mixture by the pseudo-CCD technique described by Wiberg.[16] A reaction-solution aliquot of 30 ml was distributed in equal parts into four separatory funnels, each containing 250 ml of water. Four successive 50-ml portions of cyclohexane were passed down the series of funnels and combined at the end. The cyclohexane solution was then washed with 5% sodium bicarbonate solution and with water, dried over Drierite, and concentrated to 1 ml by flash distillation. After filtration through glass wool, the solution was analyzed for ester composition by gas chromatography.

Product Analysis by Gas Chromatography.—A Model 90-P3 Aerograph gas chromatograph, equipped with a thermal detector and a Model 8000–2600 Barber-Coleman recorder, was used with a 10 ft × 0.25 in. column of 60–80 mesh Varian Aerograph Chromosorb W regular solid support coated with 15% by weight diethylene glycol succinate (column temperature 190°, helium carrier gas flow 45 ml/min). Area integrations of the chromatogram peaks were obtained by tracing the peaks using Clearprint technical paper (no. 1000PH) and a light tracing pencil and then cutting out the traces and weighing them on a Mettler analytical balance (type H16).

Calibration.—Buffer solutions similar to those for the methanolysis of *p*-nitrophenyl benzoate and benzoic phenylacetic anhydride were used for acquiring the calibration data. These buffers, containing no substrate, were heated for 4 hr at 45.00° in a constant-temperature bath, after which methyl benzoate (0.0010–0.0050 *M*), methyl phenylacetate (0.0050–0.0090 *M*), benzoic acid (0.0050 *M*), and *p*-nitrophenol (0.0100 *M*) were added to simulate the products of an actual methanolysis. The samples of esters were weighed out in small combustion boats and the entire boat was put into the calibration solution. All other samples were added by volumetric pipettes from stock solutions. The esters were then separated and analyzed by gas chromatography as described in the above paragraphs. Esterification of buffer under reaction conditions led to high values of the methyl phenylacetate:methyl benzoate ratio. Therefore a plot of peak area ratio *vs.* actual product composition had to be prepared and used to calculate true reaction-product distributions.

Registry No.—*p*-Nitrophenyl benzoate, 959-22-8; benzoic phenylacetic anhydride, 41085-80-7; thallium(I) phenylacetate, 41085-81-8; benzoyl chloride, 98-88-4.

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[16] K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill, New York, N. Y., 1960, p 187.

Stable Carbocations. CLVII.[1] Protonation of 2,4,6-Trimethoxytoluene and 2,4,6-Trimethoxy-*m*-xylene in Superacid Solutions

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Protonation of 2,4,6-trimethoxytoluene and -*m*-xylene in FSO_3H-SO_2 and in HF-SbF_5-SO_2ClF solution is reported. The structure of the formed arenium ions and methylated oxocyclohexenyl dications is based on their pmr spectroscopic study. The relative stability of these ions is discussed in terms of resonance, inductive, and steric effects.

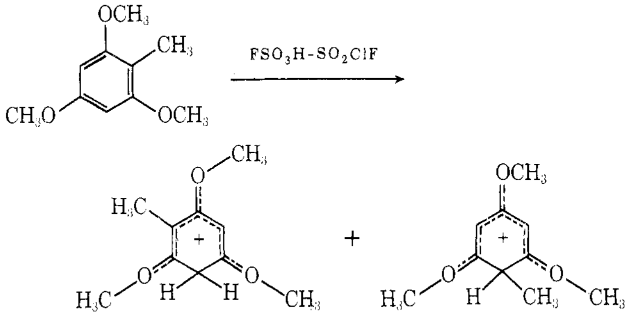
A series of stable arenium ions have been observed previously in superacid media.[3] Among them, methylbenzenium ions,[4a] fluorobenzenium ions,[1,4b] halomethylbenzenium ions,[5] and hydroxy- and alkoxybenzenium ions[6] have been reported. Recently, we have succeeded even in the direct observation of the parent benzenium ion[7] and naphthalenium ion.[8]

Protonation of arenes generally takes place at a ring position to which hydrogen is attached. Carbons bearing substituents, however, also can be protonated to give stable arenium ions, as first shown by Vaughan and his associates[9] in case of some methoxy-1,2,3-trimethylbenzenes and *o*-xylenes.

We now wish to report further such examples of arenium ions and methylated cyclohexenyl dications obtained by protonation of 2,4,6-trimethoxytoluene and 2,4,6-trimethoxy-*m*-xylene in FSO_3H-SO_2 and HF-SbF_5-SO_2ClF solution.

Results and Discussion

Protonation of 2,4,6-trimethoxytoluene in FSO_3-H-SO_2ClF gave a mixture of two benzenium ions (1 and 2). The pmr spectrum of the solution (Figure 1) is well resolved and shows in the methyl proton region (of benzenium ions) a singlet at δ 1.85 and a doublet at δ 1.59 (J = 7.5 Hz). In the vinyl region, there are two singlets at δ 6.10 and 6.27. If protonation take place at the unsubstituted position of 2,4,6-trimethoxytoluene, only one methyl and one vinylic proton absorption should be observed. These data suggest the



Temp, °C	1,%	2, %
−70	80	20
−50	77	23
−30	73	27
−20	72	28

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[1] Part CLVI: C. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 3221 (1973).

[2] Postdoctoral Research Associate, 1969–1971.

[3] For a review, see D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed. Wiley-Interscience, New York, N.Y., 1970, p 864.

[4] (a) G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 1103 (1965); (b) G. A. Olah and T. E. Kiovsky, *ibid.*, **89**, 5692 (1967).

[5] (a) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **90**, 2583 (1968); (b) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **87**, 335, 342 (1968).

[6] (a) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 5341 (1972); (b) *J. Org. Chem.*, **38**, 353 (1973); (c) A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Amer. Chem. Soc.*, **93**, 6181 (1971).

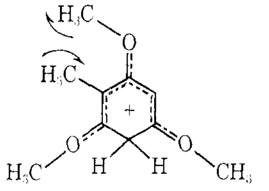
[7] (a) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970); (b) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **94**, 2034 (1972).

[8] G. A. Olah, Gh. D. Mateescu, and Y. K. Mo, *J. Amer. Soc.*, **95**, 1865 (1973).

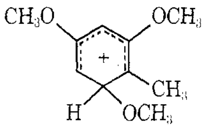
[9] M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *J. Chem. Soc. B*, 1624 (1971).

formation of ion **2** (*via* protonation of the methyl-bearing carbon). Furthermore, a quartet at δ 3.63 is also observed for the methine proton of ion **2**. It is interesting to note that the methylene proton (δ 3.90) of ion **1** is more deshielded than the methine proton of ion **2**. There are only two methoxy absorptions appearing at δ 4.03 and 4.26 in a ratio of 2:1 indicating the coincidence of the *o*-OCH_3 and of the *p*-OCH_3 in ions **1** and **2**. In addition, the ratio of **1** and **2** is temperature dependent, *i.e.*, a higher ratio is observed at lower temperature. These data indicate that **1** is thermodynamically more stable than **2**.

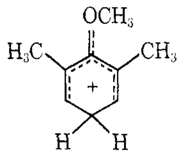
One may suggest three possible mechanisms for the reversible interconversion process ($\mathbf{1} \rightleftharpoons \mathbf{2}$). First, it could proceed by intermolecular exchange between the precursor and the benzenium ion; second, it could involve an unstable intermediate such as **1b** and a 1,2-hydrogen shift (intramolecular); and, finally, it could involve hydrogen transfer with the acid solvent FSO_3H–SO_2, which is present in large excess.



1a



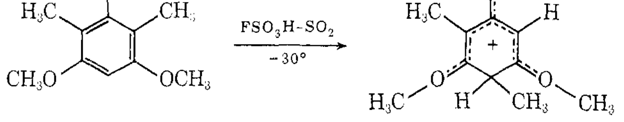
1b



3

It is known that the pmr spectrum of C-protonated anisole (4-methoxybenzenium ion) is temperature dependent, indicating the rotation of C=O partial double bond at higher temperature.[6] However, the pmr of both ion **1** and **2** (present in the same solution) is temperature independent. It is therefore suggested that the ion formed from 2,4,6-trimethoxytoluene has structure **1** rather than that of **1a** or of equibrating of ions $\mathbf{1} \rightleftharpoons \mathbf{1a}$. Ion **1a** is expected to be less stable than ion **1** owing to prevailing steric effects. This kind of steric effect has been demonstrated when 2,6-dimethylanisole was not found to be C-protonated to give 3,5-dimethyl-4-methoxybenzenium ion **3**.[6] On the other hand, the C=O partial double bond of ion **2** may be rapidly rotating even at −80°, since its double bond character is less pronounced than that of the 4-methoxybenzenium ion (or there is less charge introduced into the *p*-CH_3O group).

Protonation of 2,4,6-trimethoxy-*m*-xylene in FSO_3H–SO_2 solution at −30° gave exclusively ion **4**. The isomeric ion **5** was not observed at the temperature range −80 to −20°, indicating considerable stability difference between ions **4** and **4a**.



4

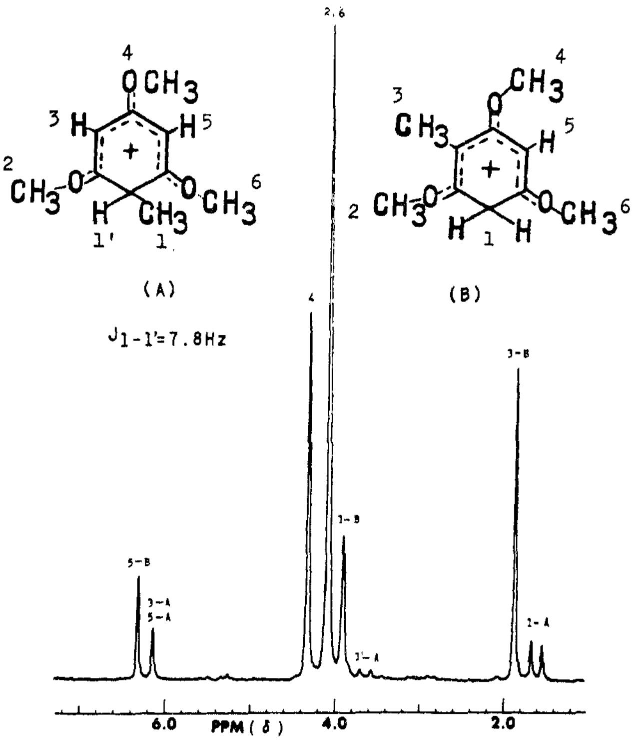
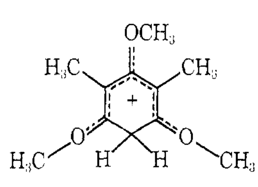
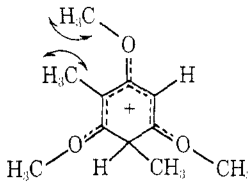


Figure 1.—Pmr spectrum of 1-methyl-2,4,6-trimethoxybenzenium ion (A) and 3-methyl-2,4,6-trimethoxybenzenium ion (B).



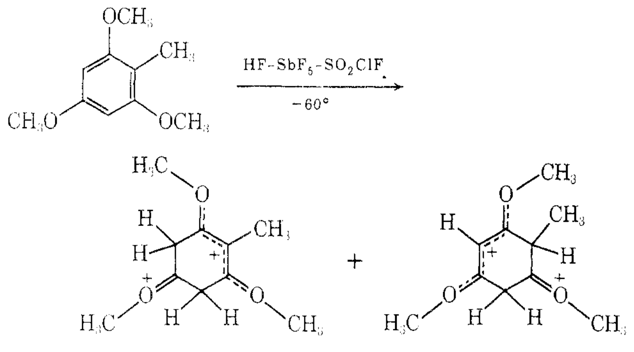
4a



5

In the pmr spectrum of ion **4** the methyl group which is attached to the sp^3 carbon shows a doublet at δ 1.62 (J = 7.5 Hz). It is coupled to the methine proton which displays a quartet at δ 3.89 (J = 7.5 Hz). The other methyl proton absorption is a slightly deshielded singlet at δ 1.86. The three methoxy groups of ion **4** are significantly deshielded and situated in different environments. Consequently, they are no longer equivalent and their signals appear at δ 4.11, 4.17, and 4.32 as three singlets. The most deshielded absorption (δ 4.32) is evidently assigned to the *p*-OCH_3. Because of the obvious steric effect, the structure of the ion obtained from protonation of 2,4,6-trimethoxy-*m*-xylene in FSO_3H–SO_2 solution must have the structure **4** and not **5**. Consequently, we can assign the more deshielded methoxy singlet at δ 4.17 to the 2-OCH_3 because of the anisotropy effect of the *p*-OCH_3.[6] Finally, it is interesting to note that the vinylic proton of **5** is more shielded (δ 6.16) than the ring protons of its precursor (δ 6.23), indicating that there is essentially no charge introduced into the meta position upon protonation.

In stronger superacidic FSO_3H–SbF_5–SO_2ClF and HF–SbF_5–SO_2ClF solution, 2,4,6-trimethoxytoluene was

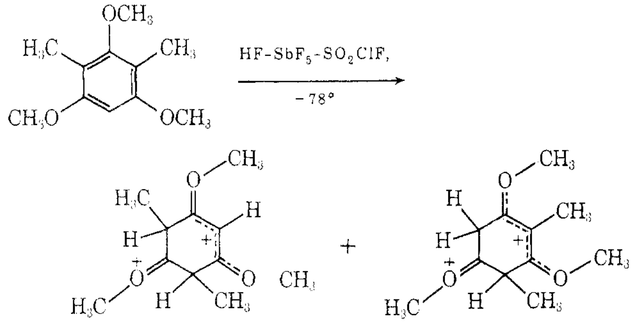


7 (20%) 6 (80%)

diprotonated to give the methylated oxocyclohexenyl dications **6** and **7** in a ratio of 4:1. The ratio of these ions is temperature independent. The pmr spectrum of the solution is different from that of 2,4,6-trimethoxytoluene when protonated in FSO_3H-SO_2 (each corresponding absorption is further deshielded). It shows in the methyl proton region (of benzenium ions) a doublet at δ 2.21 (J = 6 Hz, CH_3, of **7**) and a singlet at δ 2.41 (CH_3 of **6**). The methine proton absorption of **6** is a quartet at δ 4.20. There is a singlet absorption at δ 7.06 which can be assigned to the vinylic proton of dication **7**. The $CH_3—^+O=C$ proton absorptions of **6** and **7** are two close singlets at δ 5.50 and 5.70 (also in a ratio of 4:1). The methoxy groups attached to the terminal allylic carbons in dications **6** and **7** show a coincidental singlet at δ 4.91. The methylene protons of **6** and **7** also show a coincidental slightly broadened singlet at δ 5.0.

Methylated oxocyclohexenyl dications **6** and **7** were formed when ions **1** and **2** in FSO_3H-SO_2 solution were added to SbF_5-SO_2ClF or $HF-SbF_5-SO_2ClF$ solution at −78°. This result evidently shows that the formation of **6** and **7** takes place through additional protonation at the meta carbons of **1** and **2**. Dication **6** is the only product ion when **2** is further protonated at the unsubstituted meta positions. Both dication **6** and **7** can be formed when **1** is further protonated at C-3 and C-5, respectively. The ratio of ions **1** and **2** is 4:1 at −70°. Thus, the ratio of protonation at C-3 and C-5 is becoming 3:1, although the former protonation is sterically unfavorable. This result may be accounted for by the unusual stability of dication **6**.

Similarly, when 2,4,6-trimethoxy-*m*-xylene was protonated in $HF-SbF_5-SO_2ClF$ solution, two methylated oxocyclohexenyl dications **8** and **9** (in a ratio of 3:1) were obtained. The pmr spectrum of the solution is different from that when 2,4,6-trimethoxy-*m*-xylene was protonated in FSO_3H-SO_2 solution (each corresponding absorption peak is further deshielded). It is less resolved presumably owing to the viscosity of the medium. The methyl group attached to the central allylic carbon shows a deshielded singlet at δ 2.42. The other methyl group of dication **9** and the two symmetrical methyl groups of dication **8** show a multiplet pmr absorption at δ 2.2–2.3. The formation of dication **8** can easily be recognized by the vinylic proton singlet absorption at δ 7.01. The $CH_3—^+O=C$ of **8** and **9** show two close singlet absorptions at δ 5.64 (75%) and 5.50 (25%), respectively. The other methoxy groups and the methylene protons show a slightly broadened singlet absorption at δ 5.0. The methine protons of **8** and **9** show a multiplet at δ 4.2–4.4. Finally, it is interesting to note that the additional protonation of **5** (to form **8** and **9**) occurring at the meta carbon bearing a methyl group is again 3:1 with respect to the other unsubstituted meta carbon.



8 (75%) 9 (25%)

The study of protonation of 2,4,6-trimethoxytoluene and -*m*-xylene in superacid solutions led to the formation of the observed novel benzenium ions and methylated oxocyclohexenyl dications, indicating the importance of steric and resonance effects on the stability of arenium ions. Geminally substituted arenium ions may play an important role in electrophilic reactivity of polyalkoxybenzenes.

Experimental Section

Materials.—2,4,6-Trimethoxytoluene was commercially available material from Aldrich Chemical Co. and used without further purification. 2,4,6-Trimethoxy-*m*-xylene was prepared according to the method reported for the preparation of 1,3-dimethoxy-2-methylbenzene.[10] 2,4,6-Trimethoxytoluene (0.1 mol) was added to 200 ml of an ether solution of phenyllithium (0.1 mol). After the solution was kept for 2 days at room temperature in the dark, dimethyl sulfate (0.12 mol) was added to the solution. It was refluxed for 2 hr, then poured onto ice–water. The product was extracted with ether and isolated as a white solid, mp 60°, with correct analysis and nmr spectrum.

Fluorosulfuric acid (Allied Chemical Co.) was doubly distilled and antimony pentafluoride (Allied Chemical Co.) was triply distilled before used. HF was obtained form J. T. Baker Chemical Co. The preparation of superacid solutions has been described previously.[11]

Preparation of the Ions and Their Nmr Study.—Solutions of the ions for nmr studies were prepared by adding 0.2 g of the aromatic to 2 ml of FSO_3H-SO_2ClF ($HF-SbF_5-SO_2ClF$) solution which had been cooled at −78°. The well-stirred solutions were allowed to slightly warm till clear, slightly yellow solutions were obtained.

A Varian Associates Model A-56-60A nmr spectrometer equipped with a variable-temperature probe was used to obtain all spectra. External capillary tetramethylsilane was used for proton reference.

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

Registry No.—**1**, 42077-30-5; **2**, 42077-31-6; **4**, 42077-32-7; **6**, 42200-04-4; **7**, 42077-33-8; **8**, 42077-34-9; **9**, 42077-35-0; 2,4,6-trimethoxytoluene, 14107-97-2; 2,4,6-trimethoxy-*m*-xylene, 1521-61-5.

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[10] J. P. Lambooy, *J. Amer. Chem. Soc.*, **78**, 771 (1956)

[11] G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967).