According to the literature,[15] compound IV can be obtained from the reaction of 4-methyl-2-aminothiazole with 2,4-dinitrohalobenzene in ethanol and in the presence of sodium acetate. The melting point reported for the reaction product is 81 °C. Following this procedure, we were not able to obtain the described product. Instead the observed products (~90% yield) were 2,4-dinitrophenyl ethyl ether, unreacted DNFB and 4-methyl-2-aminothiazole, and 4-methyl-2-aminothiazolium 2,4-dinitrophenoxide.

X-ray Analysis. Preliminary lattice constants were obtained by least-squares methods from 25 reflections lying in the range $6° < \theta < 20°$. Relevant crystallographic data are summarized in Table V.[17] Intensity data were corrected for Lorentz and polarization effects but not for absorption.

For compound I 128 reflections with $F_o \le 5\sigma(F_o)$ were taken as unobserved, after data reduction. The space group was assigned from the systematic extinctions ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The structure was solved by direct methods and refined by full-matrix least-squares methods with the SHELX crystallographic program system.[16] The H atoms were geometrically positioned (assuming C–H = 1.08 Å). Isotropic refinement was performed for all nonhydrogen atoms, except for the S and C_2 atoms and the NO_2 groups. The weighting scheme was $4.27/[\sigma(Fo)^2 + 0.000092F_o^2]$. The final conventional agreement index was 0.048.

For compound IV the same procedure as described for I was used (see Table V). In this case the first map with $E \ge 1.2$ gave an unsatisfactory structure, as two molecules were present in the asymmetric unit. With $E = 1.1$, the position of the atoms was clearly revealed and a preliminary refinement allowed identification of some hydrogen atoms (H_{01B}, see Figure 2). The other hydrogen atoms were geometrically positioned by subsequent refinement. For these hydrogen atoms only, a thermal parameter was used, while all the nonhydrogen atoms were refined by isotropic U values, except for the S atom and the nitro groups. The weighting scheme was $2.93/[\sigma(F_o)^2 + 0.00053F_o^2]$ and the final conventional agreement index was 0.068.

Acknowledgment. We thank Professor G. Valle (University of Padova) for the diffractometer measurements. This work was carried out with the financial assistance of the CNR (Roma).

Registry No. I, 77825-94-6; II, 77825-95-7; III, 77825-96-8; IV, 68557-42-6; V, 77825-97-9; 2-(*sec*-butylamino)thiazole, 1438-44-4; 2-aminothiazole, 96-50-4; 4-methyl-2-aminothiazole, 1603-91-4; DNFB, 70-34-8.

Supplementary Material Available: Tables I–XI consisting of physical and spectral data, bond lengths and angles, data collection information, fractional and thermal parameters (13 pages). Ordering information is given on any current masthead page.

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[15] S. P. Gupta and S. Rani, *J. Indian Chem. Soc.*, **55**, 730, (1978).

[16] G. M. Sheldrick, "SHELX 76", University of Cambridge, Cambridge, England, 1976.

[17] Supplementary material.

Alkoxycarbenium Ions. Relative Thermodynamic Stabilities via Pairwise Equilibrations[1a,b,2]

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Alkoxycarbenium ions were synthesized by direct O-alkylation of the corresponding carbonyl compounds with trimethyloxonium ion salts and methyl fluorosulfate. The thermodynamic stabilities of the alkoxycarbenium ions were determined by stepwise equilibrations of pairs of these ions via transalkylation with the corresponding carbonyl compounds in liquid sulfur dioxide as monitored by ^1H NMR. The structures, spectra, and stabilities of alkoxycarbenium ions have been compared with those of the corresponding hydroxycarbenium ions. In general, the relative stability order for alkoxycarbenium ions parallels the order of stabilities for the corresponding hydroxycarbenium ions.

Alkoxycarbenium ions (or carboxonium ions), **1**, have been postulated as intermediates in a vast number and variety of organic reactions.[3-18] Oxonium ion chemistry has been the subject of a text[19] and a review.[20] The chemistry of structurally related species has also been reviewed.[21-27]

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[1] (a) Taken in part from the Ph.D. dissertation of C.R.G., University of Arkansas, Fayetteville, AR, 1978. (b) Presented in part at the 27th–31st Southeast–Southwest Combined Regional Meeting of the American Chemical Society, Memphis, TN, Oct 31, 1975, Abstract No. 461. (c) Present address: Michigan Molecular Institute, 1910 W. St. Andrews, Midland, MI 48640.

[2] Preliminary communication: Quirk, R. P.; Gambill, C. R. *J. Chem. Soc., Chem. Commun.* **1974**, 503.

[3] Streitwieser, A., Jr. "Solvolytic Displacement Reactions", McGraw-Hill: New York, 1962; p 103.

[4] Dusseau, C. H. V.; Schaafsma, S. E.; deBoer, T. J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 535.

[5] Cordes, E. H. *Prog. Phys. Org. Chem.* **1967**, *4*, 1.

[6] Cordes, E. H.; Bull, H. G. *Chem. Rev.* **1974**, *74*, 581.

[7] Patai, S., Ed.; "The Chemistry of the Ether Linkage"; Interscience: New York, 1967; p 309.

[8] Young, P. R.; Bogseth, R. C.; Rietz, E. G. *J. Am. Chem. Soc.* **1980**, *102*, 6268.

[9] Sheldon, R. A.; van Doorn, J. A. *Tetrahedron Lett.* **1973**, 1021.

[10] Deno, N. C.; Billups, W. E.; Kramer, K. E.; Lastomirsky, R. R. *J. Org. Chem.* **1970**, *35*, 3080.

[11] Olah, G. A.; Parker, D. G., Yoneda, N.; Pelizza, F. *J. Am. Chem. Soc.* **1976**, *98*, 2245.

[12] Ward, H. R.; Sherman, P. D. *J. Am. Chem. Soc.* **1967**, *89*, 4222; *1968*, *90*, 3812.

[13] Begue, J. P.; Charpentier-Morize, M.; Pardo, C. *Tetrahedron* **1975**, *31*, 1919, 2505.

[14] Smith, L. E. H.; Mohr, L. H.; Raftery, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 7494.

[15] Dunn, D. M.; Bruice, T. C. *Adv. Enzymol.* **1973**, *37*, 1.

[16] Ryono, D. E.; Loudon, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 1889, 1900.

[17] Olah, G.; Yoneda, N.; Parker, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 2251, 7341.

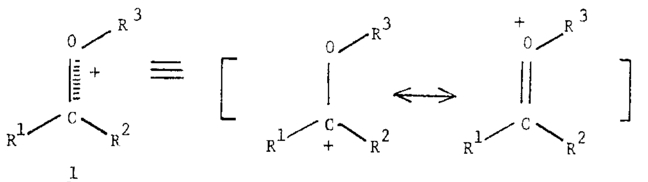
[18] Nakai, T.; Wada, E.; Okawara, M. *Tetrahedron Lett.* **1975**, 1531.

[19] Perst, H. "Oxonium Ions in Organic Chemistry"; Academic Press: New York, 1971.

[20] Perst, H. In "Carbonium Ions"; Olah, G. A., and Schleyer, P. v. R. Eds.; Wiley-Interscience: New York, 1976; Vol. V.

[21] Pittman, C. U.; McManus, S. P.; Larsen, J. W. *Chem. Rev.* **1972**, *72*, 357.

[22] Granik, V. G.; Pyatin, B. M.; Glushkov, R. G. *Russ. Chem. Rev. (Engl. Transl.)* **1971**, *40*, 747.



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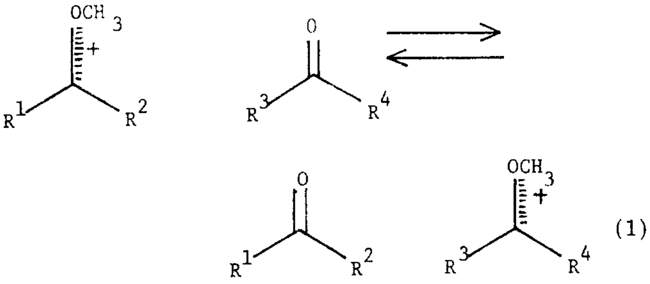
Despite the synthetic, mechanistic, and theoretical importance of alkoxycarbenium ions, little information is available regarding their thermodynamic stabilities in solution.[28,29] Since alkoxycarbenium ions can be generated and characterized in "superacid" media[23,30-33] as well as isolated and characterized as relatively stable salts,[26,34] these ions provide a unique opportunity to investigate the relationship between structure, stability, and reactivity for carbocation intermediates.

In general, a variety of kinetic and thermodynamic methods have been utilized to determine the stabilities of carbocation intermediates in solution. One of the least ambiguous methods involves the equilibration of pairs of carbocations with their covalent precursors; for example, Freedman and co-workers[35,36] have determined the relative stabilities of trityl cations using this procedure. An analogous equilibration method[37] was sought to measure the relative thermodynamic stabilities of carboxonium ions. Since it was known that carboxonium ions and related species are quite reactive as alkylating agents with nucleophiles,[19,20] it was deduced that equilibration of alkoxycarbenium ions might be effected by mixing a carbonyl base with an alkoxycarbenium ion (eq 1). Herein we report the results of equilibration studies of alkoxycarbenium ions with carbonyl bases.

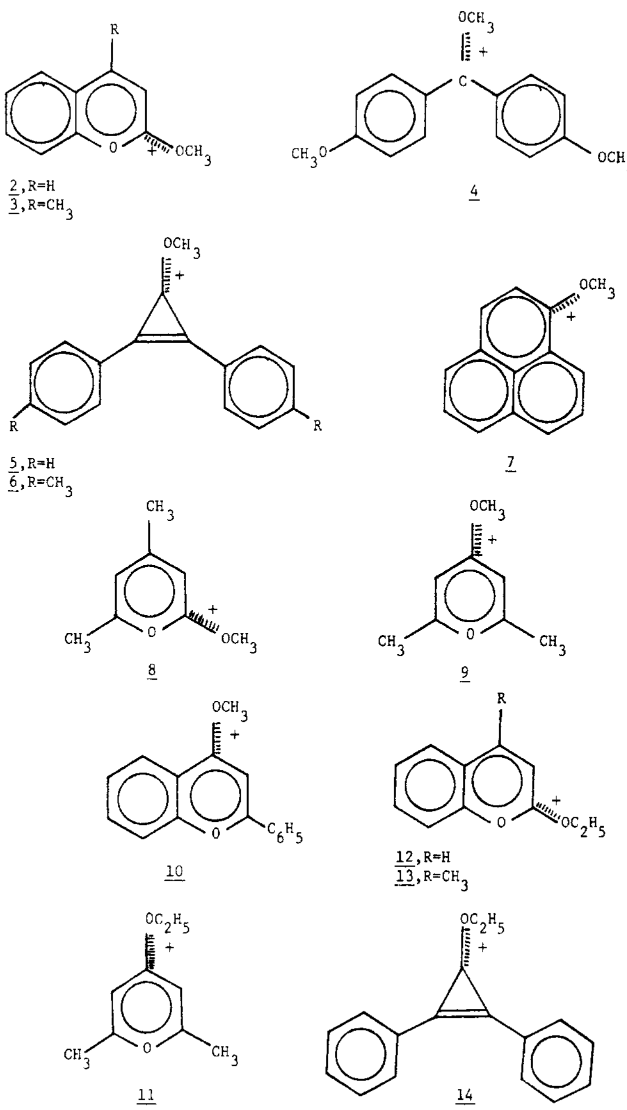


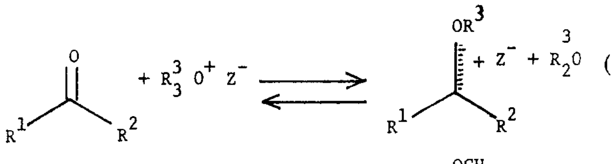
(1)

Results and Discussion

Alkoxycarbenium Ion Syntheses. The required alkoxycarbenium ions (2–14, Chart I) were all readily prepared by direct O-alkylation of the corresponding carbonyl bases using trialkyloxonium ion salts (eq 2; $R^3 = C_2H_5$, CH_3) or methyl fluorosulfate (eq 3). However, the direct

Chart I





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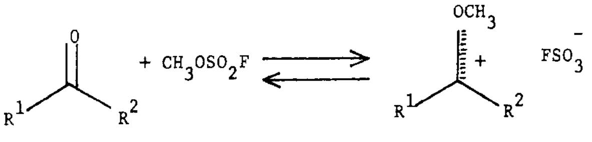

(3)

O-alkylations of xanthone, 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one, and 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one with triethyloxonium tetrafluoroborate were not observed, presumably because of steric interference from the peri hydrogens. ^1H NMR spectroscopy was conveniently used to monitor the alkylation reaction since downfield shifts of 0.19–1.42 ppm were observed for each resonance absorption, relative to the corresponding absorption in the parent carbonyl, upon formation of the alkoxycarbenium ion.

The BF_4^- salts were generally easier to prepare and handle, while the PF_6^- salts (e.g., the derivatives of coumarin and diphenylcyclopropenone) tended to fume in air

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[23] Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.

[24] Olah, G. A.; Schleyer, P. v. R., Eds. "Carbonium Ions"; Wiley-Interscience: New York, 1968–1976; Vol. I–V.

[25] Paulsen, H.; Behre, H.; Herold, C. P. "Fortschritte der Chemischen Forschung"; Springer-Verlag: West Berlin and Heidelberg, 1970; Band 14, Heft 4, p 473.

[26] Meerwein, H. In "Methoden der Organischen Chemie (Houben-Weyl)"; Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1965; Auflage 4, Bd VI/3, Sauerstoffverbindungen I, p 325.

[27] Alder, R. W. *Chem. Ind. (London)* **1973**, 983.

[28] Gas-phase data for a variety of ions are available. See for example: Kebarle, P. *Annu. Rev. Phys. Chem.* **1977**, *28*, 445.

[29] The heats of formation of oxolan-2-ylium ions generated from unsaturated ketones in strong acid media have been measured. See: Larsen, J. W.; Ewing, S. *J. Am. Chem. Soc.* **1971**, *93*, 5107.

[30] Olah, G. A.; White, A. M.; O'Brien, D. H. *Chem. Rev.* **1970**, *70*, 561.

[31] Ramsey, B. G.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 3058.

[32] Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2993.

[33] Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801.

[34] Kabuss, S. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 675.

[35] McKinley, S. V.; Rakshys, J. W.; Young, A. E.; Freedman, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 4715.

[36] Freedman, H. H. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds., Wiley: New York, 1973; Vol. IV, pp 1501.

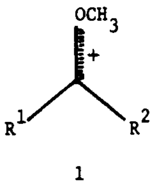
[37] Wong, C.; Jackman, L. M.; Portman, R. G. *Tetrahedron Lett.* **1974**, 921.

and were insoluble in either liquid SO$_2$ or trifluoroacetic acid. The FSO$_3^-$ salts were very simple to prepare, but they were very difficult to handle because they were hygroscopic and readily decomposed.

Characterization of Alkoxycarbenium Ion Salts. In addition to elemental analyses, various spectroscopic methods were used to characterize the alkoxycarbenium ion salts (see Table I). Infrared spectra were especially useful for assessing the purity of salts via analysis of the carbonyl region to detect unreacted carbonyl base. Mulls (Kel-F or Nujol) were used to obtain infrared spectra because initial experiments using solid-state sampling in KBr pellets produced only the spectrum of the starting carbonyl compound; analogous observations have been reported by Ramsey and Taft.[31] In all cases, the characteristic absorptions of the associated anions (BF$_4^-$, PF$_6^-$, or FSO$_3^-$) were observed. The characteristic infrared frequencies for the isolated alkoxycarbenium ion salts are listed in Table I.

Ultraviolet spectra of the alkoxycarbenium ion salts were recorded in acetonitrile[38] in order to obtain information about their electronic structure and for comparison with the analogous hydroxycarbenium ions. The available electronic absorption data are summarized in Table I. There is an excellent correspondence between the alkoxycarbenium ion data and the published spectra for the analogous carbonyl bases in 96% sulfuric acid.[41] In general, the ultraviolet absorption bands for the carboxonium ions were relatively insensitive to the nature of the counterion as shown by the data in Table I for carboxonium ion salts **8** and **9**.

^{1}H NMR spectra of the alkoxycarbenium ion salts were readily obtained in trifluoroacetic acid or in liquid sulfur dioxide. These spectra provided a principal means of characterizing the alkoxycarbenium ions. In general, the methyl group resonances ($R^+\cdots OCH_3$) for different alkoxycarbenium ions (see Table I) were sufficiently sensitive to structural factors so that distinct, sharp signals could be observed for each ion. In addition, the chemicals shifts were relatively insensitive to solvent variation as shown by the data for the ions **11**, **12**, and **5** in Table IV (available as supplementary material). Initial studies with ethyl derivatives prepared from carbonyl bases and triethyloxonium ion salts were abandoned early on in our research, because in contrast to the methyl derivatives the ethyl group resonances for pairs of ions overlapped considerably.



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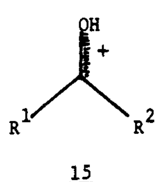

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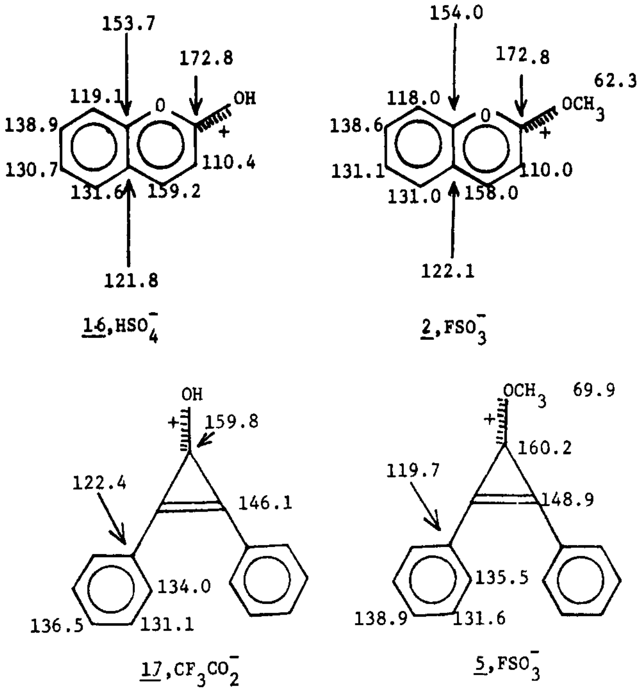
Chart II. Carbon-13 NMR Chemical Shifts (ppm) for Alkoxycarbenium Ions vs. those for Hydroxycarbenium Ions



16, HSO$_4^-$

2, FSO$_3^-$

17, CF$_3$CO$_2^-$

5, FSO$_3^-$

In order to obtain further information about structural differences between methoxycarbenium ions (**1**) and the corresponding hydroxycarbenium ions (**15**) as noted with the UV data, we determined the ^{13}C NMR spectra of the methyl fluorosulfate derivatives of 1,2-diphenylcyclopropenone and coumarin as well as the spectrum of 1,2-diphenylcyclopropenone in trifluoroacetic acid and compared these data with the data for protonated coumarin in 96% sulfuric acid.[42] The results are shown in Chart II. Considering the expected differences in solvation between these two types of carbenium ions, it is noteworthy that the ^{13}C NMR chemical shifts of the hydroxycarbenium ions are in good agreement with the shifts for the corresponding methoxycarbenium ions. The average deviations in chemical shift differences between all carbons in the hydroxy- vs. the methoxycarbenium ion are 0.7 and 2.2 ppm for the coumarin and diphenylcyclopropenone systems, respectively. In terms of the Spiesecke–Schneider relationship (160 ppm/electron of charge)[43-45] these deviations would correspond to small differences in charge distributions between these two types of ions, although solvent and counterion effects are important variables also.

Equilibration Studies. The success of our equilibration procedure for carboxonium ions (eq 1) depends on their facility in undergoing reversible alkyl group transfers with carbonyl bases in solution. Our initial studies involved preliminary equilibration experiments using various ethoxycarbenium ions (**11**,[47] **12**, **13**, and **14**[46]) and the corresponding carbonyl bases in acetonitrile and nitromethane. The following conclusions were drawn from these experiments: (a) alkyl transfer readily occurs between carbonyl compounds in solution; (b) equilibration could be established from either direction; (c) ^{1}H NMR methodology can be used to monitor these equilibrations; (d) decomposition and other complications are readily observed. Practical considerations led to the use of methoxycarbenium ion salts and liquid SO$_2$ as the solvent. The methoxycarbenium ion salts exhibited sharp ^{1}H NMR methyl resonances which were very useful in characterizing

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(38) Carboxonium ions gradually decompose after several hours in acetonitrile (see ref 31, 39, 40).

(39) Kevill, D. N.; Meichia, G.; Lin, L.; Wang, A. *Tetrahedron* **1980**, *36*, 715.

(40) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627.

(41) Filipescu, N.; Chakrabarti, S. K.; Tarassoff, P. G. *J. Phys. Chem.* **1973**, *77*, 2276.

(42) Sojka, S. A. *J. Org. Chem.* **1975**, *40*, 1175.

(43) Martin, G. T.; Martin, M. L.; Odiot, S. *Org. Magn. Reson.* **1975**, *7*, 2.

(44) Farnum, D. G. *Adv. Phys. Org. Chem.* **1975**, *11*, 123.

(45) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468; *J. Chem. Phys.* **1961**, *35*, 722.

(46) Breslow, R.; Eicher, T.; Krebs, A.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1320.

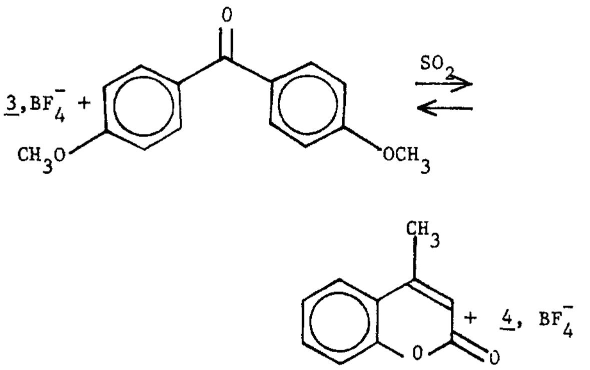
(47) Meerwein, H.; Hinz, G.; Hofman, P.; Kronig, E.; Pfeil, E. *J. Prakt. Chem.* **1937**, *147*, 257.

Table I. Physical and Spectroscopic Characterization of Alkoxycarbenium Ion Salts[a]

compd	mp, °C	characteristic bands: UV (CH_3CN) λ_{max}, nm (log ϵ)	characteristic bands: IR (Kel-F, Nujol), cm^{-1}	$R\overset{+}{-}OCH_3$ ^1H NMR chemical shifts, δ
2,BF_4^-	121-122 dec	317 (4.09), 243 (3.86), 238 (3.87)	1630, 1600, 1540, 1375, 1040, 830, 750	4.68[b]
2,PF_6^-	97		930, 880-800	insoluble
3,BF_4^-	163-164 dec	311 (4.13), 241 (4.01), 238 (4.01)	1600, 1550, 1525, 1500, 1450, 1030, 855, 790	4.57[b]
3,FSO_3^-	126-127		1630, 1595, 1510, 1300-1260, 1070, 920, 789, 720, 550-450	
5,BF_4^-	202-203	304 (sh), 297 (4.40), 285 (sh)	1885, 1585, 1500, 1100-1000, 765, 680	4.83[b]
5,PF_6^-	176-178 dec		1880, 1590, 1500, 1030, 880-800	insoluble
6,BF_4^-	197-198		1055, 815	4.88[c]
10,BF_4^-	210-211	350 (4.97), 282 (4.02), 258 (4.24)	1620, 1600, 1480, 1460, 1420, 1250, 1200, 1020-1090, 950, 850, 840, 775, 680	4.58[b]
7,BF_4^-	202-203	408 (3.76), 361 (3.70), 218 (4.96)		4.57[b]
8,BF_4^-	173-174	293 (3.96), 214 (3.36)	1250, 1020, 620	4.38[c]
8,PF_6^-	159-161 dec	294 (3.81), 214 (3.13)	1660, 1530, 1260, 900-800	4.52[c]
8,FSO_3^-	109-111 dec	293 (3.94), 214 (3.24)		4.57
9,BF_4^-	174-175	259 (4.08), 246 (4.13)	1665, 1550, 1500, 1410, 1210, 1175, 1020-1070	4.18[b]
9,PF_6^-	171-172		1665, 1210, 1170, 900-800	4.27[c]
9,FSO_3^-	166-168	255 (4.11), 244 (4.16)	1645, 1540, 1500, 1300-1110, 1070, 940, 885, 700	4.27[c]

[a] Satisfactory analytical data (±0.4% for C, H) were reported for all new compounds listed in the table except as noted. Several carboxonium ion salts were too unstable to provide satisfactory analytical data after transit. These salts were as follows: **2**,PF_6^-; **5**,PF_6^-; **6**,BF_4^-; **8**,FSO_3^-; **3**,FSO_3^-; **9**,PF_6^-; **9**,FSO_3^-. Analytical data available as Table V in supplementary material. [b] NMR spectrum for sample in liquid SO_2. [c] NMR spectrum for sample in CF_3CO_2H.

the ions (see Table I for a tabulation of these methyl peak absorptions) and quantitatively identifying them in equilibration mixtures. Thus, the ^1H NMR spectra of equilibrating systems could be interpreted in terms of the separate resonances for all four species in solution. The equilibrations proceeded to completion over a period of days or weeks; methyl transfer was slow on the NMR time scale, and distinct resonance signals were observed for each equilibrating species (independently synthesized and characterized). A representative example of an equilibration experiment is the reaction of the methoxycarbenium ion of 4-methylcoumarin (**3**,BF_4^-) with 4,4′-dimethoxybenzophenone in liquid SO_2 (eq 4; the initial and final ^1H NMR spectra for this equilibration experiment are available in Figures 1 and 2, respectively, as supplementary material). The methyl singlet resonances at δ 2.4 and 2.9 for 4-methylcoumarin and its methoxycarbenium ion, respectively, provided their concentration ratios. The methoxy singlets on the aromatic ring at δ3.83 and 3.97 for 4,4′-dimethoxybenzophenone and its methoxycarbenium ion, respectively, were used to monitor their relative concentrations. The reverse equilibration starting with the oxonium ion of 4,4′-dimethoxybenzophenone (**4**,BF_4^-) and 4-methylcoumarin could not be investigated because an analytically pure sample of this substituted



(4)

Table II. Average Equilibrium Constants for Equilibration of Pairs of Alkoxycarbenium Ions with the Corresponding Carbonyl Bases in Liquid SO_2[a]

entry	equilibration pair	av equilib constant (K_{eq})
1	**2** + 4-methylcoumarin	5.9 ± 1
2	**2** + 4,4′-dimethoxybenzophenone	1.2 ± 0.1[b]
3	**3** + 4,4′-dimethoxybenzophenone	0.15 ± 0.03
4	**3** + diphenylcyclopropenone	436 ± 277
5	**5** + bis(4-methylphenyl)cyclopropenone	4.8 ± 1.6
6	**6** + 4,6-dimethyl-α-pyrone	1.9 ± 0.8
7	**8** + 2,6-dimethyl-γ-pyrone	complete transfer
8	**9** + perinaphthenone	no transfer[b]

[a] Equilibria at 25 °C approached from both forward and reverse directions, where possible. [b] Equilibrium approached in forward direction only.

Table III. Relative Stabilities of Alkoxycarbenium Ions and Hydroxycarbenium Ions

carbonyl base	methoxycarbenium ion stability, $-\Delta(\Delta G)_{eq}$,[a] kcal/mol	hydroxycarbenium ion stability pK_a[b]	 $-\Delta(\Delta G)_{pK}$,[c] kcal/mol	 $-\Delta(\Delta H_p)$,[b] kcal/mol
coumarin	0[d]	4.8	0[d]	0[d]
4,4′-dimethoxybenzophenone	0.11 ± 0.03	4.4	0.55	
4-methylcoumarin	1.05 ± 0.01			
diphenylcyclopropenone	4.6 ± 0.41	2.5	3.10	4.3
bis(*p*-methylphenyl)cyclopropenone	5.6 ± 0.40			
4,6-dimethyl-α-pyrone	6.0 ± 0.20	3.78[e]		
2,6-dimethyl-γ-pyrone	ca. 9	−0.40	7.10	11.8

[a] This work; 25 °C. See Table II for equilibrium constants. Entry 2 in Table II was used for 4,4′-dimethoxybenzophenone. [b] See ref 52. $-\Delta(\Delta H_p)$ represents the heat of protonation of the base in FSO_3H. [c] Calculated from the pK_a values by using coumarin as the reference zero. [d] Arbitrarily chosen point of reference. [e] Tolmachev, A. I.; Shulezhko, L. M.; Kisilenko, A. A. *J. Gen Chem. USSR* (*Engl. Transl.*) **1968**, *38*, 117.

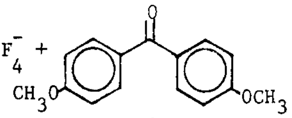
benzophenone carboxonium ion could not be prepared.

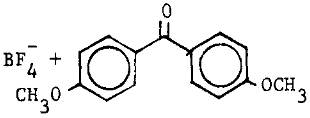
The equilibrium constant (K_{eq}) for each equilibration (eq 5) was calculated by using the concentration ratios for

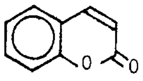
$$RCH_3^+ + R_o \overset{K_{eq}}{\rightleftharpoons} R + R_oCH_3^+ \qquad (5)$$

each carbonyl/methoxycarbenium ion pair as determined by ^1H NMR integration. A summary of all of the average equilibrations constants obtained in this work is shown in Table II. These data represent not only the average values for several independent equilibration runs but also the average of equilibrium constant values determined for both the forward and reverse processes, where possible.

A check for the internal consistency of this pairwise equilibration procedure can be obtained from the equilibrations of 4,4′-dimethoxybenzophenone with the carboxonium salts of both coumarin and 4-methylcoumarin; these equilibrations are represented in eq 6, 7, and 8.

$\underline{3}, BF_4^-$ +

$K_4 = 0.15 \pm 0.03$ (6)

$\underline{2}, BF_4^-$ +

$K_6 = 1.2 \pm 0.1$ (7)

$\underline{3}, BF_4$ +

$K_7 = 0.15 \pm 0.03$ (8)

From these equations it follows that $K_4/K_6 = K_7$; the value of K_7 calculated from K_4/K_6 is 0.12 which is in good agreement with the measured value of 0.15 ± 0.03.

The major limitation in application of this equilibration method for determining the relative stabilities of methoxycarbenium ions is the problem of finding suitable pairs of carbenium ions whose stabilities are close enough to allow ^1H NMR determination of their concentrations. For example, the equilibrium constant calculated for the 4-methylcoumarin/1,2-diphenylcyclopropenone system has an average value of 436 ± 277. The large data spread is due in part to the magnitude of the equilibrium constant. This equilibration system is at the limit of our ^1H NMR method of analysis. Similar limitations have been noted by Freedman and co-workers[35,36] for equilibrations of trityl carbenium ions. In several systems either no methyl transfer was observed or transfer was complete. These results are also shown in Table II.

Relative Stabilities of Carboxonium Ions. The principal data which are used as an index of carbenium ion stabilities are the kinetics of reactions which involve formation of these intermediates in the rate-determining step. The limitations of stability–reactivity relationships have been demonstrated by a number of studies.[48–51] The equilibration method described herein provides an opportunity to explore structure–stability relationships for a variety of alkoxycarbenium ions. The results of the present studies are shown in Table III. These results provide a limited but useful scale of methoxycarbenium ion stabilities with which to compare other methoxycarbenium ions. Also listed in Table III are proton basicities of these carbonyl bases (pK_a) determined by the Hammett acidity function method, the corresponding free energy differences [$\Delta(\Delta G)_{pK}$], and their heats of protonation in fluorosulfuric acid[52] [$\Delta(\Delta H_p)$] which provide measures of the relative stabilities of the corresponding hydroxycarbenium ions (14). The similarity between the equilibration results (carbon basicity)[53] and the equilibrium proton basicities further document the inference deduced from the spectroscopic data reported herein that alkoxycarbenium ions are reasonable models for hydroxycarbenium ions.

Experimental Section

General Methods. Melting points were obtained in sealed tubes by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained by using a Perkin-Elmer Model 337 grating spectrophotometer, and ultraviolet-visible spectra were obtained by using a Cary-14 spectrophotometer. Proton NMR spectra were determined on a Varian A-60 (60 MHz) spectrometer; chemical shifts are reported in parts per million downfield from internal tetramethylsilane (Me_4Si). Coupling constants are reported in hertz. The ^{13}C NMR spectra were recorded in the pulse Fourier transform mode on a Varian XL-100 spectrometer operating at 25.2 MHz and using a 400-ppm sweep width; this instrument utilized an external ^{19}F lock, and the probe temperature was 40 ± 2 °C. For ^{13}C spectra, trifluoroacetic acid was used as the solvent, and chemical shifts are reported in parts per million downfield from internal Me_4Si. Elemental analyses were performed by Chemalytics, Inc.

All reactions involving oxonium ions were conducted under an atmosphere of dry nitrogen or argon. Schlenk-type glassware and standard techniques[54] were used to prepare and purify the oxonium compounds.

Materials. Methylene chloride, acetonitrile, pentane, nitromethane, toluene, and 1,2-dimethoxyethane were purified as described by Perrin, Armarego, and Perrin.[55] Diethyl ether was

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(48) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1978**, *100*, 2930.

(49) Diffenbach, R. A.; Sano, K.; Taft, R. W. *J. Am. Chem. Soc.* **1966**, *88*, 4747.

(50) Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170.

(51) Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755.

(52) Arnett, E. M.; Quirk, R. P.; Larsen, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 3977.

(53) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley-Interscience: New York, 1975.

(54) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; pp 145.

distilled from lithium aluminum hydride and passed through 3A molecular sieves prior to use. Each carbonyl compound was dried overnight under vacuum prior to use in oxonium ion synthesis.

Coumarin (Eastman), 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (Aldrich), 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclopenten-5-one (Aldrich), 4,4′-dimethoxybenzophenone (Aldrich), 2,6-dimethyl-γ-pyrone (Aldrich), flavone (Aldrich), methyl fluorosulfate (Aldrich), perinaphthenone (Aldrich), trimethyloxonium hexafluorophosphate (Cationics), and xanthone (Aldrich) were used as received after spectroscopic characterization (NMR, IR). Acetophenone (Baker) was distilled prior to use. Diphenylcyclopropenone [mp 120.5–121.5 °C (lit.[46] mp 119–120 °C)] and 1,2-diphenyl-3-ethoxycyclopropenyl tetrafluoroborate [mp 185–186 °C (lit.[46] mp 195–196 °C)] were synthesized by the method of Breslow et al.[46] Bis(*p*-methylphenyl)cyclopropenone [mp 175–176 °C (lit.[56] mp 176–177 °C)] was prepared according to the procedure of Eicher and Hansen.[56] 4,6-Dimethyl-α-pyrone [mp 49–50 °C (lit.[57] mp 50–51 °C)] was prepared by decarbonylation of coumalic acid according to the method of Smith and Wiley.[57] 4-Methylcoumarin [mp 82–83 °C (lit.[58] mp 83–84 °C)] was prepared from phenol and ethyl acetoacetate by the method of Woodruff.[58] 4-Ethoxy-2,6-dimethylpyrylium tetrafluoroborate [mp 90–91 °C (lit.[47] mp 90–91 °C)] was synthesized by the method of Meerwein et al.[47] Triethyloxonium tetrafluoroborate was prepared by the method of Meerwein.[59] Trimethyloxonium tetrafluoroborate was prepared according to the procedure of Curphey.[60]

Carboxonium Ion Synthesis. Carboxonium ion derivatives of the carbonyl bases were prepared by reaction of trialkyloxonium tetrafluoroborate salts with the carbonyl bases in an inert atmosphere. A typical procedure for alkylation of coumarin is illustrated below. To a Schlenk vessel protected from light and charged with 1.21 g (7.58×10^{-3} mol) of trimethyloxonium tetrafluoroborate was added a solution of 1.40 g (9.58×10^{-3} mol) of coumarin in 25 mL of CH_2Cl_2. The mixture was stirred for 48 h, and then 20 mL of diethyl ether was added to precipitate the pyrylium salt **2**. The collected solid was washed successively with CH_2Cl_2 (20 mL) and diethyl ether (2 × 20 mL) and was then dried in vacuo to yield 1.38 g (73%) of **2** as a white solid, mp 121–122 °C dec.

Anal. Calcd for $C_{10}H_9O_2BF_4$: C, 48.43; H, 3.66. Found: C, 48.42; H, 3.64.

Physical property data for all of the oxonium ions prepared in the course of this research are listed in Table I. All carboxonium ions were characterized by elemental analyses (supplementary material available), infrared spectra, ultraviolet–visible spectra, and ^1H NMR spectra.

Equilibrations. The carbonyl base (ca. 0.1 mol) was added under a blanket of dry nitrogen to an NMR tube which contained a weighed amount (ca. 0.1 mol) of an alkoxycarbenium ion salt; the solvent (generally SO_2) was condensed into the tube (ca. 0.5 mL). After being thoroughly degassed, the NMR tube was sealed under vacuum. The equilibration at 25 °C was monitored by periodic ^1H NMR observations; when the ratio of appropriate resonance signals was constant with time, it was judged that equilibrium had been established. In general, side products were not observed by ^1H NMR during these equilibrations. When small, extraneous peaks were observed, their presence did not seem to affect the calculated equilibration constants as deduced from the reproducibility obtained for several runs. Complete equilibration required several days to weeks, depending on the equilibration system. Between 8 and 15 consecutive electronic integrations per sample were utilized to determine the relative concentrations of the various species present in solution.

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Registry No. **2** BF_4^-, 77902-74-0; **2** PF_6^-, 77902-75-1; **2** FSO_4^-, 77902-76-2; **3** BF_4^-, 77902-78-4; **3** FSO_4^-, 77902-79-5; **5** BF_4^-, 77902-57-9; **5** PF_6^-, 77902-58-0; **5** FSO_3^-, 66633-47-4; **6** BF_4^-, 77902-60-4; **7** BF_4^-, 29531-31-5; **8** BF_4^-, 77902-81-9; **8** PF_6^-, 77902-82-0; **8** FSO_3^-, 77902-83-1; **9** BF_4^-, 13938-87-9; **9** PF_6^-, 77924-72-2; **9** FSO_3^-, 52912-00-2; **10** BF_4^-, 77902-85-3; **11**, 45952-21-4; **12**, 46185-86-8; **16** HSO_4^-, 77902-86-4; **17** $CF_3CO_2^-$, 77902-61-5; 4,4′-dimethoxybenzophenone, 90-96-0; diphenylcyclopropenone, 886-38-4; bis(*p*-methylphenyl)cyclopropenone, 38377-57-0; 4,6-dimethyl-α-pyrone, 675-09-2; 2,6-dimethyl-γ-pyrone, 1004-36-0; 4-methylcoumarin, 607-71-6.

Supplementary Material Available: Figures 1 and 2, initial and final ^1H NMR spectra for equilibration of α-methoxy-4-methylbenzopyrylium tetrafluoroborate (**3**) with 4,4′-dimethoxybenzophenone in liquid SO_2; Table IV, solvent effects on the ^1H NMR parameters of several oxonium ions (**5**, **11**, **12**); Table V, supplementary elemental analysis data for new compounds (4 pages). Ordering information is given on any current masthead page.

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[55] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: London, 1966.

[56] Eicher, T.; Hansen, A. M. *Chem. Ber.* **1969**, *102*, 319.

[57] Smith, N. R.; Wiley, R. W. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 549.

[58] Woodruff, E. H. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 581.

[59] Meerwein, H. *Org. Synth.* **1966**, *46*, 113.

[60] Curphey, R. W. *Org. Synth.* **1971**, *51*, 142.

Hydrolysis of Formamide at 80 °C and pH 1–9[1]

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The rate of hydrolysis of formamide in hydrochloric acid and in various aqueous buffers was studied over the pH range 1–9 at 80 °C. The reaction is subject to general catalysis in cacodylate, acetate, propionate, and probably methoxyacetate and succinate buffers. Data extrapolated to zero buffer concentration or obtained under conditions where general catalysis should be relatively minor show that hydroxide ions are about 10 times as effective as hydrogen ions in bringing about hydrolysis. The water term in the rate equation is so small that it never contributes more than about 50% to the total reaction rate, but it appears to be real.

The kinetics and mechanism of hydrolysis of amides have been studied extensively in acidic and basic aqueous solution.[2-10] Studies in the intermediate pH range are much less common, however. In fact, it has been stated