with two 100-ml portions of chloroform, the combined extracts were washed once with water. The chloroform solution was dried over anhydrous sodium sulfate, decolorized with charcoal, and filtered. The filtrate was concentrated to a syrup, which was crystallized from 75 ml of ethanol–chloroform (25:1, v/v) by storage at −5° overnight. Recrystallization from this solvent yielded pure **9**: yield 10.9 g (82%); mp 168–169°; nmr ($CDCl_3$) δ 2.43 (s, 12, CH_3 of tosyl), 3.12 (s, 2, hydroxyls, collapses D_2O), 4.13 (s, 4, a, b), 4.60 (s, 2, c, d), 7.24–7.85 (m, 16, aromatic of tosyl).

Anal. Calcd for $C_{34}H_{36}O_{14}S_4$: C, 51.24; H, 4.55; S, 16.09. Found: C, 51.20; H, 4.33; S, 16.00.

1(*S*),4(*S*)-Dimethyl-2(*S*)-cyclobutanetriol (10).—To a suspension of **9** (5.0 g, 1 equiv) in 150 ml of ether–benzene (2:1, v/v) was added with stirring lithium aluminum hydride (3.8 g, 16 equiv). The mixture was refluxed with stirring for 4 days with an oil bath temperature of 60°. The reaction mixture was shown to contain no **9** but the presence of a major component of lower R_f by tlc in solvent D. Ethyl acetate (50 ml) was then gradually stirred into the cooled reaction mixture to decompose excess lithium aluminum hydride. Then 100 ml of ether–water (10:1, v/v) was added to complete this decomposition. The mixture was then filtered through Celite and the alkaline filtrate was neutralized with Amberlite IR-45 (H^+) resin. The exchange resin was removed by filtration, and the filtrate was concentrated under diminished pressure to a syrup (300 mg). Crystallization of this syrup failed, so it was applied to a silica gel column and eluted with solvent G. A fraction consisting mainly of the major reduction product was obtained (120 mg) and this was further purified by repeated silica gel column chromatography, again using solvent G as eluent. This product was not crystalline: yield 80 mg (11%); nmr ($CDCl_3$) δ 1.13, 1.14 (s, 6, a,b), 1.61–1.5 (m, 2, d,e), 3.60 (s, 3, hydroxyls), 3.76 (m, 1, c).

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Registry No.—**1**, 6341-07-7; **2**, 35304-04-2; **3**, 40627-21-2; **4**, 40627-22-3; **5**, 40695-92-9; **6**, 40627-23-4; **7**, 40627-24-5; **8**, 40627-25-6; **9**, 40627-26-7; **10**, 40627-27-8; D-fructose, 57-48-7; L-sorbose, 87-79-6; *p*-toluenesulfonyl chloride, 98-59-9.

A Direct Low Temperature ^1H and ^{19}F Nuclear Magnetic Resonance Study of Boron Trifluoride Complexes with 4-Cholesten-3-one, 1(5β)-Androstene-3,17-dione, 5β-Androstane-3,17-dione, and Obacunone

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A direct low temperature proton and fluorine-19 nmr study of boron trifluoride complexes with steroids **1**–**3** and a limonoid **4** is reported. In these systems ligand exchange is slow enough below −50° for observation of separate pmr signals for bulk ligand and molecules bound to the boron trifluoride. For ligands **1**, **2**, and **4**, the ^1H and ^{19}F nmr data indicate that complexing first occurs solely at the A-ring carbonyl group. In the remaining system **3** and for high BF_3/base ratios of **4**, complexing also occurs at a second site in the base, the carbonyl group in the D ring.

Complexes of boron trihalides with organic bases have been studied using several calorimetric and spectroscopic techniques to ascertain the chemical and structural features of the components which influence these interactions.[1-8] Nmr investigations of boron trihalide complexes include ligands such as trimethylamine, ethers, *N*,*N*-dimethylformamide, ureas and thioureas, and water (^{19}F and proton resonance). Recent publications have demonstrated the usefulness of the direct low temperature nmr method as a supplemental aid for these investigations.[8-12] The success of this low temperature method is based on the ability to slow ligand exchange, thereby allowing the observation of separate pmr signals for the ligand molecules bound to the boron trihalide and the bulk (uncomplexed) ligand. The information obtainable by this means includes chemical shifts induced in the ligand by complex formation, the stoichiometry of the complex, the ligand interaction site or sites, and competition between sites. Previous investigations of this type have been confined largely to ligands of relatively low molecular weight and complexity. To determine whether this low temperature technique could also be applied to larger and more complex ligands, we have now studied complexes of boron trifluoride with three steroids and a limonoid.

Experimental Section

The 2-nitropropane (2NP) used was the highest commercial grade available and was distilled before use. 4-Cholesten-3-one (**1**) and 1(5β)-androstene-3,17-dione (**2**) were generously supplied by Dr. Erich Heftmann, Western Regional Research Laboratory, Albany, Calif. 5β-Androstane-3,17-dione (**3**) was purchased from Mann Laboratories.[13] The purity of these three steroids was verified by their nmr spectra. Obacunone (**4**) was isolated from grapefruit seed meal by methods previously described.[14] Boron trifluoride (J. T. Baker) was purified by fractionation through a −110° petroleum ether (bp 30–60°)–liquid nitrogen cold trap, and its purity verified by ^{19}F nmr in anhydrous CH_2Cl_2. Van Ness Associates No. 105–7PP special purpose nmr sample tubes were employed for all measurements. These are

(1) J. M. Miller and M. Onyszchuk, *Can. J. Chem.*, **42**, 1518 (1954).
(2) E. Gore and S. S. Danyluk, *J. Phys. Chem.*, **69**, 89 (1965).
(3) M. Okada, K. Suyama, and Y. Yamashita, *Tetrahedron Lett.*, 2329 (1965).
(4) P. N. Gates, E. J. McLauchlan, and E. F. Mooney, *Spectrochim. Acta*, **21**, 1445 (1965).
(5) S. J. Kuhn and J. S. McIntyre, *Can. J. Chem.*, **43**, 375 (1964).
(6) N. N. Greenwood and B. H. Robinson, *J. Chem. Soc. A*, 511 (1966).
(7) R. J. Gillespie and J. S. Hartman, *Can. J. Chem.*, **45**, 859 (1966).
(8) A. Fratiello and R. E. Schuster, *Inorg. Chem.*, **8**, 480 (1969), and references cited therein.
(9) A. Fratiello, T. P. Onak, and R. E. Schuster, *J. Amer. Chem. Soc.*, **90**, 1194 (1968).
(10) A. Fratiello and R. E. Schuster, *Inorg. Chem.*, **7**, 1581 (1968).
(11) A. Fratiello and R. E. Schuster, *Org. Magn. Resonance*, **1**, 139 (1969).
(12) A. Fratiello, R. E. Schuster, and M. Geisel, *Inorg. Chem.*, **11**, 11 (1972).
(13) Reference to a company or product name does not imply endorsement by the U. S. Department of Agriculture to the exclusion of others that may be suitable.
(14) D. L. Dreyer, *J. Org. Chem.*, **30**, 749 (1965).

thin-walled, high resolution tubes, which can be sealed readily under high vacuum.

Stock solutions of each base were prepared and a portion of the solution was syringed into the nmr tube, placed on the vacuum line, and degassed several times before a measured amount of purified BF_3 was condensed into the tube at liquid nitrogen temperature. After the tube was sealed off under vacuum, its contents were thawed and mixed in a Dry Ice–acetone bath. It then was stored in liquid nitrogen until the spectrum could be recorded. Each sample contained a few per cent by volume of tetramethylsilane (TMS) and hexafluorobenzene (C_6F_6) for use as internal nmr chemical shift standards for the ^1H and ^{19}F nuclei, respectively.

The chemical shift and area measurements were made using a JEOL PS-100 spectrometer (operating at 94 MHz for the ^{19}F measurements) equipped with a variable temperature device permitting measurements down to −170°. The samples were cooled until separate pmr signals for bulk and complexed ligand molecules were observed. The pmr areas were determined by integration of suitable peaks in the spectrum. ^{19}F nmr data were obtained in the same manner and the signal or signals recorded at the temperature of maximum resolution.

Results

Pmr chemical shift and integration data for ligands 1–4 are presented in Table I, and representative pmr

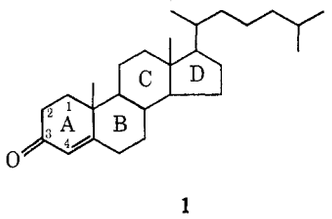
TABLE I

PROTON CHEMICAL SHIFT AND COORDINATION DATA FOR BORON TRIFLUORIDE COMPLEXES OF 4-CHOLESTEN-3-ONE, 1(5β)-ANDROSTENE-3,17-DIONE, 5β-ANDROSTANE-3,17-DIONE, AND OBACUNONE

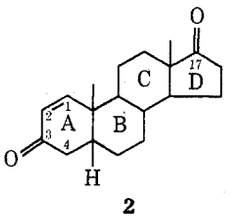
Base	Mole ratio of base/BF_3/solvent[a]	t, °C	Δν(C-B),[b] Hz H-1	H-2	H-4	H-15	Coordination no.
1	3.80:1.00:456	−50		60	80		1.0
2	3.40:1.00:408	−52	42	32			1.0
3	3.83:1.00:445	−57	Overlapping, unidentifiable				
4	4.31:1.00:517	−59	55	24		12	1.0

[a] The solvent in all cases was $CDCl_3$, and the accuracy of the mole ratios was within 1–2%. [b] The Δν(C-B) values refer to the separation in hertz between the complexed and bulk ligand protons indicated.

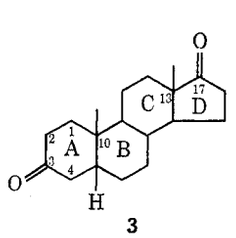
spectra of 4 complexed with BF_3, recorded at three temperatures, are shown in Figure 1. Table I lists the



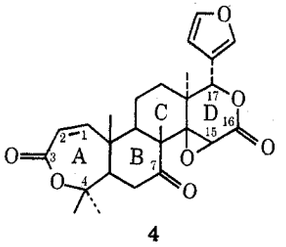
1



2



3



4

mole ratios of the systems studied and the temperatures at which the spectra were recorded. The high solvent to base ratio, 120:1 in all cases, was used to avoid intermolecular interactions between coordinated and bulk ligand molecules. Thus the chemical shift separations (for those protons able to be studied)

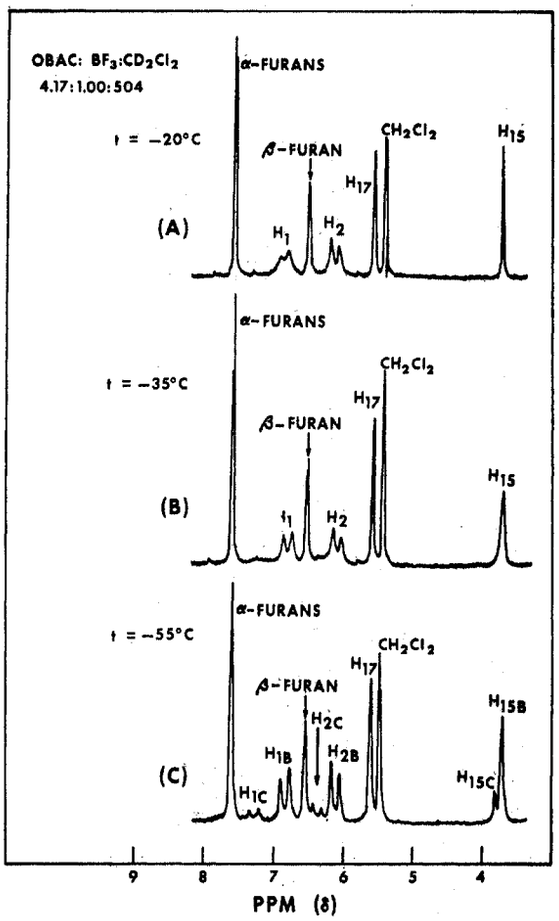


Figure 1.—The variable temperature pmr spectrum of an obacunone–BF_3 mixture in $CDCl_3$, recorded at 100 MHz. The signals arising from bulk (B) and coordinated (C) ligand molecules are labeled in the diagram and each proton is identified. Concentrations are in mole ratios.

between complexed and bulk ligand molecules, represented by the quantity Δν(C-B) in Table I, are an accurate measure of the effect of complex formation on individual protons. Since the resonance signals of complexed ligand molecules appear downfield from those of corresponding bulk molecules, the quantities under the heading Δν(C-B) in Table I are always positive. The last column of Table I lists the stoichiometry of the BF_3 complex with each base, as calculated from proton integrations. In every case data for chemical shift and area measurements represent two or more measurements with each sample and are precise to about 5% (Δν shifts) and 10% (areas), respectively.

It can be seen from Table I that it was not possible to obtain coordination data for all ligands by pmr, nor was it possible to measure Δν(C-B) values for all the protons in a particular ligand. These problems arise from spectral characteristics of the individual compounds and from the small complex to bulk chemical shift difference for protons far removed from the interaction site, and not from the inability to slow ligand exchange. Thus chemical shift differences under the heading Δν(C-B) are given only for those protons whose bulk and coordinated signals could be identified clearly.

The ^{19}F 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

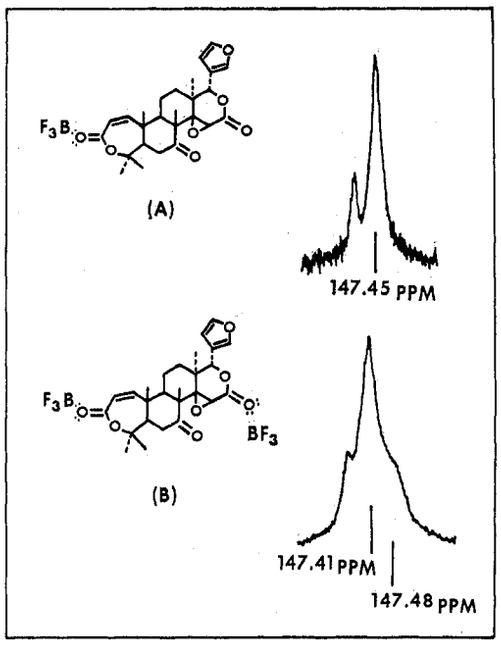


Figure 2.—The fluorine-19 nmr spectra for two obacunone/BF_3 ratios in (a) $CDCl_3$ and (b) 2-nitropropane (2NP), recorded at 94 MHz. The species present, mole ratios, and chemical shifts (δ) are labeled in the diagram.

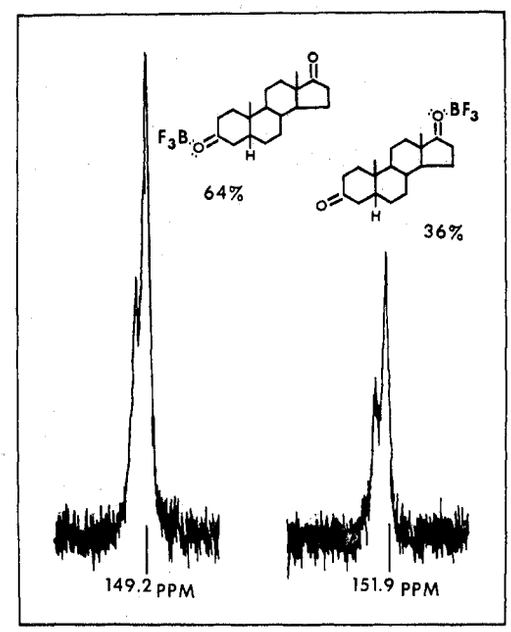


Figure 3.—The fluorine-19 nmr spectrum of a 1(5β)-androstane-3,17-dione–BF_3 mixture in $CDCl_3$, recorded at 94 MHz. The relative area of each signal and the chemical shifts (δ) are labeled in the diagram.

TABLE II

FLUORINE-19 CHEMICAL SHIFTS AND COORDINATION DATA FOR BORON TRIFLUORIDE COMPLEXES OF 4-CHOLESTEN-3-ONE, 1(5β)-ANDROSTENE-3,17-DIONE, 5β-ANDROSTANE-3,17-DIONE, AND OBACUNONE

Base	Mole ratio of base/BF_3/solvent[a]	t, °C	^{19}F chemical shifts,[b] δ, base–BF_3 complex
1	3.80:1.00:456	−46	149.6
2	3.40:1.00:408	−40	149.3
3	3.83:1.00:445	−57	149.2 (64%), 151.9 (36%)
4	4.31:1.00:517	−51	149.8
	1.02:1.00:132 (2NP)	−55	147.45
	0.68:1.00:81.5 (2NP)	−55	147.41, 147.48

[a] The solvent was $CDCl_3$, except where otherwise indicated. [b] Chemical shifts are in parts per million upfield from $CFCl_3$.

relationship, $\delta(C_6F_6) - \delta(CFCl_3) = +162.3$ ppm.[15] These chemical shifts were all upfield from $CFCl_3$ and were measured with a precision of at least 0.1 ppm. Typical ^{19}F nmr spectra are shown in Figures 2 and 3. Each BF_3–base complex signal appears as two signals due to the presence of both $^{10}BF_3$ and $^{11}BF_3$. Figure 2B illustrates the ^{19}F signals observed for the 0.68:1.00 obacunone–BF_3 system. Figure 3 shows the two ^{19}F signals, along with the relative area of each and the chemical shifts observed when two different sites in **3** are complexed by BF_3. In Table III pmr chemical shifts for two obacunone/BF_3 ratios, along with the temperature dependence of selected protons for the 0.68:1.00 obacunone–BF_3 system are listed.

Discussion

Since ^{19}F chemical shift differences are usually greater than ^1H values, separate ^{19}F signals can generally be observed at a higher temperature than bound and bulk ^1H ligand resonances. For instance, using the relationship $\tau = 10/2\pi\Delta\nu$ to approximate these rates, a lifetime of about 0.03 sec would be necessary to observe separate ^1H ligand signals, whereas for base **3** in Table II only 0.006 sec would be necessary to observe separate ^{19}F signals. These exchange rates are similar to those reported for other boron trihalide complexes with oxygen-containing bases, but are much faster than those involving nitrogen-containing bases such as pyridine, where ligand exchange is slowed enough to observe separate signals at about 0°.[8,11,12] The exchange rate may reflect the strength of these complexes.

TABLE III

PROTON CHEMICAL SHIFT DATA FOR OBACUNONE AS A FUNCTION OF TEMPERATURE

Mole ratio of obacunone/BF_3/2NP	t, °C	Chemical shift,[a] δ H-1	H-2	H-15	H-17
1.02:1.00:132	−57	7.34	6.19	3.80	5.52
0.68:1.00:81.5	−57	7.33	6.19	4.06	5.82
	−63	7.33	6.18	4.14	5.83
	−73	7.33	6.17	3.96	5.55
	−78	7.32	6.16	3.84	5.54
	−85	7.32	6.17	3.84	5.54

[a] Chemical shifts are in parts per million from internal TMS.

The ^1H and ^{19}F nmr data for **1**, in Tables I and II, provide a useful reference for the remaining three systems. As expected, the 1:1 adduct is formed with complexing occurring at the only possible interaction site, the A-ring carbonyl group. This is substantiated by the relatively large $\Delta\nu$(C-B) values for the 2 and 4 protons, the integration data, and the observation of only one ^{19}F nmr signal, occurring at +149.6 ppm. The coordination data for **2**, **3**, and **4**, however, show several interesting features. Compounds **2** and **3** have two possible interaction sites, the A- and D-ring carbonyl groups. However, **2** contains an α,β-unsaturated keto group in the A ring, whereas **3** is a com-

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

pletely saturated diketone. The data of Tables I and II indicate that complexing in **2** occurs solely in the A ring. This is shown by the large $\Delta\nu$(C-B) values for H-1 and H-2, the coordination number of 1.0, and the single ^{19}F nmr signal at +149.3 ppm, which closely agree with those observed for the BF_3 complex of **1**. In contrast, complexing of **3** occurs at both carbonyl groups. At −56° the ^{19}F nmr spectrum of a BF_3 mixture with **3** consists of two well-defined and widely separated signals, one at +149.2 ppm amounting to 64% of the total ^{19}F area and the other at +151.9 ppm. The signal at +149.2 ppm can be attributed to that fraction of BF_3 complexed in the A ring, since the shift closely parallels those observed for **1** and **2**, and the signal at +151.9 ppm arises from that complexed in the D ring. This reasoning is confirmed by ^{19}F nmr data of BF_3 complexes with cyclohexanone and cyclopentanone, which have ^{19}F resonances at +149.0 and +151.8 ppm, respectively.[16]

In the pmr spectrum of **3** the signals of the protons on carbons α to the two carbonyl groups cannot be individually identified because of strong coupling and overlap. However, the signal of the 13-methyl group adjacent to the 17-carbonyl provides an indication of complexing at this site. In the presence of BF_3 this resonance is split into bulk and coordinated signals, with a separation of 22 Hz. The corresponding signal in complexed **2**, on the other hand, is not split. These findings support the conclusion drawn from the ^{19}F spectra that complexing occurs at both carbonyl sites in **3**.

Thus in **2** the D-ring carbonyl group cannot effectively compete for BF_3 in the presence of the conjugated A-ring carbonyl group. When the A ring is saturated, as in **3**, the D-ring carbonyl group then can compete for BF_3 to the extent indicated. These observations are in agreement with proton basicity data which indicate that α,β-unsaturated ketones are more basic than the corresponding saturated ketones.[17] Unfortunately, since the interaction sites, the A- and D-ring carbonyl groups, are so far apart, it cannot be demonstrated conclusively whether these interactions occur in different molecules, at two sites in the same molecule, or both.

The value of this low temperature nmr method in yielding information about coordination sites is well illustrated by the data for obacunone (**4**), a compound which has seven possible interaction sites. The pmr coordination and chemical shift data of Table I indicate that with high base/BF_3 ratios complexing occurs solely in the A ring, as evidenced by the large $\Delta\nu$(C-B) values for the 1 and 2 protons, 42 and 32 Hz, respectively. Integration of bulk and complex signals of H-1, H-2, and H-15 uniformly yields a coordination number of unity within experimental error. This demonstrates that complexing is at only one site. This is confirmed by the ^{19}F nmr spectrum, which shows only one signal at +149.8 ppm.

Since **4** contains many possible interaction sites, it was of interest to identify the second most basic site. Since the complex precipitated from $CDCl_3$ and CD_2Cl_2 solutions with base/BF_3 ratios approaching unity, use of a more polar solvent, 2-nitropropane, was necessary to keep it in solution. Unfortunately, the large solvent peaks in the proton spectrum then prevented observation of the H-15 and H-17 complex signals; so we were unable to determine $\Delta\nu$(C-B) values for these two protons. Instead we have used the change in chemical shift of the H-15 and H-17 resonances with temperature as a measure of the effect of complexing on these protons. Above the temperature at which exchange becomes slow on the nmr time scale, separate bulk and complex signals do not appear, but rather a single broadened resonance, which is an average of the two, is observed. The maximum downfield position of this average signal is thus less than, but proportionate to, the $\Delta\nu$(C-B) value and can be used similarly to the latter in comparing complexing effects.

Table III lists ^1H chemical shift data for two obacunone/BF_3 ratios in 2-nitropropane. The first entry gives the chemical shifts of the 1, 2, 15, and 17 protons of obacunone in a 1:1 complex at −55°. The second entry illustrates the temperature dependence of these protons when excess BF_3 is present. It is apparent that the 1- and 2-proton signals, at this concentration, are not temperature dependent, further demonstrating that the A-ring carbonyl group is completely complexed. However, as the temperature is decreased, the 15- and 17-proton signals first shift to lower field, *i.e.*, the broadened average signals are observed. At lower temperatures these then split, and the bulk signals move back upfield to about the same position as in the 1:1 complex. This indicates that the second mole of BF_3 is coordinating at a site close to the 15 and 17 protons. The ^{19}F spectrum for this sample shows two signals with very similar chemical shifts, as illustrated by Figure 2B. If the second site complexed was the 7-ketone, the downfield shift of H-15 with decreasing temperature should be considerably larger than that for H-17, but the two values are approximately the same. The small chemical shift difference for the two ^{19}F signals also tends to rule out the epoxide as one of the sites complexed. Thus, the ^1H and ^{19}F nmr results both suggest that the first site complexed is the carbonyl group of the A ring, and the second site is the carbonyl group of the D ring.

Since the $\Delta\nu$(C-B) values in Table I are all positive, the complexed ligand signals always appearing at lower applied magnetic field than the bulk signals, the protons of the former must experience a decreased electronic shielding. These positive $\Delta\nu$(C-B) values may reflect changes in electron density and field effects at that particular site in the ligand upon complex formation. For example, listed in Table I are $\Delta\nu$(C-B) values for the conjugated 1 and 2 protons of **2** and **4**. The values of 42 and 32 Hz for **2** and 55 and 24 Hz for **4** are consistent with other spectroscopic[18] and chemical[19] data which indicate that polarization of α,β-unsaturated carbonyl compounds causes a reduction in the electron density at the β-carbon atom, and hence decreases the effective shielding at the β proton. Thus the $\Delta\nu$(C-B) values give some indication concerning the magnitude of such changes occurring on complex formation. Of particular interest, and not readily explained, is the appearance of a complex signal for the 15 proton of **4**.

(16) A. Fratiello, private communication.

(17) A. M. Smoczkiewicz and R. I. Zalewski, *Steroids*, **12**, 391 (1968).

(18) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1963, Chapter 5.

(19) C. Djerassi, "Steroid Reactions," Holden-Day, San Francisco, Calif., 1963.

Since complexing occurs solely at the carbonyl group of the A ring, at those concentrations given in Table I, the effect observed, $\Delta\nu$(C-B) equal to 12 Hz, must be transmitted through at least seven carbon atoms. This long-range effect is quite unexpected, since in aliphatic noncyclic bases previously studied the $\Delta\nu$-(C-B) values attenuate rapidly with distance. For example, in di-*n*-butyl ether,[20] the $\Delta\nu$(C-B) value for the methylene protons adjacent to the coordinated oxygen atom is approximately 80 Hz, whereas the terminal methyl group pmr signal is displaced only 6 Hz. Thus the 15 proton of **4** must be strongly affected by changes in the A ring.

These results demonstrate the advantages of this direct low temperature nmr method for investigating a variety of Lewis acid–base interactions involving structurally complex ligand molecules. The combination of ^{1}H and ^{19}F nmr provides a reliable method for determining the interaction site or sites in the ligand. For polyfunctional compounds the relative basicities of different sites thus can be determined. If BF_3 coordinates at each of two possible sites, they probably differ in basicity by less than 1 pK_{BH^+} unit.[8] This method could be of particular value in the steroid field, where quantitative data on basicities of functional groups are scarce.[17] Such knowledge could be used in explaining and predicting the course of acid-catalyzed reactions, although of course factors other than basicity also must be considered. For example, ketalization of **3** with methanol in the presence of *p*-toluenesulfonic acid gave largely the 3-ketal,[21] which is in accord with our finding of predominant binding of BF_3 at the 3-carbonyl. The observation of exclusive complexing at the conjugated carbonyl group of **2** and **4** also is consistent with numerous selective acid-catalyzed reactions of steroids of this type.[19] The fact that BF_3 itself frequently is used as a catalyst for steroid reactions adds to the value of the method reported here.

Acknowledgment.—We thank Dr. Anthony Fratiello for helpful discussions during the course of this work.

Registry No.—1-BF_3, 40715-58-0; 2-BF_3, 40715-59-1; **3**-2BF_3, 40715-60-4; 4-BF_3, 40758-67-6; 4-2BF_3, 40758-68-7.

(20) A. Fratiello and R. E. Schuster, *J. Org. Chem.*, **37**, 2237 (1972).

(21) W. Nagata, *et al.*, *Chem. Pharm. Bull.*, **14**, 174 (1966).

Notes

Organophosphorus Enamines. VIII. A Convenient Preparation of Diethyl β-Ketophosphonates[1]

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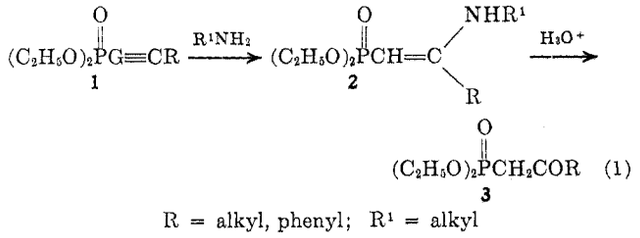
Recently we described the nucleophilic addition of aliphatic amines to the carbon–carbon triple bond in diethyl 1-alkynylphosphonates **1**,[2] giving enamine phosphonates **2** in fair to good yields.[3] Now we wish to report that an acid hydrolysis of **2** produces β-ketophosphonates **3** in excellent yields (eq 1). Compounds



(1)

R = alkyl, phenyl; R^1 = alkyl

3 prepared in this manner are listed in Table I along with their boiling points and yields.

TABLE I

Compd	R	Bp, °C (mm)	Yield,[a] %
a	*n*-C_5H_{11}	130 (0.15)	94
b	*n*-C_6H_{13}	125 (0.10)	89
c	*n*-C_7H_{15}	139 (0.1)	83
d	$(CH_3)_2CHCH_2CH_2$	137 (0.15)	91
e	*c*-C_5H_9	110 (0.10)	76
f	*c*-C_6H_{11}	151 (0.50)	81
g	C_6H_5	135 (0.10)	90
h	$C_6H_5CH_2CH_2$	162 (0.12)	91
i	$C_6H_5CH_2CH_2CH_2$	155 (0.08)	92

[a] This is the yield of the distilled material based upon the starting 1-alkynylphosphonates **1**.

The ir spectra of compounds **3a–i** display strong absorption at τ 5.85–5.90 (C=O). In the nmr spectra of **3a–i**, the *P*-methylene protons exhibit a doublet (J_{PH} = 22.5 Hz) in the region of δ 3.08–3.18. The methylenes from the *O*-ethyl groups display two quartets (J_{HH} = 7.5, J_{PH} = 9 Hz) at δ 4.12–4.20, which overlap to give a near quintet pattern. All other proton resonances were also found to be in agreement with the assigned structures. The structures were further supported by the elemental analyses of these phosphonates **3**.

The hydration of the triple bond in diethyl 1-alkynylphosphonates **1** to produce diethyl β-ketophosphonates **3** has also been reported;[4] our alternate method described here affords, under very mild conditions, a straightforward and high-yield synthesis of this very useful class of phosphonates.

(1) The work was initiated at Tulane University, New Orleans, La.
(2) M. S. Chattha and A. M. Aguiar, *J. Org. Chem.*, **36**, 2719 (1971).
(3) M. S. Chattha and A. M. Aguiar, *J. Org. Chem.*, in press.
(4) G. Sturtz and C. Charrier, *C. R. Acad. Sci.*, **261**, 1019 (1965).