

(m, 1), 6.68 (s, 3), 7.08 (m, 1), 7.7–8.8 (m, 12). NaBH_4 reduction gave cyclooctyl methyl ether (ir, nmr) with $\Delta\nu_{\text{OCH}_3} = 8.5$ cps.

In the nmr spectrum of the raw β -methoxycyclooctylmercuric chloride, some β -acetate product was seen. Although investigation of this minor constituent was not carried out, it is certainly the identical product as isolated by Sokolov.⁶

cis- and *trans*-Cyclononene.—Hydroxymercuration of *cis*- and *trans*-cyclononene gave *trans*-2-chloromercuricyclononanol in 25 and 57% yields, respectively, mp 127–128° from chloroform-pentane. *Anal.* Calcd for $\text{C}_9\text{H}_{17}\text{OHgCl}$: C, 28.65; H, 4.54. Found: C, 28.53; H, 4.27. Ir spectrum (CHCl_3) of the products from the two reactions were identical. The first overtone hydroxyl stretching frequency was 7020.2 cm^{-1} for both products. NaBH_4 reduction gave cyclononanol (ir), having a first overtone hydroxyl frequency of 7032.0 cm^{-1} .

Methoxymercuration of *cis*- and *trans*-cyclononene gave *trans*-1-methoxy-2-chloromercuricyclononane in 54 and 65% yields, respectively: mp 86.5–87.5° from $\text{CH}_3\text{OH-H}_2\text{O}$; ir spectra (KBr) of the products from the two reactions were identical; mass spectrum molecular ion at m/e 490; nmr (CCl_4) τ 6.37 (m, 1), 6.64 (s, 3), 7.02 (m, 1), 7.7–8.6 (m, 14). NaBH_4 reduction gave cyclononyl methyl ether (ir, nmr) with $\Delta\nu_{\text{OCH}_3} = 9.7$ cps.

Registry No.—Cyclobutene, 822-35-5; *trans*-2-chloromercuricyclobutanol, 39837-13-3; *trans*-1-methoxy-2-

chloromercuricyclobutane, 39837-14-4; cyclopentene, 142-29-0; *trans*-2-chloromercuricyclopentanol, 39849-94-0; *trans*-1-methoxy-2-chloromercuricyclopentane, 29581-86-0; cyclohexene, 110-83-8; *trans*-2-chloromercuricyclohexanol, 29581-85-9; *trans*-1-methoxy-2-chloromercuricyclohexane, 5274-83-9; cycloheptene, 628-92-2; *trans*-2-chloromercuricycloheptanol, 39837-19-9; *trans*-1-methoxy-2-chloromercuricycloheptane, 39837-20-2; *cis*-cyclooctene, 931-87-3; *trans*-cyclooctene, 931-89-5; *trans*-2-chloromercuricyclooctanol, 5185-85-3; *trans*-1-methoxy-2-chloromercuricyclooctane, 5185-84-2; *cis*-cyclononene, 933-21-1; *trans*-cyclononene, 3958-38-1; *trans*-2-chloromercuricyclononanol, 39837-23-5; *trans*-1-methoxy-2-chloromercuricyclononane, 39837-24-6.

Acknowledgments.—We gratefully acknowledge the help of Mr. Philip G. Marsh for synthesis of *cis*-cyclononene and cyclononyl amine hydrochloride. This work was supported in part by the National Science Foundation, NSF Grant GP-18317 (W. L. W.) and NSF Grant GP-242 (T. G. T.).

A Direct ^1H and ^{19}F Nuclear Magnetic Resonance Study of Boron Trifluoride Complexes with Cycloalkanones¹

ANTHONY FRATIELLO,*² GEORGE A. VIDULICH, AND YVONNE CHOW

Department of Chemistry, California State University, Los Angeles, Los Angeles, California 90032

Received December 27, 1972

A direct ^1H and ^{19}F nmr study of BF_3 complexes of several cycloalkanones (cyclobutanone through cyclodecanone) has been completed. At temperatures below -80° , exchange is slow enough to permit the observation of separate sets of resonance signals for coordinated and bulk ketone molecules. The appearance of the $\alpha\text{-CH}_2$ pmr peaks of coordinated cyclohexanone and cycloheptanone reflect the slowing of an additional kinetic process, possibly *cis*-*trans* isomerization at the carbonyl oxygen. The ^{19}F nmr signals of mixtures of the cycloalkanones with BF_3 were used to evaluate the relative basicities of this series of molecules. The basicities decreased in the order $\text{C}_8 > \text{C}_5 > \text{C}_7 > \text{C}_6 \approx \text{C}_9 > \text{C}_{10} \gg \text{C}_4$, a trend which was interpreted primarily in terms of steric effects.

Boron trihalide mixtures with a variety of organic bases have been studied by calorimetric^{3–7} and spectroscopic^{8–17} techniques to evaluate the energetics and structural features of the complexes formed. The organic bases involved in several representative studies of BF_3 adducts include pyridines,^{3,11} alkyl ethers, amines, and sulfides,⁴ dimethyl sulfoxide and ethyl acetate,⁵ cyclic ketones,⁶ triethylamine,⁷ ethers,⁸ dimethylformamide,⁹ benzophenone,¹⁰ ureas and thio-ureas,¹² water,¹³ trimethylamine,¹⁴ diethyl ketone,¹⁵

aromatic amine 1-oxides,¹⁶ and benzaldehydes.¹⁷ In most of the nuclear magnetic resonance (nmr) studies, the components were mixed in a 1:1 mole ratio, and the ligand chemical shifts were compared to pure base.

Recently, a direct, low-temperature nmr technique has been refined and applied to studies of boron trihalide complexes.^{18–24} In the presence of excess base, and at temperatures low enough to reduce the rate of ligand exchange, it is possible to observe separate resonance signals for bulk and coordinated ligand molecules. This observation leads to an accurate measure of the ^1H , ^{11}B , ^{19}F , and even ^{13}C ²⁵ chemical shifts produced by complex formation, the stoichiometry of the complex, steric hindrance to complex formation, and the ligand preference of a boron trihalide in a system containing more than one base. These features have been evaluated for amines and

(1) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

(2) To whom correspondence should be addressed.

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TABLE I
HYDROGEN-1 AND FLUORINE-19 CHEMICAL SHIFT AND COORDINATION DATA FOR BORON TRIFLUORIDE COMPLEXES
WITH CYCLOALKANONES

Registry no.	Base	Mole ratios			Temp, °C ^a	δ (¹ H), ppm ^b		δ (¹⁹ F), ppm ^c	Coord no.
		BF ₃	Base	CH ₂ Cl ₂		B	C		
39209-65-9	C ₄	1	3.0	30	-100	3.20	3.72	12.6	0.98
39684-87-5	C ₅	1	2.9	30	-85	2.17	2.94	11.2	0.94
29684-87-5	C ₅	1	2.9	15	-90	2.15	2.96	11.6	1.04
29684-90-0	C ₆	1	2.8	30	-90	2.34	2.93	14.8	1.04
	C ₆	1	3.0	15	-90	2.38	2.97	15.0	0.95
39209-67-1	C ₇	1	2.6	80	-85	2.52	3.12	13.4	0.95
	C ₇	1	3.1	30	-90	2.55	3.18	13.7	0.92
39209-68-2	C ₈	1	2.9	30	-90	2.42	3.05	14.1	0.98
39837-95-1	C ₉	1	3.0	30	-80	2.48	3.05	14.9	0.96
39837-96-2	C ₁₀	1	3.1	35	-80	2.57	3.15	15.0	0.89

^a These temperatures apply to the ¹H measurements which were made within a 5° range of the value shown. The ¹⁹F spectra were recorded within a 10° range of these values. ^b The chemical shifts of the α -CH₂ peaks were measured with respect to internal tetramethylsilane. ^c The chemical shifts were measured with respect to internal hexafluorobenzene, which appeared at higher field in all cases.

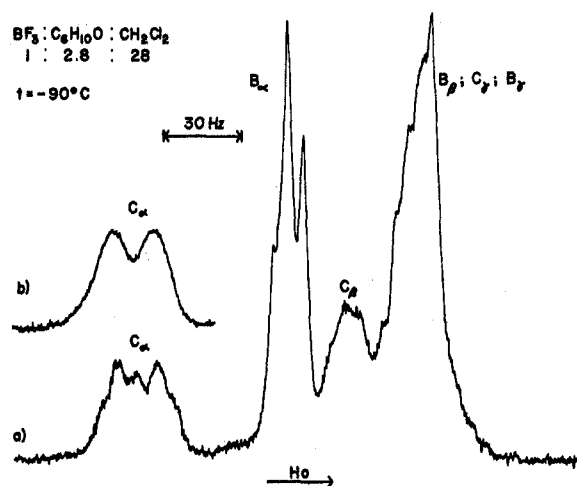


Figure 1.—The proton magnetic resonance spectrum of a mixture of BF₃ and cyclohexanone in methylene chloride, recorded on a Varian HA-100 spectrometer, is shown. The signals arising from coordinated (C) and bulk (B) cyclohexanone molecules are labeled and the particular protons are identified by the subscripts. The C_α signals in portion b result from decoupling of these protons from the C_β protons of the base. Mole ratios also are shown.

phosphines,¹⁸ oxygen-containing bases,^{19,20,25} pyridines,^{21,22} nitrogen heterocycles,²³ keto esters,²⁴ several cyclic ketones,^{26,27} and methanol.²⁸ The present study involves a series of cycloalkanones as the Lewis bases for BF₃ complexation. These compounds, cyclobutanone through cyclodecanone, have the same carbonyl functional group; yet they differ in ring size and strain, basic strength, and possible conformations. Thus, the influence of these parameters on complex formation could be evaluated. It was anticipated that a correlation of these results with available proton basicity data²⁹ would be possible, again demonstrating the utility of this direct nmr method as a complementary tool for basicity studies.³⁰

Experimental Section

Methods.—The boron trifluoride was CP grade and 99.5% pure. The cycloalkanones, acetone, and dichloromethane solvent

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were at least reagent grade and they were used after drying over CaSO₄. Proton magnetic resonance (pmr) area measurements and gas chromatography revealed a noticeable impurity only in the case of cyclononanone. Although attempts to purify this compound by vacuum distillation were unsuccessful, the presence of this impurity did not hamper the measurements. The dryness of each sample was verified by the absence of a resonance signal for BF₃-H₂O adduct in the ¹⁹F nmr spectrum. The boron trifluoride was fractionated twice at -100° and condensed *in vacuo* in the nmr sample tube. The tube was sealed, warmed in an acetone-Dry Ice mixture to dissolve the components, and stored in liquid nitrogen until the spectrum could be recorded. To avoid possible decomposition, the samples were not allowed to reach temperatures above -60°. With these precautions, decomposition was negligible in these systems as indicated by the lack of any extraneous ¹H or ¹⁹F nmr signals, even when measurements were repeated after a period of several days.

The nmr chemical shift and area measurements were made on a Varian A-60 and a Varian HA-100 spectrometer, the latter operating at 94.1 MHz for ¹⁹F nuclei. Both spectrometers are equipped with variable-temperature accessories for measurements from -150 to 200°. The procedure is described in more detail elsewhere,¹⁹⁻²⁴ and it consists essentially of cooling the sample in the probe to reduce the rate of ligand exchange. When separate coordinated and bulk ligand pmr signals, or ¹⁹F nmr signals for base mixtures, are observed, the temperature is adjusted to maximize spectral resolution. The complete spectrum is recorded at this point for chemical shift data, and area integrations are measured electronically.

Results.—The ¹H and ¹⁹F nmr chemical shift and area results for each boron trifluoride-cycloalkanone complex are listed in Table I, and representative pmr spectra are shown in Figures 1 and 2. The cycloalkanones are identified in Table I by the number of carbon atoms in the molecule, and each entry results from measurements of at least three samples. The quantities δ_B and δ_C are the separations in parts per million of the α -CH₂ pmr signals for bulk and coordinated base, respectively, with respect to internal TMS. The ¹⁹F nmr chemical shifts were referred to the internal C₆F₆ signal, which appeared upfield (lower frequency) in all cases. The δ values were calculated using the expression $10^6[(\nu_S - \nu_R)/\nu_0]$, where ν_S is the resonance frequency of the cycloalkanone or BF₃, ν_R is the reference TMS or C₆F₆ resonance frequency, each taken as zero, and ν_0 is 60 or 100 MHz for protons and 94.1 MHz for ¹⁹F nuclei. Since the α -CH₂ pmr multiplets usually were not symmetrical (see Figures 1 and 2), the center of each pattern was approximated for the chemical shift measurements. The ¹H and ¹⁹F δ values are precise to within 0.05 ppm.

As seen in Figures 1 and 2 and implied by the data in Table I, only the α -CH₂ pmr signal of the coordinated cycloalkanone could be identified unambiguously, and, consequently, this signal was used in the chemical shift and area calculations. Also, signal overlap of the bulk α -CH₂ signal with the signals from the other bulk CH₂ protons usually precluded a direct comparison of the bulk and coordinated α -CH₂ signal areas. However, the total area due to coordinated ligand was deduced from the coordinated α -CH₂ signal. The number of base molecules bound per BF₃,

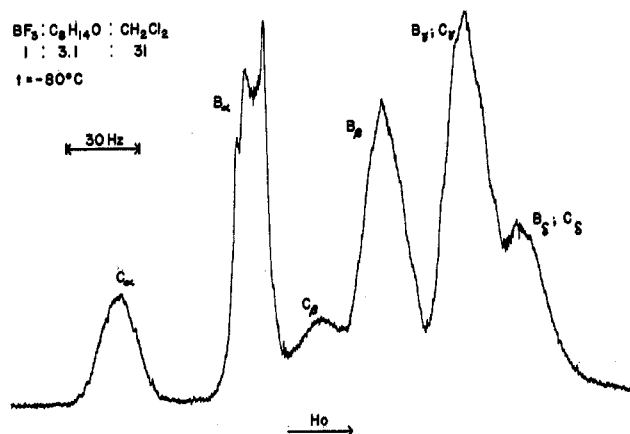


Figure 2.—The proton magnetic resonance spectrum of a mixture of BF_3 and cyclooctanone in methylene chloride, recorded on a Varian HA-100 spectrometer, is shown. The signals arising from coordinated (C) and bulk (B) cyclooctanone molecules are labeled and the particular protons are identified by the subscripts. Mole ratios also are shown.

the BF_3 "coordination number," was calculated from the expression (moles of base/mole of BF_3) \cdot (coord base area/total base area). A precision of 5% was typical for these area results. The coordination number results indicate that 1:1 complexes were formed in all cases, although low (0.9) values were obtained in the cycloheptanone and cyclodecanone solutions. Since gas chromatography, pmr areas, and ^{19}F nmr spectra showed no evidence for the presence of impurities, the two low results must be due to the more extensive signal overlap which prevails in the pmr spectra of these solutions.

The nmr chemical shift and area data for all possible pair mixtures of the cycloalkanones are listed in Table II. In these mixtures, the overlap of the coordinated $\alpha\text{-CH}_2$ signals for each base, exemplified by Figure 3 for the cyclopentanone-cyclooctanone combination, prevented an evaluation of the amount of BF_3 complexed by each ligand. Thus, from pmr spectra, only the total amount of BF_3 complexed could be determined (last column). The fractions of BF_3 complexed, listed in columns 6 and 7 of Table II, were easily measured from the much simpler ^{19}F nmr spectra, an example of which is shown in Figure 4 for the same cyclopentanone-cyclooctanone solution. Since it was difficult to prepare solutions containing the exact base mole ratios desired, the concentrations and BF_3 fractions complexed were normalized to the values shown. Although only small changes ($\sim 5\%$) were involved, a detailed justification will be presented later.

The ^{19}F δ value assignments listed in Table II were aided by the chemical shift results for the single base systems summarized in Table I. The identities of the complexes were made easily in all cases except the cyclohexanone-cyclononanone, cyclohexanone-cyclodecanone, and cyclononanone-cyclodecanone combinations. As seen in Table I, the ^{19}F chemical shifts of the complexes of these bases differed only slightly. However, from the δ value of 14.6 ppm observed for the boron trifluoride-cyclohexanone adduct in the cyclobutanone through cyclooctanone mixtures, the assignment for this species in the remaining mixtures was made. The assignment of the cyclononanone and cyclodecanone complexes was based on a comparison of the data of Table II involving these ligands. The boron trifluoride-cyclononanone complex ^{19}F nmr signal consistently appeared at higher field than that of the cyclodecanone adduct by about 0.1 ppm.

Discussion

The observation of bulk and coordinated ligand pmr signals in these cycloalkanone solutions is due to the reduced rate of intermolecular exchange at low temperatures. This observation was possible with all ketones studied, in contrast to the reported inability to achieve this slow exchange condition in BF_3 solutions of cyclohexanone.²⁶ From the chemical shift displacements produced by complex formation with

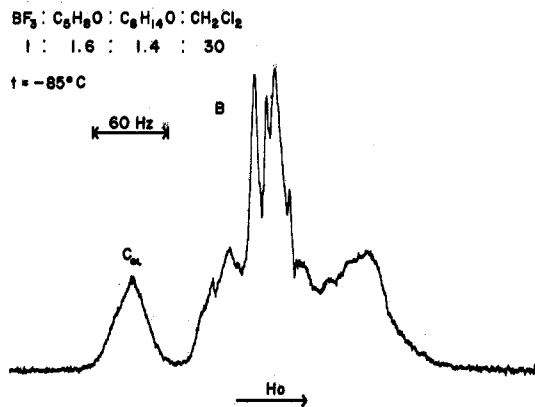


Figure 3.—The proton magnetic resonance spectrum of a mixture of BF_3 , cyclopentanone, and cyclooctanone in methylene chloride, recorded on a Varian A-60 spectrometer, is shown. The signals arising from coordinated (C) and bulk (B) base molecules are labeled. Mole ratios are shown.

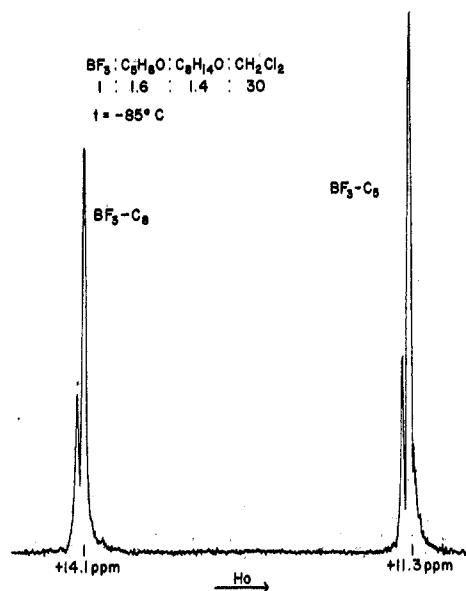


Figure 4.—The fluorine-19 nuclear magnetic resonance spectrum of a mixture of BF_3 , cyclopentanone, and cyclooctanone in methylene chloride, recorded at 94.1 MHz on a Varian HA-100 spectrometer, is shown. The complexes of the bases with BF_3 are labeled, the shifts in parts per million to lower field from internal C_6F_6 are given, and mole ratios of all components are shown.

these compounds, and the relationship $\tau \sim 10/2\pi\Delta\nu$, the lifetime of a base in a particular environment must be ~ 0.05 sec.

The more significant features of the pmr spectra of these boron trifluoride-cycloalkanone solutions at low temperature are (a) a chemical shift displacement of about 0.6 ppm, with two exceptions, for the $\alpha\text{-CH}_2$ protons of coordinated base, with an attenuation of this effect at sites further from the carbonyl group; (b) an increased line width for the bound ligand signals, again more noticeable for the $\alpha\text{-CH}_2$ proton peaks; and (c) a similar appearance of the bound and bulk ligand signals in all but two cases. The chemical shift change, represented by $\delta_{\text{CB}} = \delta_{\text{C}} - \delta_{\text{B}}$, induced at the $\alpha\text{-CH}_2$ position of these cycloalkanones, was ~ 0.6 ppm except in the cyclobutanone (0.5 ppm) and cyclopentanone (0.8 ppm) solution spectra. A comparison of the δ_{C} values shows that in reality only the cyclobutanone result could be considered anomalous.

TABLE II
HYDROGEN-1 AND FLUORINE-19 CHEMICAL SHIFT AND COORDINATION DATA FOR BORON TRIFLUORIDE COMPLEXES
IN MIXTURES OF CYCLOALKANONES

Base		Mole ratios				Temp, °C ^a	δ (¹⁹ F), ppm ^b		BF ₃ Fraction comp ^c		Coord no. ^c
A	B	BF ₃	A	B	CH ₂ Cl ₂		A	B	A	B	
C ₄	C ₅	1	1.5	1.5	30	-90	12.8	11.3	0.02	0.98	0.95
C ₄	C ₆	1	1.5	1.5	30	-90	12.8	14.6	0.05	0.95	0.93
C ₄	C ₇	1	1.5	1.5	30	-90	12.8	13.6	0.02	0.98	0.90
C ₄	C ₈	1	1.5	1.5	30	-90	12.7	14.1	0.02	0.98	1.01
C ₄	C ₉	1	1.5	1.5	30	-90	12.7	14.9	0.02	0.98	0.90
C ₄	C ₁₀	1	1.5	1.5	30	-90	12.7	15.0	0.12	0.88	0.75
C ₅	C ₆	1	1.5	1.5	30	-90	11.4	14.6	0.67	0.33	1.01
C ₅	C ₆	1	1.0	2.0	35	-90	11.3	14.6	0.50	0.50	0.98
C ₅	C ₇	1	1.5	1.5	30	-90	11.4	13.6	0.57	0.43	0.99
C ₅	C ₇	1	1.4	2.9	30	-90	11.4	13.7	0.38	0.62	1.03
C ₅	C ₈	1	1.5	1.5	30	-90	11.3	14.1	0.45	0.55	0.96
C ₅	C ₈	1	1.7	2.9	25	-90	11.3	14.1	0.37	0.63	1.04
C ₅	C ₉	1	1.5	1.5	30	-90	11.3	14.9	0.67	0.33	0.99
C ₅	C ₉	1	1.5	3.0	30	-90	11.3	15.0	0.50	0.50	1.00
C ₅	C ₉	1	3.0	1.5	30	-90	11.4	15.0	0.83	0.17	0.97
C ₅	C ₁₀	1	1.5	1.5	30	-90	11.3	15.0	0.72	0.28	0.96
C ₅	C ₁₀	1	1.5	3.0	30	-90	11.3	15.1	0.64	0.36	1.04
C ₆	C ₇	1	1.5	1.5	30	-90	14.7	13.7	0.35	0.65	0.99
C ₆	C ₈	1	1.5	1.5	30	-90	14.6	14.1	0.32	0.68	0.99
C ₆	C ₉	1	1.5	1.5	30	-90	14.6	14.9	0.50	0.50	1.04
C ₆	C ₁₀	1	1.5	1.5	30	-85	14.6	15.1	0.57	0.43	0.89
C ₇	C ₈	1	1.5	1.5	30	-85	13.6	14.1	0.44	0.56	0.98
C ₇	C ₉	1	1.5	1.5	30	-85	13.6	15.0	0.61	0.39	0.93
C ₇	C ₁₀	1	1.5	1.5	30	-90	13.6	15.1	0.67	0.33	0.93
C ₈	C ₉	1	1.5	1.5	30	-90	14.1	14.9	0.78	0.22	0.96
C ₈	C ₁₀	1	1.5	1.5	30	-85	14.1	15.0	0.75	0.25	0.89
C ₉	C ₁₀	1	1.5	1.5	30	-85	14.9	15.0	0.60	0.40	0.90

^a All shift and area measurements were made within a 5° range of the temperature shown. ^b The chemical shifts were measured with respect to internal hexafluorobenzene, which appeared at higher field in all cases. ^c These coordination numbers are based on ¹H spectra.

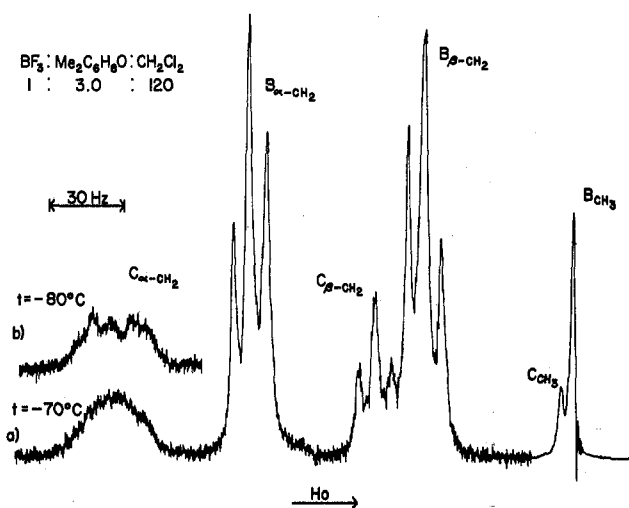


Figure 5.—The proton magnetic resonance spectrum of a mixture of BF₃ and 4,4-dimethylcyclohexanone in methylene chloride, recorded on a Varian HA-100 spectrometer, is shown. The signals arising from coordinated (C) and bulk (B) 4,4-dimethylcyclohexanone molecules are labeled and the particular protons are identified by the subscripts. The signal amplitude was reduced by a factor of 10 when recording the methyl group signals. Mole ratios also are shown.

For example, in the boron trifluoride-cyclopentanone solution spectra, the inordinately high field position of the bulk α -CH₂ pattern is responsible for the large δ_{CB} value. As will be discussed in detail later, the unusual complexing behavior of cyclobutanone is due to the severe ring strain in this molecule. The compounds in this series differ in basicity, and pre-

sumably should form complexes of varying strength. Calorimetric studies of the cyclopentanone and cyclohexanone systems, for instance, show marked differences in the heats of formation of their BF₃ complexes.⁶ Thus, the lack of dependence of the δ_{CB} values with ring size rules out a correlation of pmr chemical shift with interaction strength. Rather, complex formation produces the same extent of deshielding at the α -CH₂ sites. Similarly there is no observable trend of ¹⁹F nmr chemical shifts with molecular structure in this series of BF₃ complexes.

The line width characteristics of the coordinated ligand pmr signals are due to interactions with the quadrupole moment of the boron nucleus of BF₃. At the low temperatures required in this study, the solution viscosity is high and the lifetime of ligand molecules in the "coordination shell" of BF₃ is relatively long. Consequently, the coupling between the ¹¹B nuclei and bound ligand protons is effective, the proton T₁ values are reduced, and signal broadening results. As expected, this effect diminishes with distance from the ¹¹B nucleus.

The most interesting spectral features are exhibited by the BF₃ complexes of cyclohexanone and cycloheptanone, for which the coordinated α -CH₂ pmr peaks appear as more complicated patterns. This is illustrated in Figure 1 for the cyclohexanone complex and in Figure 5 for the BF₃ adduct of 4,4-dimethylcyclohexanone, which produces a much simpler spectrum.³¹ It also appears that two processes, one in-

(31) The authors are indebted to Professor Paul McMaster of Holy Cross College for a sample of this compound and for many helpful suggestions regarding this aspect of the study.

volving ligand exchange and another causing the pattern of the bound $\alpha\text{-CH}_2$ pmr signals, are involved. As seen in Figure 5, at -70° , ligand exchange is slow enough to observe distinct sets of signals for all protons, even those of the methyl groups, for bulk and coordinated 4,4-dimethylcyclohexanone molecules. The broadness of the coordinated $\alpha\text{-CH}_2$ peak contrasts with the sharp, well-defined $\beta\text{-CH}_2$ triplet and indicates that these molecules are still involved in some process which has a greater influence at the carbon atoms closest to the carbonyl group. Although not completely resolved, the coordinated $\alpha\text{-CH}_2$ pattern at lower temperatures (see Figures 1 and 5) seems to be a set of overlapping triplets, producing peaks with approximate area ratio 1:2:2:2:1. The three central peaks are well defined but the outer two are shoulders. If this assignment is correct, the two sets of coordinated $\alpha\text{-CH}_2$ triplets would be duplicates of the parent bulk signal. When the coordinated $\beta\text{-CH}_2$ protons are decoupled, the coordinated $\alpha\text{-CH}_2$ multiplets collapse into two singlets of equal area.

These features could result from a reduced rate of cis-trans isomerization at the boron trifluoride-carbonyl linkage. This process would produce two coordinated $\alpha\text{-CH}_2$ triplets of equal area, since there is no thermodynamic preference for either isomer. A precedent is provided by the diethyl ketone-boron trifluoride adduct, for which cis-trans isomerization is slow at -120° .¹⁵ Although a carbonyl group is involved in both cases, the structural differences between this ketone and the cycloalkanones can account for the ability to observe slow isomerization at higher temperatures in the latter systems. It is not clear why this process should be more rapid in the larger ($\text{C}_8\text{-C}_{10}$) cycloalkanones, a situation which seems to prevail.

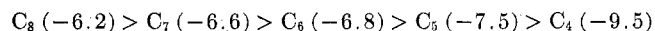
A slow chair-chair interconversion also might give rise to the spectra of Figures 1 and 5, but several points minimize this possibility. Ring strain produces an essentially planar configuration for cyclobutanone³²⁻³⁴ and a rigid, "half-chair" structure for cyclopentanone,³⁵ precluding this kind of conformational motion in these smaller members of the series. In the larger members, barriers to interconversion are very low and this motion proceeds easily. For example, interconversion is slow on the nmr time scale only at -160° for cyclooctanone ($\Delta H^\ddagger \cong 7$ kcal)^{36,37} and all attempts to slow chair-chair interconversion for cyclohexanone have been unsuccessful, even at -170° .^{38,39} These results led to a postulate of a barrier of only 5 kcal for interconversion of this molecule. Unless the hybridization of the carbonyl carbon in the BF_3 complex resembles that of cyclohexane, where chair-chair interconversion proceeds with a ΔH^\ddagger of about 10

kcal,^{40,41} this process does not seem to be the cause of the spectra observed with cyclohexanone and cycloheptanone. This process also should produce a more complex $\alpha\text{-CH}_2$ spectrum as a result of axial-equatorial coupling, although this could be obscured by coupling with the boron quadrupole.⁴² Measurements with substituted cyclohexanones are planned in an attempt to clarify these points.

The coordination data of Table II emphasize the utility of this direct nmr method for evaluating in a qualitative manner the relative basic strengths of a series of compounds toward a common Lewis acid.¹⁸⁻²⁴ As will be discussed later, at equal concentrations of each base, the fraction of BF_3 complexed depends only on the basicity of the ligand. For example, in all mixtures, cyclobutanone was able to complex only a small fraction of the BF_3 , a good indication that it is the weakest base in this series. Cyclopentanone binds more than half of the BF_3 in the presence of any other member of this series except cyclooctanone. From a comparison of such results obtained with mixtures containing bases at equal concentrations, the following trend of decreasing relative basicity toward BF_3 can be constructed for these cycloalkanones.



Here the subscript indicates the number of carbon atoms in the ring. This trend may be compared to the available protonation data for this series, which yield the following order of decreasing basicity expressed as $\text{p}K_{\text{BH}^+}$ values at 25° .²⁹



It is evident that, in both systems, cyclobutanone is the weakest base. This can be attributed to the effect of the severe ring strain of this molecule on the nature of the carbonyl bond. It has been suggested that the C-C-C bond angle at the carbonyl group in cyclobutanone produces an increase in the s character of the carbon-oxygen σ bond, and a consequent decrease in the basic strength of the oxygen atom.⁴³ This effect decreases with increasing ring size, but it probably is the cause of the relatively low $\text{p}K_{\text{BH}^+}$ value of cyclopentanone.

In contrast to the smooth increase of basicity with ring size toward the proton, the order with respect to BF_3 is much more complicated. The main difference between the two groups of studies is the steric factor introduced by the use of the more bulky BF_3 . For example, the position of cyclononane and cyclodecanone in this BF_3 basicity series is not surprising when the conformational possibilities for these molecules are considered. The size of these two rings may introduce steric hindrance to complex formation at the carbonyl group, by methylene groups at the opposite end of the molecule. This steric hindrance also should prevail in the cyclooctanone ring but to

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a lesser extent. Also, the preferred conformations of this molecule place the carbonyl group in a somewhat favorable position for complex formation.^{34,36} Since these steric effects would be minimal in smaller rings, one would predict that cycloheptanone and cyclohexanone, respectively, should follow cyclooctanone in the BF_3 basicity series.

Thus, as a function primarily of steric factors, cyclopentanone emerges as a strong complexing agent for BF_3 , in spite of its low proton basicity as compared to other members of this series. Previous studies in these laboratories²⁰⁻²⁴ have implied that, if $\text{p}K_{\text{BH}^+}$ values for two bases differ by one or more units, essentially all the BF_3 will be complexed by the stronger ligand. Since cyclopentanone can compete with all the larger cycloalkanones in BF_3 solution, steric factors reduce the effective basicity of the latter by at least a factor of 10.

In addition to the relative basicity, which is a fundamental molecular property, the fraction of BF_3 complexed by each base in a mixture depends on the concentration of the components. For instance, when cyclopentanone and cyclohexanone are mixed in equal concentrations, cyclopentanone complexes approximately two-thirds of the BF_3 . However, these bases complex equal fractions when the cyclohexanone concentration is twice that of cyclopentanone (see Table

II). In other words, the relationship, $f \propto b \cdot c$, where f is the BF_3 fraction complexed, b is the relative basicity of the molecule toward BF_3 , and c is the base concentration, seems to hold for these systems. Thus, at equal concentrations, $f_1/f_2 = b_1/b_2$ provides a measure of the relative basic strength of these compounds. Assuming that basicity is not concentration dependent, the fraction of BF_3 complexed at various base concentrations can be estimated from $f_1/f_2 = \text{constant}$ (c_1/c_2). This relationship holds within 10-20% when tested in these mixtures and it provides a justification for the normalization procedure used in the development of the Table II data.

Registry No.—Adduct of BF_3 and 4,4-dimethylcyclohexanone, 39209-78-4.

Acknowledgments.—This work was supported in part by Research Grant GP-9517 from the National Science Foundation, a National Science Foundation Instrument Grant, GP-8347, for the purchase of the Varian HA-100 nmr instrument, a Holy Cross College Faculty Fellowship (G. A. V.), and a National Institutes of Health Research Career Development Award, 5-K4-GM42334-04 (A. F.). The authors are indebted to Mr. Richard Perrigan for his assistance in recording several of the spectra.

On the Dehydroxylation of Phenols by Cleavage of Their Diethyl Phosphate Esters with Alkali Metals in Liquid Ammonia¹

ROBERTO A. ROSSI² AND JOSEPH F. BUNNETT*

University of California, Santa Cruz, California 95064

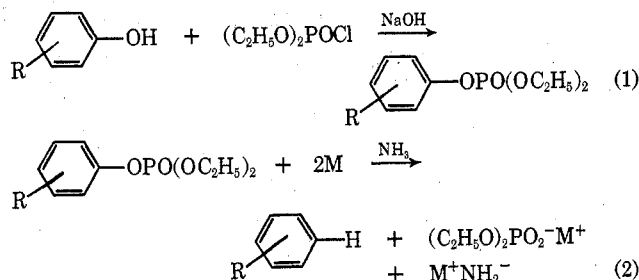
Received November 7, 1972

In a method due to Kenner and Williams, the phenolic hydroxyl group is replaced by hydrogen in a two-step process: the phenol is converted to an aryl diethyl phosphate ester, which is then cleaved with an alkali metal in ammonia. Reinvestigation of the method with use of glpc shows it to be convenient and to give high yields of dehydroxylation products. Complications are encountered in the dehydroxylation of 1-naphthol, but allyl, acetyl, and (in part) nitro substituents survive the procedure unscathed.

A communication by Musliner and Gates,³ announcing a new method for the dehydroxylation of phenols, started with the sentence: "Up to the present time, no general method has been available for the removal of phenolic hydroxyl groups." The communication goes on to describe the method they developed, which involves conversion of phenols to heterocyclic ethers (especially 1-phenyl-5-tetrazolyl ethers) which are then cleaved by hydrogenolysis over 5% palladium on carbon. However, it fails to mention an attractive method of considerable generality which had been described 11 years earlier. We have reinvestigated the older method, and have formed a high opinion of it.

The method to which we refer, due to Kenner and Williams,⁴ involves conversion of the phenol to the corresponding aryl diethyl phosphate ester, and then cleavage of the latter with an alkali metal in liquid am-

monia. The modification of it which we employed is sketched in eq 1 and 2. Kenner and Williams re-



ported high yields of dehydroxylation products from several alkoxy-, alkyl-, or acetamido-substituted phenols.

The method was also studied and employed by Pelletier and Locke⁵ for the small-scale dehydroxylation of several phenols, most of which were derived from polycyclic aromatic systems. The yields that they ob-

(1) Research supported in part by the National Science Foundation.

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