erythro-**Diethyl 2-*p*-Nitrophenyl-3-phenylsuccinate (I-NO_2).**—The *p*-amino ester, I-NH_2, was oxidized to I-NO_2 using the procedure of Emmons:[21] mp 105–106° (from ethanol) (lit.[22] mp 101°); nmr ($CDCl_3$) δ 7.1–8.3 (m, 9, aromatic), 4.34 (d) and 4.51 (d) (2, benzylic), 3.86 (q) and 3.88 (q) (4, $-OCH_2-$), 0.92 (t) and 0.96 (t) (6, $-CH_3$).

Equilibration Procedure.—To a solution of 0.12 g (3.24×10^{-4} mol) of I-NO_2 in 20 ml of absolute ethanol was added 1 ml (3.24×10^{-5} mol of NaOEt) of a solution prepared from 7.4 mg of sodium dissolved in 10 ml of absolute ethanol. Upon addition of the base, the yellow ester solution turned light brown. The solution was heated at reflux under nitrogen for 24 hr. The reaction was terminated by acidification of the solution with dilute HCl and then pouring it into a beaker of ice. The brown color disappeared when the acid was added. The water–ethanol was milky white at this point. The ethanol was evaporated and the remaining aqueous mixture was washed three times with ether. The ether extracts were combined, dried over magnesium sulfate, and filtered. Evaporation of the ether left 113.9 mg of an oily, yellow solid. This material was analyzed as described in the discussion of the equilibrations.

Equilibrations of I-H, II-H, I-Cl, and I-OMe were carried out using the same procedure. However, no color changes accompanied these equilibrations and these esters were easily collected by suction filtration of the melted ice solution as opposed to the extraction procedure described above.

The nmr spectra were taken using Varian A-60 and Varian HA-100 spectrometers. $CDCl_3$ containing TMS was used as the solvent in all cases.

Acknowledgment.—Our thanks to the National Science Foundation for its support of this research. K. B., S. H., E. H., and R. L. were National Science Foundation Undergraduate Research Participants (GY-7540).

Registry No.—I-H, 13638-89-6; I-OMe, 41915-54-2; I-Cl, 41915-55-3; I-NH_2, 41915-56-4; I-NO_2, 41915-57-5; II-H, 41915-58-6; II-OMe, 41939-32-6; II-Cl, 41915-59-7; II-NO_2, 41915-60-0; *erythro*-2-*p*-acetamidophenyl-3-phenylsuccinonitrile, 41915-61-1; benzyl cyanide, 140-29-4; *p*-acetamidobenzaldehyde, 122-85-0; *erythro*-2-*p*-methoxyphenyl-3-phenylsuccinic acid, 41915-62-2; *erythro*-2-*p*-chlorophenyl-3-phenylsuccinic acid, 41915-63-3; *threo*-2,3-diphenylsuccinic acid, 41915-64-4; *erythro*-2,3-diphenylsuccinic acid, 41915-65-5; *erythro*-2-*p*-aminophenyl-3-phenylsuccinic acid, 41915-66-6.

(21) W. D. Emmons, *J. Amer. Chem. Soc.*, **76**, 3470 (1954).
(22) J. Hoch and D. Legay, *C. R. Acad. Sci., Ser. C*, **255**, 2975 (1962).

Catalytic Mechanism of Intermolecularly Carboxylate-Assisted Acyl Transfer[1,2]

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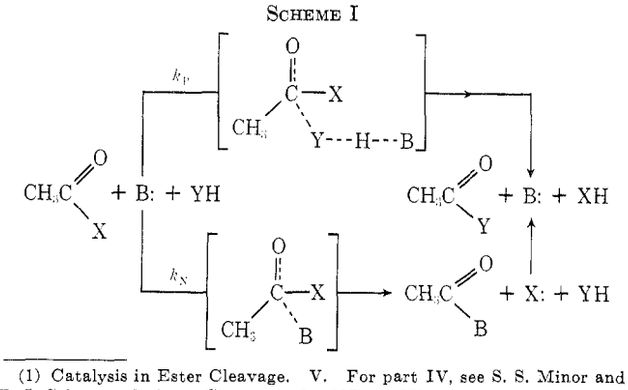
The methanolysis of *p*-nitrophenyl benzoate in methanolic buffers of sodium phenylacetate and phenylacetic acid is general base catalyzed and leads to both methyl benzoate (in 17–54% yield, depending on the buffer-component concentrations) and methyl phenylacetate (in corresponding 83–46% yield). This shows that at least a part of the catalyzed reaction occurs by a nucleophilic mechanism to generate benzoic phenylacetic anhydride, which then rapidly methanolyzes. Synthesis of this anhydride and its methanolysis shows the yield of methyl phenylacetate, under conditions of the kinetic study, to be 96.5 ± 0.6%. The data cited above show that the yield of this product from the phenylacetate-catalyzed part of the ester methanolysis is identical with that from the anhydride methanolysis, demonstrating that the sole mechanism of general-base catalysis in this system is the nucleophilic mechanism. This further supports the view that alcoholysis reactions prefer nucleophilic rather than protolytic general catalysis, in comparison to hydrolysis reactions.

The discrimination of the protolytic (k_P) and nucleophilic (k_N) mechanisms (Scheme I) of general base catalyzed acyl transfer processes,[5] which are usually kinetically indistinguishable, is of interest not only from standpoint of solution chemical dynamics, but also because of the role of such catalysis in the action of enzymes[6] and in medicinal chemistry.[7] For example, it appears that the imidazole ring of the active-site His-57 of α-chymotrypsin can function either as a protolytic catalyst or as a nucleophilic catalyst in the acylation of the nearby Ser-195 hydroxyl group, with the choice of catalytic mechanism depending on the structure of the substrate.[8] Very good leaving groups favor the nucleophilic mechanism, as is expected from the comprehensive investigation of Gold, Oakenfull, and Riley.[9] These workers studied the acetate-catalyzed hydrolysis of a series of aryl acetates, trapping the acetic anhydride intermediate formed in nucleophilic catalysis with aniline, and found that leaving groups more reactive than *p*-nitrophenoxide give preferential nucleophilic catalysis and less reactive leaving groups give preferential protolytic catalysis: *p*-nitrophenoxide itself produced 56% nucleophilic and 44% protolytic catalysis. The direct application of these results to enzymic systems such as α-chymotrypsin and the other "serine

SCHEME I



(1) Catalysis in Ester Cleavage. V. For part IV, see S. S. Minor and R. L. Schowen, *J. Amer. Chem. Soc.*, **95**, 2279 (1973).
(2) This research was supported by a grant from the National Institutes of Health and was carried out in part at the Computation Center of the University of Kansas. Further details may be found in A. E. Williams, M. S. Thesis in Chemistry, University of Kansas, 1972.
(3) Education Professions Development Act Fellow, 1970–1972.
(4) Holder of a Research Career Development Award of the National Institute of General Medical Sciences.
(5) (a) S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967); (b) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969; (c) M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins," Wiley-Interscience, New York, N. Y., 1971.
(6) R. M. S. Smellie, Ed., "Chemical Reactivity and Biological Role of Functional Groups in Enzymes," Academic Press, New York, N. Y., 1970.
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(8) C. D. Hubbard and J. F. Kirsch, *Biochemistry*, **11**, 2483 (1972).
(9) V. Gold, D. G. Oakenfull, and T. Riley, *J. Chem. Soc. B*, 515 (1968).

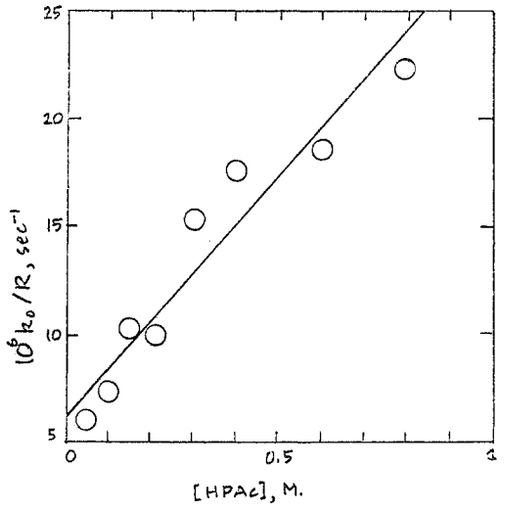


Figure 1.—Graphical test of eq 3. Data are from Table I.

hydrolases" is complicated by the fact that the acyl transfer is to an alcoholic function (the hydroxyl of serine) in the enzymic reactions but to water in the model reaction. Since the acyl acceptor is present in the transition state, at least for protolytic catalysis, its structure could easily affect the relative rate of the two forms of catalysis. Indeed, Behn discovered that acetyl transfer from *p*-nitrophenyl acetate to methanol gave less than 14% of protolytic catalysis, in contrast to 44% in the aqueous reaction, and suggested a steric destabilization of the protolytic transition state by the methyl group of the acyl acceptor.[10] We now report the dissection of nucleophilic and protolytic routes in another methanolytic reaction, determined using a different substrate, catalyst, and analytical technique from those of Behn.

Results

Kinetics.—The methanolysis of *p*-nitrophenyl benzoate (eq 1) in buffers of phenylacetic acid and sodium

$$C_6H_5CO_2C_6H_4NO_2 + CH_3OH \longrightarrow C_6H_5CO_2CH_3 + HOC_6H_4NO_2 \quad (1)$$

phenylacetate yielded the first-order rate constants of Table I. If the reaction is general base catalyzed with only terms in phenylacetate and methoxide ions being important in the rate law, then eq 2 should hold. We

$$k_0 = k_B[\text{NaPAc}] + k_M[\text{NaOCH}_3] \quad (2)$$

define the buffer ratio R by $R \equiv [\text{NaPAc}]/[\text{HPAc}]$ and note that $[\text{NaOCH}_3] = KR$. Substitution of these relations into eq 2 produces eq 3, which shows that a plot

$$k_0/R = k_B[\text{HPAc}] + k_M K \quad (3)$$

of k_0/R *vs.* [HPAc] should be linear with slope of k_B and intercept $k_M K$ if the assumptions are correct. Figure 1 exhibits the requisite linearity, whence $k_B = 2.28 \pm 0.33 \times 10^{-5}\ M^{-1}$ sec^{-1} and $k_M K = 6.0 \pm 1.2 \times 10^{-6}$ sec^{-1}.

Products.—Scheme II shows the relationship of reaction products to reaction mechanism. Methyl benzoate (MB) is formed by the reaction of substrate with methoxide ion (k_M), through protolytic catalysis by phenylacetate (k_P) and from that fraction g_{MB} of anhydride formed along the nucleophilic catalysis route (k_N) which undergoes attack at the benzoyl carbonyl group. Methyl phenylacetate (MPA) can be formed only from that fraction g_{MPA} of the anhydride formed along the nucleophilic catalysis route which undergoes attack at the phenylacetyl carbonyl group. The fraction f_{MPA} of methyl phenylacetate formed as product in the methanolysis of *p*-nitrophenyl benzoate under any set of circumstances will then be given by the ratio of the rate of nucleophilic catalysis times g_{MPA} to the total rate (eq 4). If k_0, f_{MPA}, and g_{MPA} could

$$f_{MPA} = k_N[\text{NaPAc}]g_{MPA}/k_0 \quad (4)$$

all be determined at a given sodium phenylacetate concentration, k_N could then be calculated from eq 4.

To determine g_{MPA}, benzoic phenylacetic anhydride was synthesized and methanolyzed in dummy reaction solutions from which only *p*-nitrophenyl benzoate was omitted. The product composition was then determined gas chromatographically as explained in the Experimental Section. For two quite different sets of conditions ([HPAc] = 0.400 *M*, [NaPAc] = 0.200 *M*, [$LiClO_4$] = 0.100 *M* and [HPAc] = 0.150 *M*, [NaPAc] = 0.300 *M*), the same result was obtained: $g_{MPA} = 0.965 \pm 0.006$. This was therefore accepted as the general value of g_{MPA}.

The products from methanolysis of *p*-nitrophenyl benzoate were similarly determined, as shown in Table II. Each experiment in Table II may be matched with one in Table I to obtain the corresponding value of k_0 and thus we can calculate five values of k_N from eq 4.

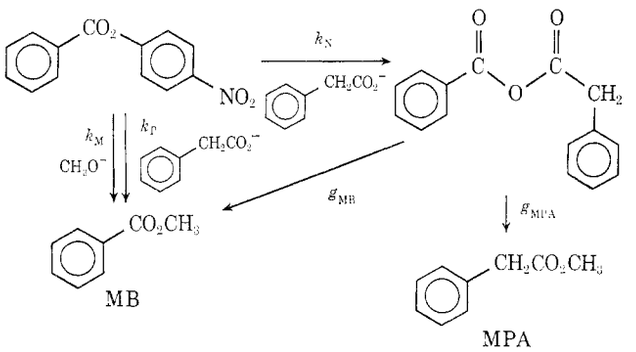
TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE METHANOLYSIS OF 0.01 *M* *p*-NITROPHENYL BENZOATE IN METHANOLIC BUFFERS OF SODIUM PHENYLACETATE (NaPAc) AND PHENYLACETIC ACID (HPAc) AT 45.00 ± 0.05° (μ = 0.300 *M*)[a]

[NaPAc], *M*	[HPAc], *M*	$10^6 k_0$,[b] sec^{-1}
0.100	0.050	11.8 ± 0.1
0.100	0.100	6.1 ± 0.1
0.100	0.200	4.2 ± 0.1
0.100	0.400	3.4 ± 0.1
0.200	0.100	16.7 ± 1.8
0.200	0.200	11.2 ± 0.1
0.200	0.400	10.7 ± 0.1
0.200	0.800	5.6 ± 0.1
0.300	0.150	20.5 ± 0.8
0.300	0.300	15.3 ± 0.3
0.300	0.600	9.2 ± 0.1

[a] Ionic strength maintained by added lithium perchlorate. [b] Error limits are standard deviations.

SCHEME II



(10) R. L. Schowen and C. G. Behn, *J. Amer. Chem. Soc.*, **90**, 5839 (1968).

TABLE II

PRODUCT COMPOSITION IN THE METHANOLYSIS OF 0.01 *M* *p*-NITROPHENYL BENZOATE IN METHANOLIC BUFFERS OF SODIUM PHENYLACETATE (NaPAc) AND PHENYLACETIC ACID (HPAc) AT 45.00 ± 0.05° (μ = 0.300 *M*)[a]

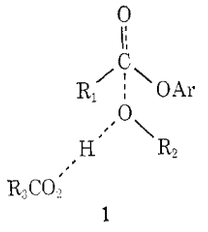
[NaPAc], *M*	[HPAc], *M*	(c_{MPA}/c_{MB})[b]	f_{MPA}[c]
0.100	0.200	0.85 ± 0.03	0.46 ± 0.02
0.100	0.400	1.94 ± 0.09	0.66 ± 0.04
0.200	0.400	1.98 ± 0.07	0.66 ± 0.03
0.200	0.800	4.81 ± 0.19	0.83 ± 0.04
0.300	0.600	1.88 ± 0.07	0.65 ± 0.03

[a] Ionic strength maintained by added lithium perchlorate. [b] Ratio of concentration of methyl phenylacetate to methyl benzoate, determined as described in the Experimental Section. Error limits are standard deviations. [c] Fraction of methyl phenylacetate in product.

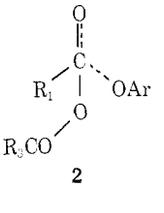
In the order of the entries in Table II, we calculate 10^5 k_N (M^{-1} sec^{-1}) = 2.00, 2.33, 3.66, 2.40, 2.07. Discarding the value of 3.66, we have k_N = 2.20 ± 0.17 × 10^{-5} M^{-1} sec^{-1}. This is equal to the value of k_B (2.28 ± 0.33 × 10^{-5} M^{-1} sec^{-1}) determined above, which shows the mechanism of catalysis to be solely nucleophilic.

Discussion

As before,[10] we presume the activated-complex structures along the protolytic and nucleophilic routes to be **1** and **2**, respectively. In the previously studied



1



2

acetate catalysis of *p*-nitrophenyl acetate (R_1 = R_3 = CH_3) solvolysis, the shift from nearly equal free energies of **1** and **2** in hydrolysis (R_2 = H)[9] to a lower relative free energy for **2** in methanolysis (R_2 = CH_3)[10] is interpreted most simply as a steric destabilization of **1** relative to **2** by the methyl group. Two changes were made in transforming to the system used in the present study: R_3 was changed from CH_3 to $C_6H_5CH_2$ and R_1 from CH_3 to C_6H_5. At first glance, R_1 should have little effect on the relative free energies of **1** and **2**, while the change in R_3 to a more electron-withdrawing group should favor **1**, in which the center of negative charge is closer to R_3. Since only catalysis *via* **2** is observed, this effect is apparently insufficient to overcome the steric destabilization of **1** by the methyl at R_2.

It is of course possible that **1** is more crowded near R_1 and is therefore destabilized by C_6H_5 *vs.* CH_3, thus cancelling the tendency at R_3. Indeed this reaction is about 23-fold slower than the acetate-catalyzed reaction of the acetate ester at the same temperature (we calculate k_N = 4.73 × 10^{-4} M^{-1} sec $^{-1}$ from Behn's data[10]): the question is, how much of this factor comes from the weaker basicity of the catalyst? To estimate this contribution, we assume the difference in pK_a of acetic and phenylacetic acids to be the same in methanol and water (ΔpK_a = 0.47, or a factor of 3). If **2** strongly resembles the tetrahedral intermediate, then this factor of 3 should roughly represent the expected factor in rate, since the $R_3CO_2^-$ moiety in **2** would resemble that in R_3CO_2H. As **2** more closely resembles the anhydride product, however, the rate factor should increase to a limit[11] of $3^{1.72}$ or 6.3. Thus the residual effect to be attributed to the phenyl group is between 23/3 ~ 4. Since some of this surely arises from destruction of reactant-state conjugation between phenyl and carbonyl, on activation, it seems unlikely that phenyl exerts a decisive differential steric effect in determining the lower free energy of **2** in the present case.

The conclusion is that nucleophilic catalysis of acyl transfer to alcohlic functions is preferred over protolytic catalysis, when compared to acyl transfer to water. Other things being equal, this conclusion leads us to expect nucleophilic catalysis in the chymotrypsin active site as observed by Hubbard and Kirsch[8] for activated esters. Needless to say, other things are radically not equal in active sites of serine acyltransferases, but our findings indicate that, when an enzyme undergoes protolytically accelerated acyl transfer to serine, its catalytic power must by capable of overcoming an extra barrier not apparent from model studies in aqueous solution.

Experimental Section

Materials.—All commercially obtained materials were used with no additional purification unless otherwise specified. Absolute methanol (anhydrous, Mallinckrodt) was purified according to the method of Lund and Bjerrum.[12] Methyl phenylacetate, prepared by refluxing of phenylacetic acid (Matheson Coleman and Bell, recrystallized) in methanol for 1 hr, had bp 213–214° (lit.[13] bp 215°). *p*-Nitrophenyl benzoate was prepared by the reaction of benzoyl chloride (Mallinckrodt, redistilled) and *p*-nitrophenol (Matheson Coleman and Bell, practical grade, recrystallized once from 0.5 *N* HCl) in cold pyridine (Baker Analyzed Reagent) for 15 min. The slightly yellow crystals obtained were recrystallized from an ethanol–methanol (1:7, v/v) mixture, yielding white crystals, mp 140–141° (lit.[14] mp 140–142°). Thallium(I) phenylacetate was prepared by adding 12.47 g (0.05 mol) of thallium(I) ethoxide, 98% (Aldrich), all at once to a stirred solution of 7.49 g (0.055 mol) of phenylacetic acid in ether under dry nitrogen. The white crystals were recrystallized from aqueous ethanol, mp 156–157°.

Benzoic phenylacetic anhydride, apparently not previously described, was prepared by allowing 10 g (0.029 mol) of an ether suspension of thallium(I) phenylacetate to react with 4.13 g (0.029 mol) of benzoyl chloride at 35° for 5 hr.[15] After the thallium chloride was filtered from the solution and the ether was evaporated, benzoyl chloride was removed by distillation at a pressure of 0.1 mm. The residue was washed quickly with 10 ml of 5% aqueous sodium bicarbonate solution and then with 10 ml of water, dried over Drierite for 30 min, and dissolved in warm benzene. Enough petroleum ether (bp 20–40°) was added to cause cloudiness and the solution was left in the refrigerator for about 10 hr. The white crystals, mp 62–63°, showed ir and nmr spectra and elemental composition (*Anal.* Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 76.07; H, 5.25.) consistent with the presumed structure. Samples were prepared immediately before use to avoid disproportionation.

Kinetic Procedure.—Reaction rates were determined by following the increase in absorption at 395 nm, owing to the formation of *p*-nitrophenol, with a Gilford Multiple Sample Absorbance Recorder (Model 2000).

Product Recovery by Multiple-Contact Pseudocountercurrent Extraction.—The product esters were separated from the reaction

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(12) H. Lund and I. Bjerrum, *Ber.*, **64**, 210 (1931).
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(15) E. C. Taylor, G. W. McLay, and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2422 (1968).

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.

(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.

(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).
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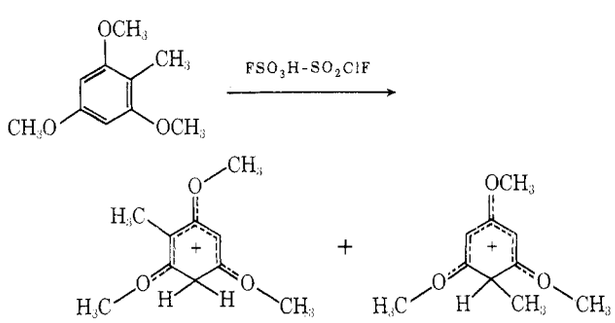
(6) (a) G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 5341 (1972); (b) *J. Org. Chem.*, **38**, 353 (1973); (c) A. J. Kresge, S. G. Mylonakis, Y. Sato, and V. P. Vitullo, *J. Amer. Chem. Soc.*, **93**, 6181 (1971).
(7) (a) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *J. 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).

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



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

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