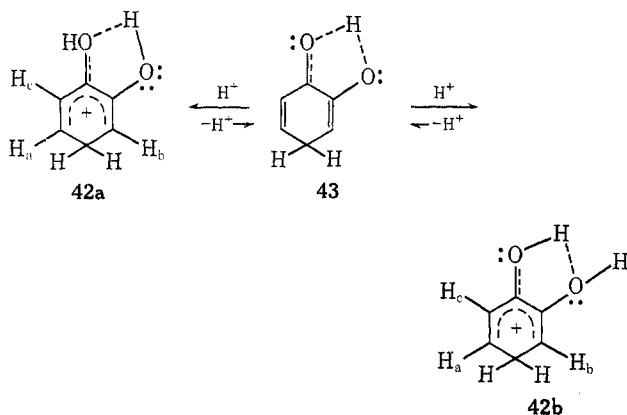


39:40 is dependent on the ratio of the molar concentration of HF-SbF₅ and **38**. Dication **40** was formed predominantly at higher concentration of HF-SbF₅ in the solution. The formation of dication **40** is indicated by its substantially deshielded pmr absorptions. The pmr spectrum shows (besides the absorption lines of ion **39**) a singlet due to the two methyl groups at δ 3.62 (6 H), a methoxy singlet at 5.60 (3 H), a slightly broadened methylene singlet at 5.5 (4 H), and a vinyl singlet at 8.66 (1 H).

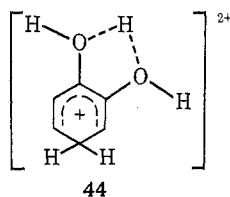
Protonation of Dihydroxybenzenes. A. Catechol (41) is C-protonated in superacids II and III to give the 3,4-dihydroxybenzenium ion **42**. The pmr spectrum



is temperature independent ranging from -90 to -20° , indicating the absence of isomeric cisoid and transoid ions of **42** and no 1,2-hydrogen shift of the methylene protons. Furthermore, the hydroxylic protons were not observable, presumably because of rapid protonation-deprotonation equilibrium (exchange), even though the hydroxylic proton of C-protonated phenol² was observed under identical conditions. Apparently, intra- and intermolecular hydrogen bonding seem to be responsible for such observation. A possible mechanism for the rapid proton exchange involves the *p*-quinoidal intermediate (**43**). On the other hand, di-



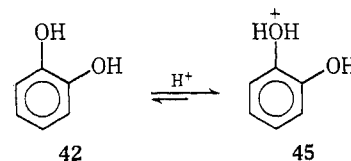
protonated catechol (**44**) as an intermediate could



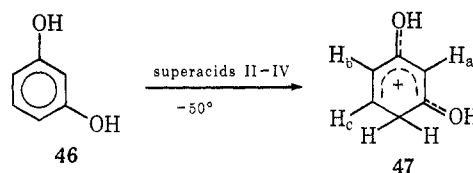
equally well explain the rapid proton exchange of **42** with the superacid systems. The pmr spectrum of ion **42** shows a slightly broadened singlet at δ 4.6 (2 H, CH₂), a doublet at 7.74 (1 H, H_a, $J_{HH} = 9$ Hz), a triplet at 8.03 (1 H, H_b, $J_{HH} = 2$ Hz), and a doublet of triplets at 8.90 (1 H, H_c, $J_{HH} = 9$ and 2 Hz). The shielding (0.9 ppm) of the ortho proton by the adjacent hydroxyl group should be noted.

When **41** was protonated in superacid IV, the pmr spectrum indicated the formation of ion **42** and an

additional sharp singlet at δ 7.44. This sharp singlet can be tentatively assigned to the aromatic protons of O-protonated catechol (**45**) undergoing rapid hydrogen exchange with the solvent system.

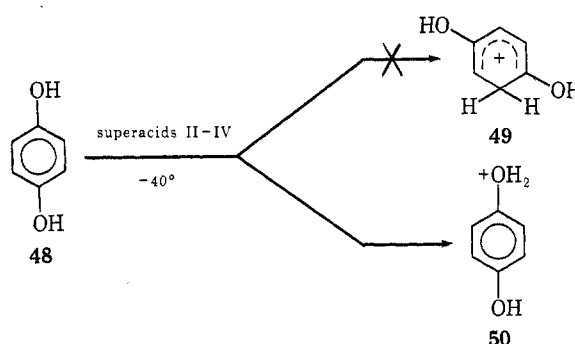


B. Resorcinol (46) is the strongest base among the three dihydroxybenzenes. It is completely C-protonated in superacids II-IV at -50° to give the 2,4-dihydroxybenzenium ion (**47**). Alder and Taylor^{2c}

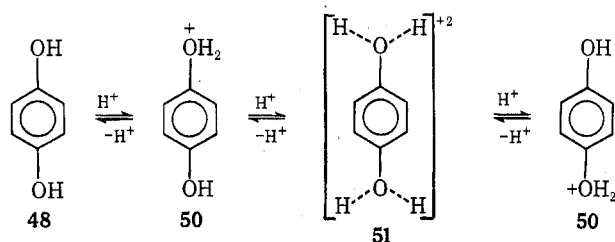


also found that **46** was C-protonated in BF₃-HF sulfonane solution, but gave no report on either peak multiplicities or coupling constants. The pmr spectrum of ion **47** as obtained in our work shows a doublet at δ 4.73 (CH₂, $J_{HH} = 3.5$ Hz), a singlet at 6.82 (H_a), a doublet at 7.31 (H_b, $J_{HH} = 10$ Hz), and a doublet of triplets at 8.10 (H_c, $J_{HH} = 10$ and 3.5 Hz). The shielding effect of the H_a proton in ion **47** by the two OH groups is noteworthy. The well-resolved doublet of triplets of the H_c proton clearly shows the rapid conformational interconversion about the benzenium ring. The hydroxylic protons are again not observed, implying rapid exchange (*via* intra- and intermolecular processes).

C. Hydroquinone (48) is not C-protonated in any of the superacids to give the 2,5-dihydroxybenzenium ion **49**. The pmr spectra of **48** in superacids II, III,



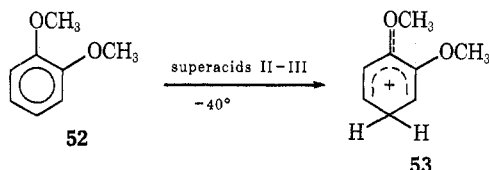
and IV (at -40°) show a sole singlet absorption at δ 8.52, 7.91, and 7.50, respectively. These results imply a rapid O-protonation-deprotonation process (**48** \rightleftharpoons **50**). In the strongest of the three superacid systems (*i.e.*, II), the equilibrium is shifted to the right and the singlet absorption is deshielded by about 1.5 ppm from that of the precursor **48**. Furthermore, the hydroxylic protons cannot be observed even at -90° , indicating that **48** \rightleftharpoons **50** is an extremely rapid and low activation energy process. One possible mechanism for the proton exchange reaction may be involvement of the dipositive ion (or transition state) **51**.



Protonation of **41**, **46**, and **48** in superacid I at -78° all gave only unidentified polymeric products. The reason for this difference in chemical behavior is not readily apparent, although superacid I is the strongest of the superacid systems used and may cause the most exothermic, difficult to control reactions, with possibility of local overheating causing polymerization.

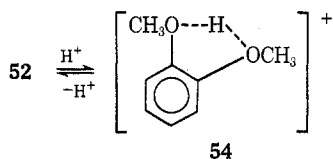
Protonation of Dimethoxybenzenes.—In many respects, protonation of dimethoxybenzene in the four superacid systems is similar to the protonation of dihydroxybenzenes. The only obvious difference is that no polymerization takes place when any of the dimethoxybenzenes is protonated in any of the four superacids.

A. *o*-Dimethoxybenzene (veratrole) (52) was found C-protonated in superacids II and III, giving the 3,4-dimethoxybenzenium ion **53**. The pmr spectrum of



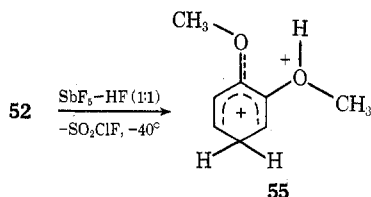
ion **53** shows the methylene proton absorption at δ 4.8 (slightly broadened). The assignment of the ring protons is similar to those of C-protonated catechol **52** (also see Table II).

In $\text{HSO}_3\text{F}-\text{SO}_2\text{ClF}$ (IV), **52** undergoes both C- and O-protonation. However, the O-protonated ion **54**

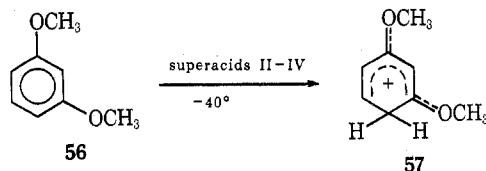


is in equilibrium with **52**. It is likely that the acidic proton is attached to both methoxy oxygens *via* hydrogen bonding.

In $\text{HF}-\text{SbF}_5(1:1)-\text{SOClF}$, (I) **52** was C-protonated. The pmr spectrum of the solution shows a similar pattern to that of ion **53**, but all the absorption lines are deshielded by 0.43–1.24 ppm (see Table II). The deshielding effect is probably coming from additional protonation of the oxygen atom (ortho OCH_3) of ion **57** to give the dication **55**, but rapidly exchanging with the acid solvent.

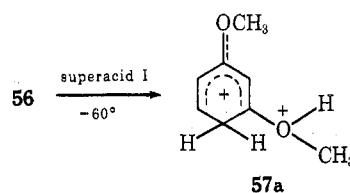


B. *m*-Dimethoxybenzene (56) was C-protonated in superacids II-IV to give 2,4-dimethoxybenzenium ion (**57**). Brouwer and coworkers^{2b} also found ion **57** when

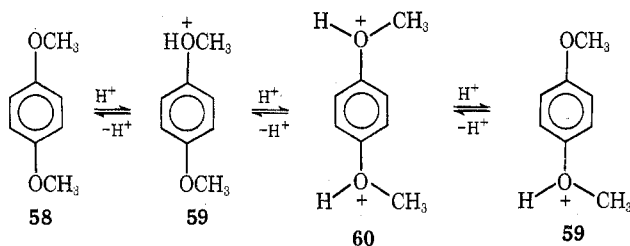


56 was treated with HF at -70° . The pmr spectrum of ion **57** is similar to that of ion **47** except that there are two additional sharp singlet absorptions at δ 4.52 and 4.63 for the ortho and para OCH_3 , respectively.

56 in superacid I at -40° gave a pmr spectrum similar to that of ion **57** but all the resonance lines were deshielded by ~ 1 ppm (see Table II). In addition, a broadened, deshielded absorption was found at δ 12.2. These data suggest that a diprotonated species is formed. The second proton is likely attached to the ortho OCH_3 rather than the para OCH_3 group. These data indicate that **56** was diprotonated to give dication **57a**, which, however, exchanges with the solvent system.



C. *p*-Dimethoxybenzene (58) was O-protonated in all the four superacids. In the weakest acid (IV), the pmr spectrum shows two singlet absorptions at δ 4.46 and 7.58 for the methoxy and the aromatic protons, respectively. When the acidity is increased in III and II, the methoxy singlet absorptions were deshielded to δ 5.23 and 5.30, as were the aromatic singlet absorptions to δ 8.10 and 8.18, respectively. These results are similar to those derived for the protonation of hydroquinone **48**, which involves a O-protonation-deprotonation process. No polymerization took place when **58** was treated in superacid I, and indeed, the



dication **60** was observed. The pmr spectrum of dication **60** shows the methoxy doublets at δ 5.48 ($J_{\text{HH}} = 3$ Hz), an aromatic singlet absorption at δ 8.24, and the deshielded hydroxyl quartets at δ 11.92 ($J_{\text{HH}} = 3$ Hz).

Conclusion

The sites of protonation of mono- and dihydroxybenzenes as well as their substituted derivatives were found to be dependent on the acid media used. Generally, O-protonation is favored in weaker acid media, while C-protonation was usually achieved in stronger

superacid media (for example, in the case of protonation of phenol, anisole, *m*- and *p*-cresols, and 2,4,6-dimethylanisole). In some cases, a mixture of O- and C-protonated species were observed in the same solution and their relative ratio is related to the acid media used. The ratio of stereoisomer (*cis* and *trans*) formation is also dependent on the acid media used.

Based on their protonating ability the decreasing acidity of the four superacid systems used is I > II > III > IV.

Substituent effects play an important role in the course of protonation. In FSO₃H-SO₂ClF solution, *m*-methylanisole (17) was completely C-protonated (18) while *m*-cresol (19) was partially O-protonated (25%) to 20a under identical experimental conditions. These results suggest that a methoxy group can stabilize a benzenium ion better than a hydroxy group. In contrast, we found in the protonation of 3,5-dimethoxyphenol that the site of protonation is four times more favorable at the carbon atom para to the hydroxyl than para to the methoxyl groups.¹⁰ Similarly, *p*-cresol (9a) is completely C-protonated in superacid II to give ion 10a, while 9b is partially C-protonated under identical conditions. The reason for these differences is not yet completely understood. It is known that methoxyl groups activate the aromatic ring in electrophilic substitutions. However, we were not able to C-protonate *p*-dimethoxybenzene (58) even in the strongest superacid I medium, as it gave only the O-diprotated dication 60.

It is reasonable to assume that initial kinetic protonation is on oxygen, which, however, in many systems is a completely reversible process and O-protonated ions can be observed only in low-nucleophilicity media (*i.e.*, superacids), but even in these their exchange processes frequently remain rapid. In contrast C-protonated ions [hydroxy(alkoxy)benzenium ions] show considerably less tendency to exchange with solvent.

Finally, three different types of dications were observed in the protonation of studied hydroxy (alkoxy) aromatic compounds. These are (i) di-O-protonated *p*-dimethoxybenzene (60), (ii) di-C-protonated 3,5-dimethylanisole (40), and (iii) O- and C-diprotated 2,4-dimethylanisole (26), *o*- and *m*-dimethoxybenzenes

(55 and 57a). Diprotonation was only achieved in the strongest superacid I. The nature of these dications is further discussed in our subsequent paper.^{10b}

Experimental Section

Materials.—All the mono- and dihydroxybenzenes and their methyl ethers were commercially available in high purity and were used without further purification. Antimony pentafluoride (Allied Chemical Co.) was refluxed for 12 hr while passing a stream of dry nitrogen through it to remove HF. The material was then twice distilled (bp 150°). Fluorosulfuric acid (Allied Chemical Co.) was twice distilled (bp 160–164°) before use. Hydrogen fluoride was obtained from Baker Chemical Co., sulfuryl chloride fluoride from Allied Chemical Co.

Preparation of Ions.—Superacids were prepared by mixing antimony pentafluoride and HF or HSO₃F at –78° in Teflon bottles. The resulting solutions were then diluted with sulfuryl chloride fluoride. Ions for nmr studies were prepared by adding ~50 mg of the aromatic compound to be protonated in an nmr tube to 1 ml of the above superacid solutions (at –78°), with good stirring, which was continued until a clear solution was obtained. Following their nmr study the solutions were quenched (as previously described³) and starting hydroxy (methoxy) compounds were recovered (as indicated by nmr, ir, and glc studies) showing that no side reactions took place otherwise as described.

Nmr Spectra.—A Varian Associates Model A-56/60A nmr spectrometer equipped with a variable-temperature probe was used for ¹H nmr spectra. Carbon-13 INDOOR spectra¹² were obtained on a Varian Associates Model HA100 nmr spectrometer as described.

Registry No.—2, 37145-55-4; 4, 19527-06-1; 6, 37396-37-5; 10a, 37396-38-6; 10b, 37396-39-7; 11, 37145-49-6; 12, 37145-50-9; 14a, 37145-56-5; 16a, 37145-57-6; 18, 37145-58-7; 20, 37145-59-8; 20a, 37396-35-3; 22, 37145-60-1; 24, 37145-61-2; 25, 37145-51-0; 26, 37145-62-3; 28, 37396-40-0; 30, 37145-52-1; 31, 37145-63-4; 34, 37145-64-5; 36, 33516-56-2; 39, 37145-66-7; 40, 37145-67-8; 42 (ion), 37145-68-9; 43, 37145-69-0; 45, 37145-70-3; 45a, 37396-36-4; 47, 37145-714; 50, 37145-53-2; 57, 37145-72-5; 57a, 37396-41-1; 60, 37145-54-3.

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

(12) A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, **91**, 2943 (1969).