positively charged imidazolium nucleus and the partially negative phenyl ring in the adducts. In order to decide between these two possibilities, it will be necessary to examine the affinities of a series of nitrogenous bases for an alkylboronic acid.

Finally, it is interesting to note that our results show that the affinities of nitrogen, sulfur, and carbon nucleophiles for trigonal boron are not much greater than that of an oxygen nucleophile of the same basicity. This finding is different from that for a carbonyl carbon, for which nitrogen, sulfur, and carbon nucleophiles have a greater affinity than an oxygen nucleophile of the same basicity.[17] Thus, in this sense trigonal boron is more similar to the proton than to trigonal carbon in its chemistry.

Registry No.—Boric acid, 10043-35-3; benzeneboronic acid, 98-80-6; 1-methylimidazole, 616-47-7.

[17] E. G. Sander and W. P. Jencks, *J. Amer. Chem. Soc.*, **90**, 6154 (1968).

A Direct ^{1}H and ^{19}F Nuclear Magnetic Resonance Study of Boron Trifluoride Complexes with Acetylacetone, Methoxyacetonitrile, Methoxypropionitrile, Methylacetoacetate, Methylmethoxyacetate, Methoxymethylacetate, 2-Methoxyethylacetate, and Methylpyruvate

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A direct proton and fluorine-19 nuclear magnetic resonance chemical shift and area study of boron trifluoride complexes with acetylacetone, methylacetoacetate, methoxyacetonitrile, methoxypropionitrile, methylmethoxyacetate, methoxymethylacetate, 2-methoxyethylacetate, and methylpyruvate has been completed. In these systems ligand exchange is slow enough below −50° to permit the direct observation of pmr signals for bulk ligand and molecules bound to the boron trifluoride. In the nitrile solutions the ^{1}H and ^{19}F nmr spectra indicate complete complexing at the methoxy linkage. The most stable complexes in solutions of acetylacetone and methylacetoacetate involve the enol tautomers of these molecules. In the remaining systems, complexing at more than one site in the base is indicated by the ^{1}H and ^{19}F nmr data. The competition by each oxygen site is influenced by basicity differences, steric hindrance, and resonance.

Studies of boron trihalide complexes with organic bases have been undertaken by several calorimetric[1-4] and spectroscopic[5-11] techniques to ascertain the chemical and structural features of the components which influence these interactions. Recent measurements have demonstrated the utility of the direct nuclear magnetic resonance method as a supplementary tool for these investigations.[12-16] The success of this method is based on the ability to slow ligand exchange, thereby allowing the observation of separate nmr signals for bulk ligand and ligand bound to the boron trihalide. When this observation is possible, quantitative measurements of the chemical shifts induced by complex formation, the stoichiometry of the complex, the ligand interaction site, steric effects, and ligand preference can be made. A correlation of these results with those obtained by other techniques frequently is possible.

The present study involves a series of ligands which contain more than one possible interaction site, an oxygen atom in most cases. It was hoped that a measure of competitive complex formation would be possible with several of these molecules. If so, the influence of properties such as molecular complexity, the relative basic strengths of the functional groups present, tautomerism, and molecular resonance structures could be ascertained.

Experimental Section

Methods.—All organic chemicals were of the highest commercial grade available, and they were distilled before use. The boron trifluoride was fractionated at −110°. The samples were prepared *in vacuo* and the nmr tube was sealed and stored in liquid nitrogen until the spectrum could be recorded. Each sample contained a few per cent by volume of tetramethylsilane (TMS) and hexafluorobenzene for use as internal nmr chemical shift standards for ^{1}H and ^{19}F nuclei, respectively.

The chemical shift and area measurements were made with a Varian HA-100 spectrometer, operating at 94.1 MHz for the ^{19}F experiments. With each sample, the nmr measurements for each nucleus were repeated at least a day later to ensure that decomposition had not occurred. This was not a problem with any system reported here. The procedure has been described in more detail in previous publications and it involves observing the nmr spectrum as the sample is cooled in the spectrometer probe.[12-16] In most of the systems studied, exchange was slow enough only at temperatures below −50° to permit the observation of separate bulk and bound ligand signals.

Results.—A summary of all pmr chemical shift and integration data is presented in Table I. As mentioned in the table, the concentrations in all cases were maintained at mole ratios of 1:3:60, BF_3 to base to dichloromethane. Such dilutions were used to avoid intermolecular interactions between ligand molecules. Thus, the chemical shift separations between bound and bulk ligand molecules, represented by the quantity $\Delta\nu(C - B)$ in Table I, are an accurate measure of the effect of complex formation by BF_3 with these bases.

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[1] H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956).

[2] T. D. Coyle and F. G. A. Stone, *ibid.*, **83**, 4138 (1961).

[3] M. F. Lappert and J. K. Smith, *J. Chem. Soc.*, 7102 (1965).

[4] N. N. Greenwood and T. S. Srivastava, *J. Chem. Soc. A*, 267, 270 (1965).

[5] J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1954).

[6] E. Gore and S. S. Danyluk, *J. Phys. Chem.*, **69**, 89 (1964).

[7] M. Okada, K. Suyama, and Y. Yamashita, *Tetrahedron Lett.*, 2329 (1965).

[8] P. N. Gates, E. J. McLauchlan, and E. F. Mooney, *Spectrochim. Acta*, **21**, 1445 (1965).

[9] S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1964).

[10] N. N. Greenwood and B. H. Robinson, *J. Chem. Soc. A*, 511 (1966).

[11] R. J. Gillespie and J. S. Hartman, *Can. J. Chem.*, **45**, 859 (1966).

[12] A. Fratiello, T. P. Onak, and R. E. Schuster, *J. Amer. Chem. Soc.*, **90**, 1194 (1968).

[13] A. Fratiello and R. E. Schuster, *Inorg. Chem.*, **7**, 1581 (1968).

[14] A. Fratiello and R. E. Schuster, *Org. Magn. Resonance*, **1**, 139 (1969).

[15] A. Fratiello and R. E. Schuster, *Inorg. Chem.*, **8**, 480 (1969).

[16] A. Fratiello, R. E. Schuster, and M. Geisel, *ibid.*, **11**, 11 (1972).

TABLE I

PROTON CHEMICAL SHIFT AND COORDINATION DATA FOR BORON TRIFLUORIDE COMPLEXES WITH ORGANIC BASES

Base[a]	Temp, °C	Δν(C − B), Hz				BF_3 Fraction Complexed			
		CH_3C	CH_3O	CH_2C	CH_2O	C=O	COC	C≡N	COH
$(CH_3)_2O$	−100		62				1.0		
$(CH_3)_2CO$	−95	65				1.0			
$CH_3CO_2CH_3$	−90	53	52			1.0			
CH_3OH[b]	−100		17						1.1
CH_3CN	−85	Not separated							
$CH_3OCH_2CH_2CH_2CH_3$	−85	6	53	Overlap	84		1.0		
$(CH_3CH_2CH_2CH_2)_2O$	−50	6		Overlap	78		1.1		
$CH_3COC_6H_4OH$[c] 2-Hydroxyacetophenone	−50	27							1.1
$CH_3COCH_2COCH_3$ Acetylacetone	−90	Not separated							
$CH_3COCH_2CO_2CH_3$ Methylacetoacetate	−85	Not separated							
$CH_3OCH_2CO_2CH_3$ Methylmethoxyacetate	−100		42[d]		65	Overlap			
$CH_3CO_2CH_2OCH_3$ Methoxymethylacetate	−100	50	43		Overlap	0.80	0.17		
$CH_3CO_2CH_2CH_2OCH_3$ 2-Methoxyethylacetate	−100	55	67		(2-CH_2) 79 (1-CH_2) 46	0.65	0.44		
	−70					0.41	Broad		
$CH_3COCO_2CH_3$ Methylpyruvate	−100	Not separated							
CH_3OCH_2CN Methoxyacetonitrile	−110	Not separated							
$CH_3OCH_2CH_2CN$ Methoxypropionitrile	−105		65	30	83		1.0		

[a] The solvent in all samples was dichloromethane, and the component mole ratios were 1:3:60, BF_3:base:solvent, within 1–2%. [b] The hydroxyl proton signal was a single line at all temperatures. [c] The hydroxyl proton signal was a single line at all temperatures and the ring proton pattern was too complex to identify bound ligand signals. [d] The 42-Hz separation listed was observed for the methoxy signal. The remaining methyl signal was split about 40 Hz but overlap with the bulk methoxy signal prevented an accurate measure.

Several of the compounds listed in Table I, specifically 2-hydroxyacetophenone and those containing only one oxygen or nitrogen atom, were chosen to provide a chemical shift and integration calibration for both the pmr and ^{19}F nmr measurements. Since several of these species had been studied previously, samples of these reference compounds were prepared in duplicate. All other samples were prepared in triplicate. In every case the chemical shift and area data are the result of two or more measurements with each sample, and they are precise to about 5 (shifts) and 10% (areas), respectively.

It can be seen in Table I that it was not possible to observe bound and bulk signals for all ligands, presumably because exchange is too rapid even at temperatures in the range of −100°. Also, although this observation was possible in the methylmethoxyacetate system, signal overlap prevented an accurate integration. However, as indicated by the data of Table II, the use of ^{19}F nmr as a complementary tool provides another means of determining the structure of these complexes. For example, in the methylmethoxyacetate sample mentioned above, two ^{19}F nmr signals were observed and the separation was large enough to permit an accurate area evaluation.[17]

The nmr chemical shifts listed in Table II were measured with respect to internal C_6F_6, and referred to $CFCl_3$, the usual standard for ^{19}F studies, by the relationship $\delta(C_6F_6) - \delta(CFCl_3) = +162.3$ ppm.[18] The chemical shifts were measured with a precision of at least 0.1 ppm. Since all the BF_3 is bound to a ligand, the area results for those systems exhibiting two or more ^{19}F signals are relative values and they were measured with a precision of at least 5%. The pmr and ^{19}F nmr coordination results were consistent in all cases where a quantitative comparison could be made. Although it was possible to measure signal areas over a much wider temperature range in those systems of multiple ^{19}F peaks, a significant variation was observed only in the 2-methoxyethylacetate system. In some instances, for example the acetylacetone solution, changes in the ^{19}F nmr spectrum with time reflected a slow approach to equilibrium. The results in Table II represent the equilibrium situation in all cases. These examples will be described in detail later.

Discussion

It is evident from the data of Tables I and II that it frequently is possible to observe distinct ^{19}F nmr signals for each BF_3 complex in solution, while only one set of averaged signals is observed in the pmr spectrum of the same sample. This is probably due to factors such as rapid intramolecular proton exchange, small, nonresolvable bulk-bound ligand proton shift differences, and the rate of intermolecular exchange. Since the ^{19}F chemical shift differences are greater than the ^1H values by about a factor of ten, this could determine the upper limit for ligand exchange which can be tolerated. For instance, using the relationship $\tau \simeq 10/2\pi\Delta\nu$ to approximate these rates,[19] a lifetime of about 0.03 sec would be required for the observation of separate ^1H peaks, but only 0.003 sec in the ^{19}F case. These relatively rapid exchange rates are typical of systems involving complex formation at an oxygen atom and it may reflect the strength of these complexes. For example, separate bound and bulk ^1H and ^{19}F nmr signals can be observed at temperatures in the range of 0°, for BF_3 complexes of pyridines and other nitrogen-containing heterocycles.[14–16] These

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[17] Typical ^1H and ^{19}F nmr spectra will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington. D. C, 20036, by referring to code number JOC-72-2237. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[18] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," 1st ed, Vol. 2, Pergamon Press, New York, N. Y., 1966, Table 11.26.

[19] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

TABLE II

FLUORINE-19 CHEMICAL SHIFT AND COORDINATION DATA FOR BORON TRIFLUORIDE COMPLEXES WITH ORGANIC BASES

Registry no.	Base[a]	Temp, °C	δ, ppm	BF$_3$ Fraction Complexed
353-42-4	$(CH_3)_2O$	−90	+159.0	1.0
661-27-8	$(CH_3)_2CO$	−85	+148.9	1.0
7611-14-5	$CH_3CO_2CH_3$	−90	+149.8	1.0
373-57-9	CH_3OH	−100	+156.4	1.0
420-16-6	CH_3CN	−85	+144.2	1.0
34804-31-4	$CH_3OCH_2CH_2CH_2CH_3$	−85	+156.0	1.0
593-04-4	$(CH_3CH_2CH_2CH_2)_2O$	−50	+140.8	1.0
34804-32-5	$CH_3COC_6H_4OH$ 2-Hydroxyacetophenone	−50	+133.5	1.0
637-99-0	$CH_3COCH_2COCH_3$ Acetylacetone	−90	+135.9	1.0
34804-34-7	$CH_3COCH_2CO_2CH_3$ Methylacetoacetate	−85	+155.9	0.25
			+150.0	0.17
			+138.3	0.58
34804-35-8	$CH_3OCH_2CO_2CH_3$ Methylmethoxyacetate	−105	+155.8	0.82
			+149.2	0.18
34804-36-9	$CH_3CO_2CH_2OCH_3$ Methoxymethylacetate	−100	+155.0	0.15
			+149.3	0.85
34804-37-0	$CH_3CO_2CH_2CH_2OCH_3$ 2-Methoxyethylacetate	−60	+155.9	0.61
			+149.2	0.39
		−67	+156.0	0.58
			+149.2	0.42
		−76	+156.1	0.55
			+149.3	0.45
		−84	+156.3	0.50
			+149.4	0.50
		−92	+156.4	0.47
			+149.5	0.53
		−100	+156.5	0.43
			+149.6	0.57
		−105	+156.6	0.37
			+149.6	0.63
34804-38-1	$CH_3COCO_2CH_3$ Methylpyruvate	−80	+155.5	0.61
			+150.4	0.24
			+149.1	0.15
34804-39-2	CH_3OCH_2CN Methoxyacetonitrile	−115	+154.6	1.0
34804-40-5	$CH_3OCH_2CH_2CN$ Methoxypropionitrile	−100	+156.1	1.0

[a] The solvent in all samples was dichloromethane, and the component mole ratios were 1:3:60, BF$_3$:base:solvent, within 1–2%.

heterocycles are much stronger bases than the molecules under study here.

In general the ^{1}H and ^{19}F nmr data for the eight reference compounds of Tables I and II provide a foundation for reasonable analogies to the remaining compounds of this study. However, even with this series of reference species several interesting features are noticeable. As expected, with only one possible interaction site in a molecule, or in the case of 2-hydroxyacetophenone where the more basic hydroxyl group dominates, simple 1:1 adducts are formed with complexation occurring at the single site. This is verified by the pmr integration data and the observation of only one ^{19}F nmr signal in the spectra of these samples. Only in the acetonitrile system was exchange too rapid to observe the bound ligand signal. Also, pmr signals for methyl groups one or two bonds removed from the interacting oxygen are displaced about 50–60 Hz upon complex formation, with an attenuation to a small displacement of a few hertz if the group is further removed (butyl ethers). The exception is methanol, for which this effect had been noticed and described previously.[12]

The pmr reference data would not have been conclusive in the assignment of interaction sites without the ^{19}F nmr results of Table II. Chemical shifts involving this nucleus are extremely sensitive to the structure of the molecule, even for compounds containing the same functional group. For example, the ^{19}F nmr shift of dimethyl, methyl-*n*-butyl, and *n*-butyl ether appear at progressively lower field, probably the result of steric hindrance. The proton nmr shift displacements are much smaller and, in some cases, similar for different molecules. An excellent illustration of these contrasts is provided by the dimethyl ether and acetone systems, in which the ^{1}H shift results are practically identical, while the ^{19}F shifts differ by 10 ppm. From the data of Table II, reference ^{19}F chemical shifts for BF$_3$ complexes at carbonyl (acetone, +149 ppm), carboxyl (methylacetate, +150 ppm), nitrile (acetonitrile, +144 ppm), hydroxyl (2-hydroxyacetophenone, +133 ppm), and ether (methyl-*n*-butyl ether, +156 ppm) functional groups were concluded. In view of the variations of ^{19}F shifts previously noted for the ethers, methyl-*n*-butyl ether was chosen because its structure more closely resembles the methoxy compounds studied. In these cases, a methoxy group was bonded to a fragment containing several carbon atoms. Consequently, similar steric effects should be observed. Similarly, 2-hydroxyacetophenone was chosen as a hydroxyl-group reference compound to provide a more meaningful comparison to the BF$_3$–enol complexes encountered in this study. In the latter cases (acetylacetone and methylacetoacetate) internal hydrogen bonding is possible with the enol tautomers. This situation also is possible in 2-hydroxyacetophenone, but not with simple alcohols, such as methanol.

From Tables I and II, definitive results were obtained with the BF$_3$ complexes of methoxyacetonitrile and methoxypropionitrile. Although separate bound and bulk pmr signals were observed only in the latter case, as seen in Figure 1,[17] the large CH$_3$ and CH$_2$ shift displacements indicate complexing at the methoxy site. Also, in this system, the pmr integration result of 1.0 reflected total complexing within experimental error at this site. Further, the one ^{19}F signal observed in each system was positioned at ∼+155 ppm, closely paralleling the reference shift of the BF$_3$–methyl-*n*-butyl ether complex, but differing sharply from the value observed for BF$_3$–acetonitrile. Thus, in compounds containing methoxy and nitrile functional groups, the exclusive interaction site would be the oxygen unshared electron pair. This behavior parallels protonation data which indicate a much greater basicity for methoxy compounds as compared to nitriles.[20]

In several of the remaining systems of Tables I and II, complexing by BF$_3$ occurred at more than one site in the base. Unfortunately, it cannot be demonstrated conclusively whether these interactions are occurring in different molecules, or at two or more sites in the same molecule. A possible criterion is the temperature dependence of the ligand signal line widths. If complexing is complete at one site, as it is in the ref-

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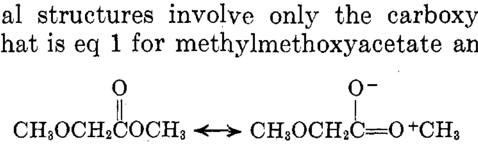
(20) E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 223 (1963).

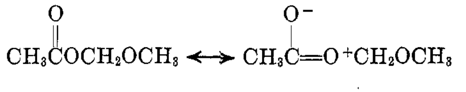
erence samples included here, all line widths reflect the same exchange rate, with a possible added factor of quadrupole broadening at nuclei close to the interaction site. When complexing occurs at more than one site, however, the simultaneous occurrence of several exchange paths creates a much more complicated situation. For example, in the BF_3–methoxymethylacetate solution spectra, the $-CH_2OCH_3$ pmr signals definitely show a much greater temperature dependence than the signals of the CH_3CO_2- fragment. Similarly, in the ^{19}F nmr spectra of this system, the signal at +156 ppm, corresponding to bonding at the methoxy group, shows the greater temperature dependence. This situation also prevailed for the other compounds involved in multiple site interactions. Depending on the exchange mechanism, this line width behavior could result from either complexing possibility mentioned above.

A consideration of steric and thermodynamic factors, however, points to complexing with different molecules. Either situation would produce similar entropy changes, so this parameter would not dominate. However, the charge withdrawal which accompanies complexing at one site in a molecule would diminish the basic strengths and complexing tendencies of other sites in the same molecule. Finally, the steric problems posed by BF_3 complexation at two and even three sites (methylacetoacetate, methylpyruvate) in the same molecule argue strongly against this possibility.

The results for methylmethoxyacetate, methoxymethylacetate, and 2-methoxyethylacetate reflect the consequences of differences in functional group basicity, canonical structures, and steric hindrance. For example, in the ^{19}F nmr spectra of the BF_3–methylmethoxyacetate and BF_3–methoxymethylacetate solutions, signals corresponding to binding at the carbonyl (+149 ppm) and methoxy (+156 ppm) linkages are observed. However, while 80% of the BF_3 is bound at the methoxy site in the methylmethoxyacetate system, only 20% is bound at this site in the case of methoxymethylacetate. The ^1H integration data in the latter system agree well with these ^{19}F nmr results. In the absence of steric hindrance, proton basicity studies would predict that complexing at the ether linkage would dominate. However, a previous BF_3 ligand preference study of acetone–ethyl ether mixtures demonstrated that steric hindrance was a factor even in the case of this ether.[13] Similar steric considerations with molecular models of these compounds reveals some hindrance at the methoxy site in both cases, a comparable hindrance at the carbonyl site in methylmethoxyacetate, and severe hindrance at the carbonyl oxygen atom of methoxymethylacetate. Thus, the surprisingly high fraction of BF_3 complexed at this last site must reflect the presence of another process. For both molecules the canonical structures involve only the carboxyl fragment, that is eq 1 for methylmethoxyacetate and eq 2



$$\mathrm{CH_3OCH_2\overset{O}{\overset{\|}{C}}OCH_3} \longleftrightarrow \mathrm{CH_3OCH_2\overset{O^-}{\overset{|}{C}}{=}O^+CH_3} \qquad (1)$$

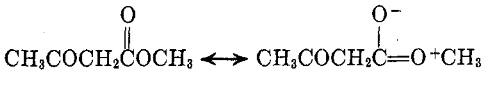


$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OCH_2OCH_3} \longleftrightarrow \mathrm{CH_3\overset{O^-}{\overset{|}{C}}{=}O^+CH_2OCH_3} \qquad (2)$$

for methoxymethylacetate. The methoxy site basicity would be essentially unaffected by **1**, whereas this site would experience a diminution of its basic strength by the proximity of the partial positive charge in **2**. The data of Tables I and II are consistent with this interpretation.

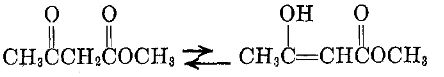
A consideration of the spectra for the BF_3–2-methoxyethylacetate system[17] must include the temperature dependence of the integration data. Thus, complexing dominates at the carbonyl oxygen (60%) at −100°, and at the methoxy site (60%) at −60°. It may be assumed that group basicities and resonance in this molecule would parallel the situation which prevails in its closest structural analog, methoxymethylacetate. This would explain the dominance of the carbonyl site at the lowest temperature. However, molecular models clearly demonstrate that the increased size of 2-methoxyethylacetate results in strong steric hindrance at both the carboxyl and methoxy sites. The lack of temperature dependence for the data of the BF_3–methoxymethylacetate complex implies that basicity and resonance effects are not influenced by this parameter over these small (~40°) temperature ranges. Rather, modifications of the strong steric hindrance must be responsible for the BF_3–2-methoxyethylacetate results. It was not possible to extend the temperature range with this sample because of viscosity and exchange broadening. However, these results are sufficient to emphasize the need for considering all processes which affect complex formation and their possible temperature dependence. It is conceivable, for example, that an organic reaction pathway could be influenced markedly by this behavior.

The results for acetylacetone and methylacetoacetate, particularly the ^{19}F nmr shift and area data of Table II, reflect the ability of these compounds to undergo keto–enol tautomerism. The enol tautomer is the more stable form of pure acetylacetone, ~75%, but the resonance of the ester group of methylacetoacetate occurs at the expense of the enol form and reduces its concentration to a few per cent.[21] In other words, the



$$\mathrm{CH_3COCH_2\overset{O}{\overset{\|}{C}}OCH_3} \longleftrightarrow \mathrm{CH_3COCH_2\overset{O^-}{\overset{|}{C}}{=}O^+CH_3} \qquad (3)$$

resonance (eq 3) results in a displacement of the tautomeric equilibrium (eq 4) to the ketone form.



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_3} \rightleftharpoons \mathrm{CH_3\overset{OH}{\overset{|}{C}}{=}CH\overset{O}{\overset{\|}{C}}OCH_3} \qquad (4)$$

The data shown in Tables I and II for the BF_3–acetylacetone system were attained after the sample had thoroughly equilibrated. In contrast to the other compounds studied here, the spectral features for this system and to a smaller extent that of the methylacetoacetate sample demonstrated a slow approach to equilibrium. Initially, bound ligand pmr signals were observed in the methyl group region of the BF_3–acetylacetone solution spectrum, and ^{19}F nmr peaks were observed at +136, +148, and +152 ppm, the latter corresponding to BF_3 fractions of 30, 20, and 50%, respectively. After 24 hr at low temperature, the bound ligand signals in the pmr spectrum and the ^{19}F nmr peaks at +148 and +152 ppm were no longer observ-

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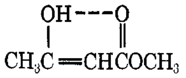
[21] L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, Chapter 4.

able. These spectra remained unchanged from that point on. The ^{19}F nmr signals at +148 and +136 ppm, respectively, can be attributed to the BF_3–keto complex and the BF_3–enol complex with bonding at the hydroxyl oxygen. This latter conclusion is based on a comparison to the results obtained with 2-hydroxyacetophenone, a structurally similar molecule. The remaining ^{19}F peak observed initially at +152 ppm cannot be assigned quantitatively. At any rate, as the system equilibrates, the most stable complex by far is the BF_3–enol species giving rise to the ^{19}F signal at +136 ppm.

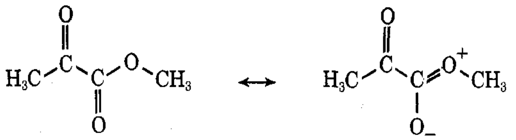
A similar situation prevails in the BF_3–methylacetoacetate solution except, as indicated above, the enol form is not as stable with this molecule. Initially, one ^{19}F nmr peak at +150 ppm was observed for this sample, this position corresponding closely to a BF_3–keto complex. After equilibration, this signal decreases in intensity, and two stronger signals appear at +138 (~58%) and +156 ppm (25%). Thus, complex formation stabilizes the enol form of this compound resulting in the peak at lowest field (+138 ppm). In addition, a BF_3–keto complex is still present at equilibrium and, surprisingly, a complex corresponding to bonding at the ether-type oxygen of the ester group (+156 ppm). This last point is not satisfactorily interpreted but it may be due to the presence of a hydrogen-bonded species of the type



$$CH_3C{=}CHCOCH_3$$

with subsequent complex formation at the ester group.

Finally, a partially successful attempt was made to study the BF_3–methylpyruvate system, because this molecule presents the interesting structural feature of neighboring carbonyl and ester groups. As with several of the compounds listed in Table I, bound ligand signals could not be observed in the pmr spectra. As seen in Table II, however, three ^{19}F nmr peaks were observed, corresponding to complexing at a carbonyl group (+149 and +150 ppm) and an ether-type oxygen (+156 ppm). These results indicate that the primary factor regulating complex formation in this system must be the basic nature of the particular sites. For example, models show no significant steric hindrance to bonding at any site in the molecule. Also, if resonance were the dominant factor, the canonical forms



would repress complex formation at the ester oxygen, a situation which contradicts the observed result. Thus, the overriding factor in this system is the inherently greater basicity of an ether-type linkage as compared to a carbonyl group.

Experimentally these results demonstrate the advantages of slowing ligand exchange to permit the direct study of solution complexes, and the desirability of correlating different types of nmr data, in this case ^{1}H and ^{19}F measurements. More importantly, the conclusions drawn emphasize the need for considering as many molecular properties as possible, for example, functional group basicity, resonance, tautomerism, and steric hindrance, when trying to determine the mechanism of complex formation. The molecules studied here all exhibit these features to some extent, and an expansion of the program to more complicated ligands is underway.

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