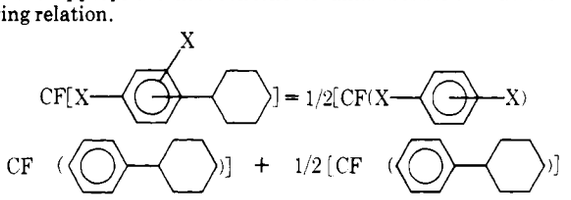
hexane were used and DTBP was obtained from Columbia Organics and used without further purification.

Cyclohexylation of Dihalobenzenes in Competition with Benzene in Excess Cyclohexane. A mixture of 0.032 mol of the dihalobenzene, 0.032 mol of benzene, 0.320 mol of cyclohexane, and 0.0064 mol of DTBP was weighed into a Fischer-Porter aeresol compatibility vessel. The valve was closed and the vessel was frozen in a Dry Ice–isopropyl alcohol bath. The valve was then opened to an aspirator and the vessel was pumped for 15 min, resealed, and warmed under the hot water tap until thawed. The freeze–evacuation–thaw cycle was repeated twice more and the reaction vessel was immersed in an oil bath in the dark at 90° for 8 days. The reaction vessel was then removed from the bath, cooled, opened under nitrogen, and stored in a brown bottle until analyzed by glpc. Product mixtures were analyzed on a Varian Aerograph HiFi 600D, equipped with a linear column temperature programmer and a 10.5 ft × 0.125 in. 15% Carbowax 6000–Chromosorb W column at a temperature program of 60–190° at 2°/min. (A program of 4°/min was used for the *o*-dibromobenzene reaction products.) Retention times were measured relative to the leading edge of cyclohexane, and individual peaks were identified by comparison with authentic samples. Quantization was accomplished by averaging triangulation and peak height times width at half height integrations. The areas were normalized to the total area of the on-scale peaks (all but cyclohexane). The normalized areas were then divided by molar correction factors, which were determined from known solution with benzene = 1.00, and the resulting areas were then used to determine the competitive data. Molar corrections factors (CF) for the cyclohexylated aromatics were estimated on the basis of the response of cyclohexylbenzene and the appropriate halobenzene or dihalobenzene from the following relation.



Cyclohexylation of Dihalobenzene in Competition with Benzene with Aromatic in Excess. The same procedure was used as in excess cyclohexane, but with the following amounts of reagents: 0.064 mol of dihalobenzene, 0.064 mol of benzene, 0.064 mol of cyclohexane, and 0.0064 mol of DTBP, as compared to 0.032 mol of the dihalobenzene, 0.032 mol of benzene, 0.320 mol of cyclohexane, and 0.0064 mol of DTBP, in excess cyclohexane.

The production of hydrogen halide was tested by opening the sealed tubes into a silver nitrate trap with an aspirator pulling on the other side of the trap. No precipitate formed in the silver nitrate solution, indicating that no hydrogen halide was produced in the reaction.

Synthesis of Authentic Cyclohexylated Aromatics. Both monohalo- and dihalocyclohexylbenzenes were synthesized by Friedel-Crafts cyclohexylation of the appropriate aromatic using cyclohexylchloride and aluminum chloride according to the method of Mayes and Turner.[18] The isomeric products were separated by preparative glpc on a Matronic 500 dual column instrument equipped with a 15 ft × 0.25 in. Carbowax 6000–Chromosorb W column. Sufficient quantities of each isomer could be isolated by this method for ir and retention time analysis. Infrared analysis was performed on a Beckman IR-8 spectrometer.

Synthesis of *tert*-Butyl Cyclohexyl Ether. The method of Lawesson and Yang was used.[19] Crude product was isolated by vacuum distillation (62–67°, aspirator pressure) and purified by preparative glpc on a 15 ft × 0.25 in. 15% Carbowax W column with column temperature 86°, injection point temperature 152°, detector temperature 140°, and carrier gas pressure 30 psi.

Other Authentics. Cyclohexanone and cyclohexanol were purchased from Matheson Coleman and Bell. Bicyclohexyl was obtained from Eastman Organics. All were used without purification.

Acknowledgment. We are grateful to the Goodyear Tire and Rubber Co. for partial support of this investigation.

Registry No.—*o*-$C_6H_4Cl_2$, 95-50-1; *o*-$C_6H_4Br_2$, 583-53-9; *p*-$C_6H_4Cl_2$, 106-46-7; *p*-$C_6H_4Br_2$, 106-37-6; C_6H_{12}, 110-82-7; C_6H_5Cl, 108-90-7; C_6H_5Br, 108-86-1.

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Stable Carbocations. CLXVIII.[1] Protonation and Cleavage of Dialkyl Pyrocarbonates in FSO_3H–SbF_5 (Magic Acid)–SO_2 Solution

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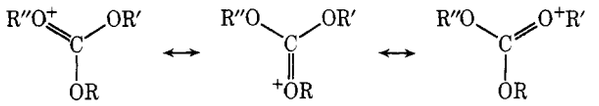
The protonation and cleavage reactions of dimethyl, diethyl, di-*n*-propyl, and diisopropyl pyrocarbonate in FSO_3H–SbF_5 (magic acid) solution have been studied by pmr and cmr spectroscopy. Cleveage products formed are protonated alkyl hydrogen carbonates, alkyl fluorosulfonates, and carbon dioxide. Di-*n*-propyl and diisopropyl pyrocarbonate give, in addition, a mixture of hexyl cations. In all cases small amounts of protonated carbonic acid and protonated alcohol were also formed. The mechanism of the cleavage reactions is discussed based on experimental data. Cmr parameters of dialkyl pyrocarbonates are also reported.

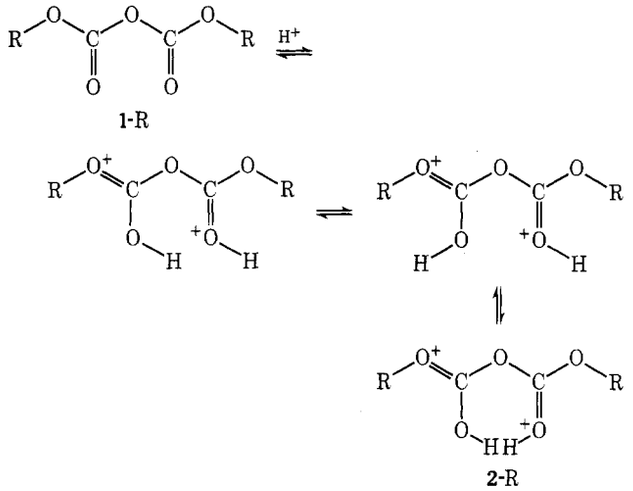
In the course of our investigation of heteroatom-substituted carbenium ions,[4] we have observed in FSO_3H–SbF_5 (magic acid) solution, by nmr spectroscopy, mono- (R = R′ = H), di- (R = H), and trialkoxycarbenium ions, including the parent ion (R = R′ = R″ = H).

Mono- and dialkoxycarbenium ions are formed by the



protonation of alkyl hydrogen carbonates and dialkyl hydrogen carbonates, respectively. Trialkoxycarbenium ions were first prepared by Meerwein by the alkylation of dialkyl carbonates and the acid cleavage of tetraalkyl orthocarbonates.[5]

We wish to report now the results of an attempt to prepare the related dications **2** by the protonation of dialkyl pyrocarbonates **1** in FSO_3H-SbF_5 (magic acid) solution under stable ion conditions.



1-R

2-R

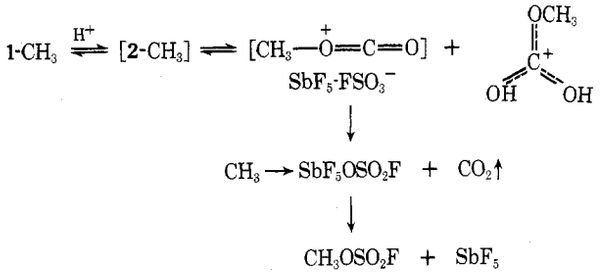
R = CH_3, C_2H_5, C_3H_7, i-C_3H_7

In addition, we wish to report the cmr spectra of the dialkyl pyrocarbonates studied. The structure of these compounds is of particular interest owing to recent reports concerning the biological consequences of the use of the enzyme inhibitor and bactericidal agent, diethyl pyrocarbonate, as a nuclease inhibitor.[6] Moreover, diethyl pyrocarbonate, a preservative in wines and beverages, has been found to react with ammonia to form carcinogenic urethan.[7-9]

Results and Discussion

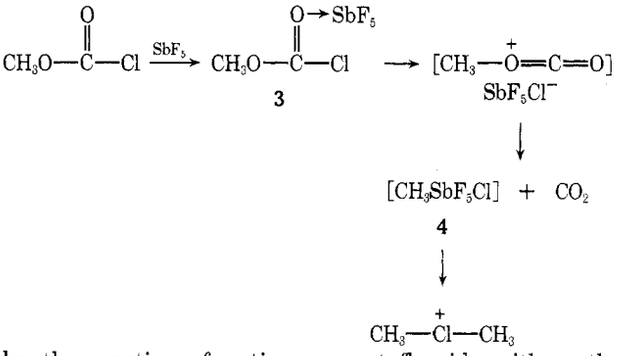
Dimethyl, diethyl, di-*n*-propyl, and diisopropyl pyrocarbonate were studied in FSO_3H-SbF_5-SO_2 at −78°. **Dimethyl pyrocarbonate** (**1**-CH_3) in 1:1 FSO_3H-SbF_5-SO_2 solution at −70° gave a pmr spectrum consisting of singlets at δ 12.9, 11.8, 11.4, 4.5, and 5.4. On standing at this temperature, the most deshielded signal moved upfield to approximately δ 10.5, while the signal at δ 5.4 increased in intensity until it almost reached that of the signal at δ 4.5 (3 H compared with each of the signals at δ 11.8 and 11.4). At −50°, an observed decrease in the signal at δ 5.4 was concurrent with the appearance and gradual increase of another signal at δ 4.3. Peak area integration indicated that the combined intensity of these two signals was equal to that of the singlet at δ 4.5. Ultimately the peak at δ 5.4 disappeared, so that the nmr spectrum of the final product consisted of peaks at δ 11.8 (1 H), 11.4 (1 H), 4.5 (3 H), and 4.3 (3 H) (excluding solvent acid peaks). The products were identified by the addition of authentic samples of assumed product ions to the reaction mixture: protonated methyl hydrogen carbonate (δ 4.5, 11.4, and 11.8) and methyl fluorosulfate (δ 4.3.). Also, a singlet at −31.0 ppm in the ^{19}F nmr spectrum of the sample confirmed the assignment of the latter signal (δ 4.3) to methyl fluorosulfonate.[10]

It is envisaged that the cleavage of dimethyl pyrocarbonate by FSO_3H-SbF_5 proceeds in the following way.

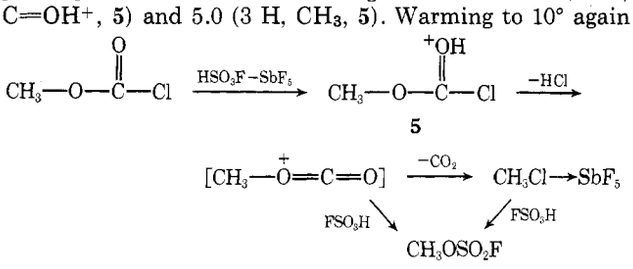


The structure of protonated dimethyl pyrocarbonate (**2**-CH_3) cannot be determined from the pmr data. Protonation most likely occurs on the carbonyl oxygen atoms, as in the case of protonated esters.[7,11] The data, however, show a rapid exchange process with the superacid system. Most likely it is the carbonyl diprotonated species which cleaves to give protonated methyl hydrogen carbonate. As in the case of cleavage of esters of primary alcohols by superacid, this cleavage is also probably of AAcl type. The signal at δ 5.4 does not arise from protonated methyl hydrogen carbonate, since its reported spectrum[12] shows a singlet for the methyl protons at δ 4.47. The reason that only one signal is observed in this region of the spectrum must be due to the methyl proton signal of the rapidly exchanging protonated dimethyl pyrocarbonate being coincident with the methyl proton reasonance of protonated methyl hydrogen carbonate in the early stages of the cleavage reaction. The above reaction was carried out below −50°, in order to avoid the decomposition of protonated methyl hydrogen carbonate to protonated methanol and carbon dioxide, a process which occurs above this temperature in FSO_3H-SbF_5-SO_2.

We propose that the singlet at δ 5.4 arises from methyl fluoroantimonate. This is suggested from results of our recent studies[13] carried out on the fragmentation reaction of methyl chloroformate with antimony pentafluoride. Initially two methyl proton signals at δ 5.10 and 5.28 are observed in the pmr spectrum of complex **3**, which is formed



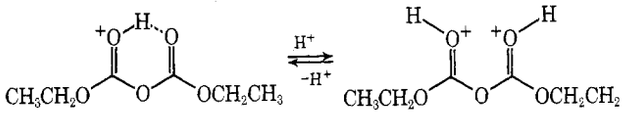
by the reaction of antimony pentafluoride with methyl chloroformate in SO_2ClF at −70°. These peaks were assigned to the cis and trans isomers. On warming to 10°, a peak at δ 5.7 appeared, which was assigned to methyl chlorofluoroantimonate (**4**). This compound reacts further according to the above scheme to give the dimethylchloronium ion. Methyl chloroformate also reacts with excess FSO_3H-SbF_5 in SO_2ClF at −70° to give a solution whose pmr spectrum consisted of singlets at δ 14.2 (1 H, C=OH^+, **5**) and 5.0 (3 H, CH_3, **5**). Warming to 10° again



results in the appearance of a transient signal at δ 5.7, followed by the appearance of a singlet at δ 4.4, which was shown to be due to methyl fluorosulfate. This behavior is analogous to that observed in the cleavage with FSO_3H–SbF_5 of dimethyl pyrocarbonate and confirms the proposed mechanism.

The pmr spectrum of a solution of **diethyl pyrocarbonate** in 1:1 *M* FSO_3H–SbF_5–SO_2 at −70° consisted of two quartets at δ 5.0 (2 H) and 4.9 (2 H), two triplets at δ 1.60 (3 H) and 1.52 (3 H), and two singlets at δ 11.28 (1 H) and 11.67 (1 H). Cleavage products were identified (by the addition of authentic products to the sample) as ethyl fluorosulfate and protonated ethyl hydrogen carbonate. In addition a triplet at δ 9.45 in the spectrum was attributed to the presence of protonated ethanol[14] (arising from acyl–oxygen cleavage of ethyl hydrogen carbonate), although the corresponding methyl and methylene proton signals were obscured by signals from the major products. This result contrasts with those from the cleavage of ethyl hydrogen carbonate with FSO_3H–SbF_5,[5] where alkyl–oxygen cleavage occurred and the *tert*-butyl cation and protonated carbonic acid were the observed products.

In FSO_3H–SO_2 protonated diethyl pyrocarbonate could be observed at −80°, before cleavage had occurred. The quartet at δ 4.05 (4 H) and the triplet at δ 1.00 (6 H) move downfield on protonation to δ 4.75 and 1.35, respectively. The species is undergoing rapid proton exchange with the acid medium because there is only one other signal in the spectrum at δ 11.2. The appearance of a single $=OH^+$ absorption could indicate either an intermolecularly rapidly exchanging monoprotonated species **6a**, a diprotonated species **6b**, or an equilibrium of the two. Both

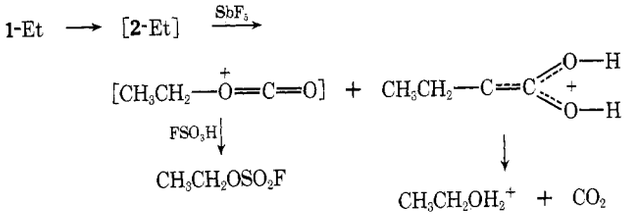


6a **6b**

would show equivalence of the two carbonyl groups. The smaller than expected deshielding of the $=OH^+$ absorptions compared with structurally related protonated carbonyl compounds would seem to indicate an equilibrating system. Pmr data, however, do not allow a clear differentiation (see, however, indication of subsequently discussed cmr studies). On the addition of SbF_5–SO_2ClF at −80°, cleavage of diethyl pyrocarbonate occurs immediately, as is evident from the appearance of peaks due to the two major products. Furthermore a quartet and triplet (decoupling experiments confirmed that they were part of the same molecule) were observed at δ 6.05 (2 H) and 1.8 (3 H). The combined intensity of these signals, together with those of ethyl fluorosulfate, was equal to that of the signals arising from protonated ethyl hydrogen carbonate. In analogy with the acid cleavage of dimethyl pyrocarbonate, these two deshielded signals were assigned to ethyl fluoroantimonate. The cleavage reaction of diethyl pyrocarbonate is thus (apart from alkyl–oxygen cleavage of the alkyl hydrogen carbonate) identical with that of dimethyl pyrocarbonate.

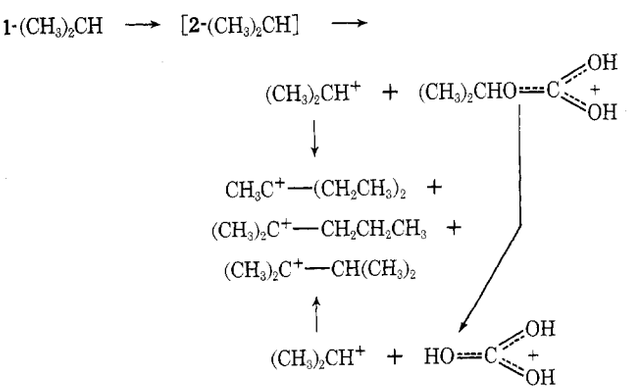
The proton-decoupled cmr spectrum of protonated diethyl pyrocarbonate in FSO_3H–SO_2 at −80°, recorded by the pulsed Fourier transform method, showed absorptions at $\delta(^{13}C)$ 12.8, 76.6, and 162.9. The latter signal was assigned to the carbonyl carbons, and indicated a downfield shift from the corresponding resonances in the precursor of 14.7 ppm. Slightly larger shifts in the carbonyl resonances of esters are observed upon their protonation (~20 ppm),[15] so that the above smaller value could possibly indicate that diethyl pyrocarbonate in FSO_3H–SO_2 is not completely protonated, but exists as a rapidly equilibrating mixture of monoprotonated and diprotonated species.

We also recorded the cmr spectrum of 1-CH_2CH_3 in FSO_3H–SbF_5–SO_2 at −80°, where peak area integration of the pmr spectrum indicated approximately 50% cleavage of the protonated diethyl pyrocarbonate. The major peaks in the cmr spectrum are at $\delta(^{13}C)$ 11.2, 12.8, 13.6, 14.2, 75.5, 77.3, 78.4, 89.5, 94.6, 124.8, 161.8, and 162.9. The products, identified by comparison with the cmr spectra of authentic samples of assumed product ions, were protonated diethyl pyrocarbonate [$\delta(^{13}C)$ 162.9, 77.3, 12.8], protonated ethyl hydrogen carbonate [$\delta(^{13}C)$ 161.8, 78.4, 12.8], ethyl fluorosulfonate [$\delta(^{13}C)$ 75.5, 13.6], and ethyl fluoroantimonate [$\delta(^{13}C)$ 94.6, 14.2]. The set of peaks at $\delta(^{13}C)$ 124.8, 89.5, and 11.2 may arise from the ethyl carboxonium ion, initially formed in the decomposition of protonated diethyl pyrocarbonate.



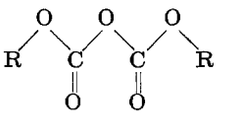
Protonated diisopropyl pyrocarbonate cleaves rapidly at −70° with the formation of a mixture of hexyl cations. (The formation of hexyl ions was established by ^1H nmr, based on comparison with the nmr assignments of these ions.)[16]

Also observed were two new peaks of equal area at δ 10.88 and 11.33 as well as the peak due to protonated carbonic acid. In addition, the methyl and methine regions became more complex, although it was impossible to resolve separate resonances. On allowing the reaction to proceed at −70° for an extended period of time, the δ 10.88 and 11.33 peaks in the –OH region disappeared and the resulting spectrum contained only absorptions corresponding to protonated carbonic acid and a mixture of tertiary hexyl cations. The new species appearing in the early stages of cleavage is assigned as protonated isopropyl hydrogen carbonate, which, like methyl hydrogen carbonate, would be expected to show two separate –OH resonances. The proposed mechanism for the cleavage is as follows.



If a solution of **di-*n*-propyl pyrocarbonate** in FSO_3H–SbF_5–SO_2 was allowed to stand for 24 hr at −80°, the final products, identified as above, were *n*-propyl hydrogen carbonate, dimethylisopropylcarbenium ion, and small amounts of protonated carbonic acid and 1-propanol. The nmr spectrum of the first species consisted of singlets at δ 11.17 (1 H) and 11.53 (1 H) due to the two nonequivalent –OH protons, a triplet at δ 4.83 (2 H) due

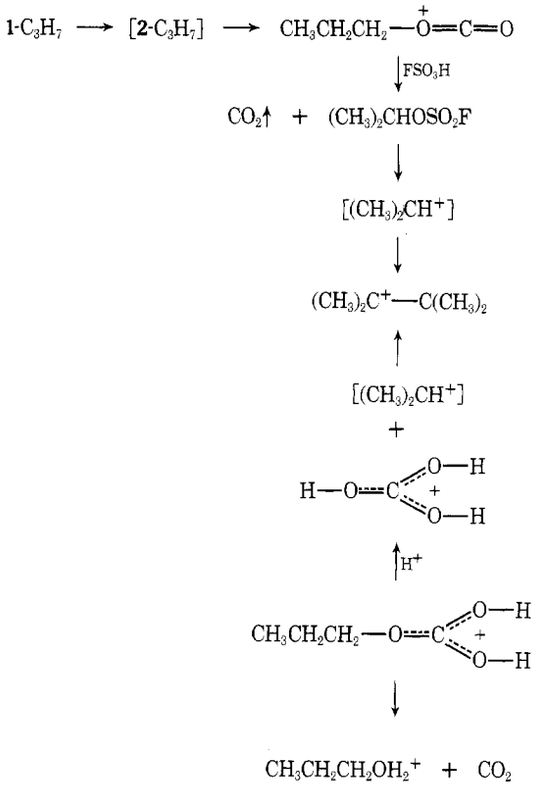
Table I
Carbon-13 Chemical Shifts in Dialkyl Pyrocarbonates[a]



R	C=O	C_α	C_β	C_γ
CH_3	147.9	58.3		
C_2H_5	148.2	66.3	14.1	
C_3H_7	148.0	71.4	21.6	10.4
i-C_3H_7	148.6	74.5	21.7	

[a] Parts per million from tetramethylsilane. Measured as neat liquid at ambient probe temperature (37°) from capillary of 60% ^{13}C-enriched methyl iodide (lock signal) and converted using $\delta(CH_3I)$ −18.5.

to the α-methylene protons, a multiplet centered at δ 1.92 (2 H) due to the β-methylene protons, and a triplet at δ 0.97 (3 H) arising from the methyl protons. Examination of the nmr spectrum during the course of the above cleavage showed that isopropyl fluorosulfate was an intermediate. This may result directly from alkylation of fluorosulfonic acid by protonated di-*n*-propyl pyrocarbonate, or it may involve the intermediacy of *n*-propyl carboxonium ion, although its presence was not detected during the course of the reaction. The cleavage reaction may be summarized as follows.



Carbon-13 Nmr Spectra of Dialkyl Pyrocarbonates. The proton-decoupled carbon-13 nmr spectra of dialkyl pyrocarbonates were obtained by the Fourier transform method on a Varian HA-100 nmr spectrometer, and the results are summarized in Table I. Assignments were made by the usual methods, which included "off-resonance" proton decoupling, the application of previously observed substituent effects, as well as symmetry and relative intensity considerations. The C_β and C_γ shieldings in Table I are similar to the *O*-alkyl β- and γ-carbon shieldings in aliphatic esters.[17] C_α shieldings, however, are deshielded 5.9–8.9 ppm from the corresponding absorptions in aliphatic esters.

The most notable feature of the data in Table I is the highly shielded carbonyl absorptions in dialkyl pyrocarbonates (approximately 25 ppm shielded from the ester carbonyl shifts). The carbonyl shieldings are very similar to those in the closely related carbonates.[13,18]

Experimental Section

Materials. All compounds used to generate the ions studied were either commercially available or were prepared by a standard literature method. Dialkyl pyrocarbonates were prepared by the reaction of Na_2CO_3 with alkyl chloroformates[19,20] or by treating *p*-toluenesulfonyl chloride with sodium methyl carbonate.[21] Alkyl hydrogen carbonates (as the sodium salts) were prepared from the reaction of carbon dioxide with the appropriate sodium alkoxide. The method used for the generation of the ions in HSO_3F–SbF_5–SO_2 has been described in detail in a previous paper.[22]

Proton Nmr Spectra. Pmr spectra were obtained using a Varian Associates Model A56/60A equipped with a variable-temperature probe. External tetramethylsilane (capillary) was used as reference.

Carbon-13 Nmr Spectra. Proton decoupled carbon-13 nmr spectra were obtained using a Varian Associates Model HA-100 nmr spectrometer equipped with a Fourier transform accessory (V-4357 Pulsing and Control Unit), broad-band proton decoupler, and variable temperature probe. The instrument, lock, and referencing systems have been described in more detail elsewhere.[23] The cmr spectra of protonated diethyl pyrocarbonate was obtained by the pulsed Fourier transform method, using a Varian Associates Model XL-100 nmr spectrometer.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—1-CH_3, 4525-33-1; 1-C_2H_5, 1609-47-8; 1-C_3H_7, 43086-15-3; 1-i-C_3H_7, 24425-00-1; magic acid, 23854-38-8.

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