A 3-g sample of the solid complex was dissolved in 250 ml of CH_2Cl_2 and the silver salt was extracted with 4×100-ml portions of distilled water. The organic layer was dried with $MgSO_4$ and CH_2Cl_2 removed by evaporation. The remaining liquid, 0.8 g (53%), had identical spectral properties with those of 1.

Complexes of Silver Fluoborate with Simple Aliphatic and Aromatic Ketones. The Carbonyl Group as an n vs. π Donor Based on Carbon-13 Nuclear Magnetic Resonance Spectroscopy[1]

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Abstract: Cyclohexanone and acetophenones were found to form complexes with $AgBF_4$ in methylene chloride as shown by enhanced solubility of the silver salt, infrared shifts of carbonyl bands to lower frequencies, and downfield nmr shifts of α protons. Downfield ^{13}C shifts of $COCH_2$ carbons upon complexation were very similar for both aliphatic and aromatic systems, indicating that the site of complexation is the carbonyl group in both cases. The carbonyl group appears to act as an n donor toward silver ion, since upon complexation the downfield ^{13}C shifts of the carbonyl carbon compared favorably with those for the α carbons of known n donors such as diethyl ether and amines and were in the opposite direction from those for known π donors such as cyclohexene, toluene, and styrene. The nature of this silver-oxygen bond, considered to be rather weak, was best elucidated by spectroscopic studies under nonhydroxylic conditions such as employed in the present work.

It is well known that silver ion forms stable complexes with unsaturated alkenes and aromatic systems as π donors.[2] Enhanced solubility in the presence of silver salts has been accepted as due to formation of complexes, which have been characterized by ir,[3] Raman,[3a,4] uv,[4,5] and proton[3b,6] and ^{13}C nmr[7] methods. The nature of bonding, described in terms of σ bonding to Ag^+ with back-bonding from d orbitals to the ligand,[8] has recently been investigated by extended Hückel methods,[9] and spectroscopic results have been explained theoretically by perturbation[4] and CNDO-MO calculations.[10] Silver salts also complex with n donors such as amines[11] and, less strongly, ethers.[12]

Much less is known about Ag^+ interactions with carbonyl compounds, though a solid complex with acetone has been isolated.[12b] In some reported cases, the bonding site is probably another functional group, as in amides,[13] urea,[14] or olefinic ketones.[15] Formation constants in aqueous media have been reported for acetone[16] and acetophenone,[17] but perhaps due to the low concentrations, these complexes were not characterized further. In a proton nmr study of cyclohexene · $AgBF_4$ in organic solvents, the use of acetone-d_6 precluded observation of ketone · Ag^+ interactions.[6b]

We now report the first spectroscopic data on complexes of $AgBF_4$ with representative aliphatic and aromatic ketones which can be formed in stoichiometric amounts in methylene chloride. Since the carbonyl group contains the electronic features of both π and n donors, model systems were also investigated in order to determine the site of complexation.

(1) Research supported in part by a National Science Foundation Traineeship grant to one of us (G. J. J.).

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Table I. Carbon-13 Chemical Shifts[a] for Cyclohexanone in Methylene Chloride with Added Salts[b]

Added salt	Mole ratio, [salt]/[ketone]	C₁ δ_{obsd}	C₁ $\Delta\delta$[d]	C₂ δ_{obsd}	C₂ $\Delta\delta$[d]	C₃ δ_{obsd}	C₃ $\Delta\delta$[d]	C₄ δ_{obsd}	C₄ $\Delta\delta$[d]
None	0.0	211.1		42.2		27.5		25.5	
AgBF₄	0.452	221.7	10.6	43.4	1.2	27.3	−0.2	24.8	−0.7
AgClO₄	0.26[c]	216.4	5.3	42.8	0.6	27.4	−0.1	25.1	−0.4
Bu₄NBF₄	0.50	211.0	−0.1	42.2	0.0	27.5	0.0	25.5	0.0
LiClO₄	0.30[c]	216.3	5.2	42.0	−0.2	27.2	−0.3	25.2	−0.3

[a] Downfield from internal TMS. [b] Solutions containing 0.920 g of ketone and the indicated amounts of salts in 5 g of solution. [c] Saturated solutions. [d] $\Delta\delta = \delta_{obsd} - \delta_{ketone}$ for corresponding carbon atoms.
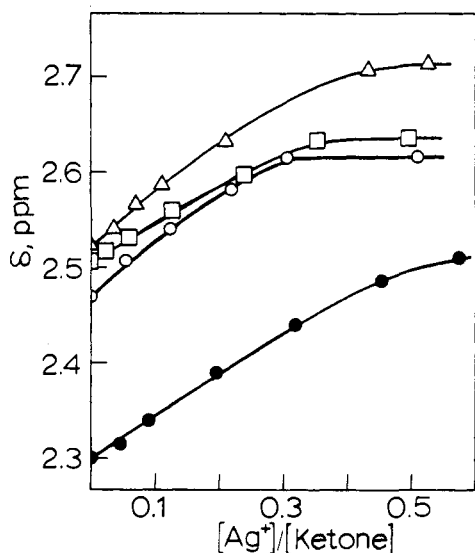

Figure 1. Dependence of α and acetyl proton chemical shifts of various ketones on moles of AgBF₄ per mole of ketone: (●) cyclohexanone; (○) p-methylacetophenone; (□) acetophenone; (△) p-chloroacetophenone.

Figure 2. Effect of AgBF₄ on the carbonyl stretching frequency of cyclohexanone in methylene chloride. Mole ratios of [AgBF₄]/[ketone] were: (a) 0.0; (b) 0.105; (c) 0.443.

Results

Aliphatic Ketones. With methylene chloride solutions containing ca. 15% cyclohexanone it was found that adding anhydrous AgBF₄ produced a deep red color and a new carbonyl stretching frequency at 1675 cm⁻¹ and also caused a downfield shift in the nmr multiplet corresponding to α-CH₂ protons. These results were taken as evidence for complex formation involving a specific interaction of AgBF₄ with the carbonyl bond. The possibility that these spectroscopic data represented the dimeric 2-cyclohex-1-enylcyclohexanone formed by an aldol reaction was unlikely, because 83% of unchanged cyclohexanone was recovered from these solutions by simple extraction of the silver salt.

The chemical shifts of α-CH₂ protons were found to increase as AgBF₄ was added as shown in Figure 1.[18] At high ketone concentration (low mole ratio of AgBF₄) the observed δ is a weighted average of chemical shifts of the free ketone and its complex.[19] However, this value began to level off at a $\Delta\delta$ value of ca. 0.19 at a 0.5 mol ratio corresponding to a 2 (ketone)·AgBF₄ complex (see below). At this ratio there is essentially no free

Ag⁺ present, since the amount in solution is 220 times greater than the amount that can be dissolved in pure chloride (per gram of solvent). Also at this ratio nearly all of the ketone is complexed as shown by the ir spectrum of Figure 2c. Consequently the observed δ at a 0.5 mol ratio of AgBF₄ can be considered as characteristic of the complex itself,[20] and any small errors resulting from this assumption here and for other cases described below will not alter the general conclusions. Natural abundance ¹³C chemical shifts for cyclohexanone and its complex are given in Table I where it can be seen that the carbonyl carbon underwent the largest downfield shift on complexation ($\Delta\delta$ of 10.6 ppm) with a smaller shift (1.2 ppm) for the α carbon.

The effects of other salts show that spectral changes are due to Ag⁺ and not the BF₄⁻ counterion. Though AgNO₃ was insoluble, AgClO₄ produced a $\Delta\delta$ commensurate with its lower solubility (Table I) and a new ir band at 1680 cm⁻¹. These results are in agreement with the known order of complexing ability,[3c,4] with AgBF₄ > AgClO₄ > AgNO₃. In contrast, added tetrabutylammonium fluoborate had no effect on ir or nmr spectra. An interaction of Li⁺ with cyclohexanone is indicated by a downfield shift of the carbonyl carbon although the degree of complexation is much less as judged by ir.[21]

Low-temperature studies were carried out with methyl ethyl ketone and diethyl ketone. As shown in

(18) The indicated δ is actually the center of a multiplet which moved downfield without changing peak shape or intensity. Separate multiplets for free ketone and complex could not be detected. This was more clearly evident in the case of methyl ethyl ketone, diethyl ketone, and the acetophenones.

(19) R. Foster and C. A. Fyfe, *Progr. Nucl. Magn. Resonance Spectrosc.*, **4**, 1 (1969).
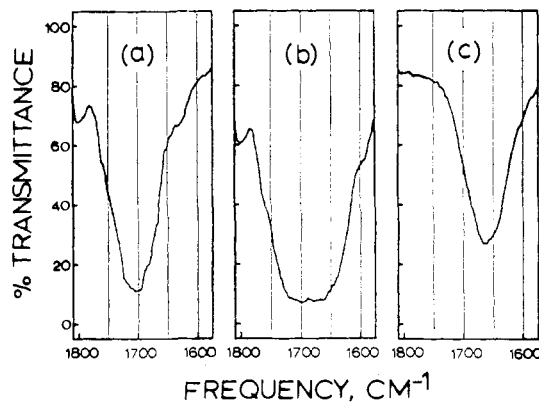
(20) The approach of ref 6b was not appropriate, since their results pertained to 1:1 complexes and to dilute solutions not as suitable for obtaining ¹³C spectra. Their results do predict little dissociation in methylene chloride, though their formation constants included solvent competition (ref 19, p 38) and unpredictable salt effects.

(21) No new ir absorption band was observed for LiClO₄ with cyclohexanone. Also, for this case, it seems unlikely that ClO₄⁻ bonds to the C₁ carbon, since one would then expect the carbonyl carbon to experience an upfield nmr shift.
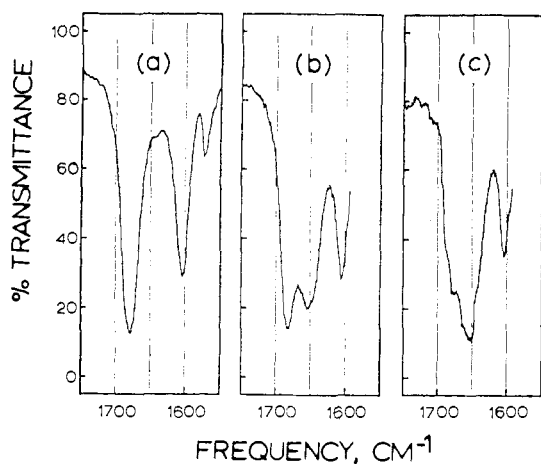
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Figure 3. Effect of $AgBF_4$ on the carbonyl stretching frequency of p-methylacetophenone in methylene chloride. Mole ratios of $[AgBF_4]/[\text{ketone}]$ were: (a) 0.0; (b) 0.220; (c) 0.536.

Table II. Effect of Temperature on Chemical Shifts[a] of α Protons of Methyl Ethyl Ketone and Diethyl Ketone and Complexes in Methylene Chloride

Species obsd	Temp, °C	δ_{obsd} (—CH_3—)	$\Delta\delta^b$ (—CH_3—)	δ_{obsd} (—CH_2—)	$\Delta\delta^b$ (—CH_2—)
MeCOEt	33	2.19		2.55	
2MeCOEt·AgBF_4	33	2.47	0.28	2.78	0.23
MeCOEt	−90	2.28		2.65	
2MeCOEt·AgBF_4	−90	2.55	0.27	2.90	0.25
Et_2CO	33			2.55	
2Et_2CO·AgBF_4	33			2.71	0.16
Et_2CO	−90			2.63	
2Et_2CO·AgBF_4	−90			2.83	0.20

[a] Measured on a Varian A-60 to ±0.04 ppm and temperature calibrated by the method of A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970). [b] $\Delta\delta = \delta_{obsd} - \delta_{ketone}$ for corresponding protons.

Table II, complex formation occurred at 33°, since $\Delta\delta$ values for α protons were comparable to those observed for cyclohexanone. The fact that a given $\Delta\delta$ value did not change significantly on lowering the temperature to −90° is another indication of quantitative complex formation at room temperature.[3b,22] However, the important feature of the low-temperature spectra is that no changes in peak multiplicity or coupling constants occurred on cooling.

Aromatic Ketones. Similar results were found for p-methylacetophenone, acetophenone, and p-chloro-acetophenone which gave red-orange solutions in methylene chloride having green fluorescence when $AgBF_4$ was added. With the p-methyl derivative, this new absorption was observed at 462 nm with a fluorescence band occurring at 510 nm (excitation at 377 or 497 nm). More indicative of complex formation were ir spectra which showed that $AgBF_4$ caused new absorptions corresponding to weaker carbonyl stretching frequencies. For example, with p-methylacetophenone having ν_{CO} at 1680 cm^{-1}, a new band at 1655 cm^{-1} appeared and increased in intensity as more silver salt was added (Figure 3).[23] Data with $AgBF_4$ mole ratios

(22) However, as pointed out in ref 6b, the same result would obtain if ΔH for complex formation is small, as might be expected here.

(23) The residual band corresponding to uncomplexed ketone for a 0.526 mol ratio of $AgBF_4$ is probably due to p-methylacetophenone formed by decomposition of the complex when the ir spectrum was taken, since its relative intensity increased with subsequent scans and free silver was deposited on the cell walls.

greater than ca. 0.5 could not be obtained, since in all cases this represented the (greatly enhanced) solubility limit of $AgBF_4$. On cooling a saturated solution of p-methylacetophenone, crystals formed which gave an analysis for 2(ketone)·$AgBF_4$ and which showed only the new band at 1665 cm^{-1} (with some decomposition).[23]

Chemical shifts of acetyl methyl protons increased with the mole ratio of $AgBF_4$ as shown in Figure 1. Changes for all other protons, though smaller, followed similar patterns and their downfield shifts upon complexation ($\Delta\delta$) are given in Table III. It should be

Table III. Proton Chemical Shifts for Various Donors (D) and $AgBF_4$ Complexes in Methylene Chloride[a]

	Mole ratio,[b] $[AgBF_4]/[D]$	Position	δ_{donor}	$\delta_{complex}$	$\Delta\delta^c$
CH_3CO—⟨⟩	0.50	CH_3CO	2.51	2.64	0.13
		ArH	7.91	7.98	0.07
CH_3CO—⟨⟩—CH_3	0.51	CH_3CO	2.47	2.62	0.15
		H_2	7.79	7.87	0.08
		H_3	7.19	7.28	0.09
		p-CH_3	2.33	2.37	0.04
CH_3CO—⟨⟩—Cl	0.53	CH_3CO	2.52	2.71	0.19
		H_2	7.84	7.91	0.07
		H_3	7.38	7.40	0.02
CH_3—⟨⟩	0.50	CH_3	2.28	2.37	0.09
		ArH	7.13	7.29	0.16
⟨⟩	0.60	H_1	5.65	6.53	0.88
		H_2	1.99	2.26	0.27
		H_3	1.60	1.72	0.12

[a] All solutions contained 7.5 mmol of donor and the indicated amounts of $AgBF_4$ in 4 g of solution. [b] Saturated in $AgBF_4$ except for cyclohexene. [c] $\Delta\delta = \delta_{complex} - \delta_{donor}$ for corresponding protons.

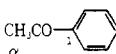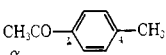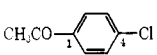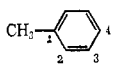noted that even at high ketone concentrations, methyl signals appeared as sharp singlets. Thus, although both free and complexed ketone can be observed by ir spectroscopy in these solutions, there is fast exchange between donor molecules on the nmr time scale. The apparent curvature shown in Figure 1 may be due to formation of 3(ketone)·$AgBF_4$ complexes[12b] at high ketone concentration analogous to nmr results reported by Foster.[24] Downfield shifts were not due to an aldol-type product, 1,3-di(4-methylphenyl)-3-buten-1-one, which was independently synthesized and found to have an nmr spectrum markedly different from that of the ketone–$AgBF_4$ solutions.

Natural abundance ^{13}C spectra of ketones and complexes (Table IV) showed that the largest $\Delta\delta$ values, those for the carbonyl carbons, were relatively constant at ca. 6.5 ppm, and all acetyl methyl carbons were shifted downfield by ca. 1.2 ppm.

Model Systems. For comparison purposes, the spectroscopic behavior of $AgBF_4$ complexes with known π and n donors in methylene chloride was investigated, though some data have been reported for other solvents. When $AgBF_4$ was added to cyclohexene, observed downfield shifts in vinyl protons increased with added $AgBF_4$, with curvature at the 0.5 mol ratio region indicating formation of a 2(cyclo-

(24) M. I. Foreman, J. Gorton, and R. Foster, *Trans. Faraday Soc.*, **66**, 2120 (1970).

Table IV. Carbon-13 Chemical Shifts[a] for Various Donors (D) and AgBF$_4$ Complexes in Methylene Chloride[b]

Donor	Mole ratio,[c] [AgBF$_4$]/[D]	Position	δ_{donor}	$\delta_{complex}$	$\Delta\delta^d$
CH$_3$CO—⟨phenyl⟩ (α)	0.50	α-CH$_3$	26.6	27.8	1.2
		CO	197.6	203.6	6.0
		C$_1$	137.6	137.1	−0.5
CH$_3$CO—⟨phenyl⟩—CH$_3$ (α)	0.51	α-CH$_3$	26.6	27.7	1.1
		CO	197.2	203.4	6.2
		C$_1$	135.4	134.4	−1.0
		C$_4$	144.0	146.3	2.3
		p-CH$_3$	21.6	21.7	0.1
CH$_3$CO—⟨phenyl⟩—Cl	0.53	α-CH$_3$	26.5	27.7	1.2
		CO	196.4	203.3	6.9
		C$_1$	136.1	135.0	−1.1
		C$_4$	139.6	141.0	1.4
CH$_3$—⟨phenyl⟩	0.50	C$_1$	138.2	141.4	3.2
		C$_2$	129.4	128.9	−0.5
		C$_3$	128.6	125.7	−2.9
		C$_4$	125.7	121.9	−3.8
⟨cyclohexene⟩	0.60	C$_1$	127.5	125.5	−2.0
		C$_2$	25.6	26.1	0.5
		C$_3$	23.3	22.5	−0.8

[a] Downfield from internal TMS. [b] All solutions contained 7.5 mmol of donor and the indicated amounts of AgBF$_4$ in 4 g of solution. [c] Saturated solutions except for cyclohexene. [d] $\Delta\delta = \delta_{complex} - \delta_{donor}$ for corresponding carbons.

hexene)·AgBF$_4$ complex in these concentrated solutions.[25] All proton and ^{13}C values are given in Tables III and IV, respectively. For cyclohexene ^{13}C shifts are somewhat smaller than those reported in aqueous solution[7c] but follow the same trend with *upfield* shifts for olefinic carbon atoms. Upfield shifts were also found for benzene (−1.0 ppm) and the ortho, meta, and para carbons of toluene. For diethyl ether complexation caused downfield shifts for α and β carbons of 2.1 and 0.5 ppm, respectively.[26]

Discussion

The study of model systems showed that all protons undergo downfield shifts on Ag$^+$ complexation, with those nearest the bonding site experiencing the largest effects. However, the nature of ^{13}C shifts depended greatly on the type of donor and hence are more instructive. With n donors such as ether and amines,[26] downfield shifts are observed, presumably due to electron withdrawal from the n orbital in forming a σ bond to the empty 5s orbital of Ag$^+$. With alkene donors, on the other hand, the sp^2 carbon atoms at the site of complexation undergo upfield shifts. This effect can be interpreted[7c] in terms of back donation of filled silver d electrons to low-lying antibonding orbitals of the donor or increased paramagnetic shielding because of changes in the excitation energies. For benzene as a π donor, the observed upfield shifts might be expected[27] from cyclohexene results, since Ag$^+$ is localized over two carbon atoms of the ring.[2] For toluene (see structure I below for ^{13}C $\Delta\delta$ values) localization over two carbon atoms is also apparent from the very large increased shielding associated with the meta–para bond.

(25) See ref 6b for concentration conditions favoring the 1:1 complex, though 2(alkene)·AgBF$_4$ complexes are more stable for acyclic alkenes.[3b]

(26) D. R. Crist, G. J. Jordan, and J. A. Hashmall, *J. Amer. Chem. Soc.*, **96**, 4927 (1974).

(27) For an example showing such a comparison in reverse, see ref 6a.

Styrene provides a very useful example which helps justify the use of monofunctional models in predicting the site of complexation in polyfunctional compounds. From II it can be seen that α and β carbons undergo large upfield shifts similar to the effects of complexation with localized π bond of cyclohexene, while unsubstituted ring carbons undergo downfield shifts unlike the effects of complexation with the aromatic ring of toluene. From these models ^{13}C data clearly show complexation with the olefinic bond of styrene, as found by completely different experimental methods.[5,28]

Aliphatic ketones form complexes having Ag$^+$ associated with the carbonyl bond as demonstrated by enhanced solubility and a weakening of the CO stretching frequency. The site of complexation can be assigned by comparison with the complexes of diethyl ether and cyclohexene. The $\Delta\delta$ value for C$_1$ of cyclohexanone indicates that the carbonyl group is acting as an n donor toward Ag$^+$ giving the characteristic downfield shift of carbon bearing complexed oxygen and opposite to the upfield shift for a carbon involved in π bonding to Ag$^+$. Thus the interaction of Ag$^+$ with ketones leading to complex formation can be described as a silver–oxygen bond.

In support of the result that a downfield $\Delta\delta$ implies an n donor CO, Olah found that the proton nmr of protonated diethyl ketone showed nonequivalent ethyl groups, which could be explained by H$^+$ bonded to n electrons in a sp^2 orbital rather than symmetrically located above the π bond.[29] Also, for the case of protonated acetone, ^{13}C nmr showed that the carbonyl carbon underwent a large *downfield* shift of 43 ppm upon protonation.[30] The structural similarity of Li$^+$ to H$^+$ suggests that it should bond to n electrons, and indeed added Li$^+$ caused a downfield shift of the carbonyl carbon of cyclohexanone. It might be pointed out that since the degree of complexation appears to be low for Li$^+$, the chemical shift corresponding to the complex itself could be quite large, i.e., comparable to that observed for protonated ketones.

One consequence of this conclusion is that syn and anti isomers of the complex should exist as shown for methyl ethyl ketone (eq 1). However, our low-temper-

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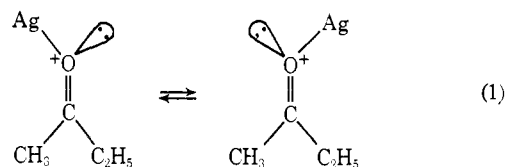
ature study indicates that this exchange is fast on the nmr time scale even at −90° or alternatively that the nature of the silver–oxygen bond is such as to cause negligible chemical shift differences.

With aromatic ketones, complex formation is also apparent, but three sites of complexation are possible: in the molecular plane bonded to n electrons of oxygen, localized above the carbonyl bond, or over two carbons

(28) (a) T. Fueno, T. Okuyama, T. Deguchi, and J. Furukawa, *J. Amer. Chem. Soc.*, **87**, 170 (1965); (b) T. Fueno, T. Okuyama, and J. Furukawa, *Bull. Chem. Soc. Jap.*, **39**, 2094 (1966).

(29) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, **89**, 3586 (1967).

(30) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969); (b) G. A. Olah and A. M. White, *ibid.*, **90**, 1884 (1968); (c) to the extent that this is a better model for the CO group as an n donor, it may be possible to have a significant amount of the π complex in equilibrium with the n complex.

of the aromatic ring. The striking similarity in nmr shifts of acetophenones and cyclohexanone (which does not even have an aromatic ring) strongly indicates that *in methylene chloride* Ag$^+$ is associated with the C=O bond in both cases. For example, the largest proton shifts were for α protons, with values of *ca.* 0.16 and 0.19 for acetophenones and cyclohexanone, respectively. The largest ^{13}C shifts were for the carbonyl carbon, with values of *ca.* 6.4 and 10.6 ppm for acetophenones and cyclohexanone, respectively, and values for carbons α to the carbonyl group are *ca.* 1.2 for both. The fact that ring carbon $\Delta\delta$ values for acetophenone (III) were comparable to those for styrene (II)[31] and in a different direction from those for toluene (I) provides further evidence that Ag$^+$ is com-

I   II   III
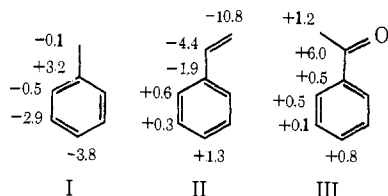
plexed with the carbonyl bond and not the aromatic ring.[32] As in the case of cyclohexanone, the carbonyl group appears to be acting as an n donor toward Ag$^+$, since the downfield shift of the carbonyl carbon is in the same direction as that for diethyl ether and protonated ketones and opposite to that for cyclohexene and styrene.

Nature of the Silver–Oxygen Bond. From the extensive literature on π complexes with Ag$^+$ and in consideration of the HSAB theory,[33] one might have expected the soft Ag$^+$ to bond to "softer" π electrons rather than the "harder" n electrons of the carbonyl bond. However, the present results indicate instead that Ag$^+$ behaves like a proton and probably like Friedel–Crafts catalysts which are known to form complexes with ketones.[34] An important factor may be the large steric requirements of Ag$^+$ which would favor complexation at the less hindered site.

The silver–oxygen bond is undoubtedly rather weak, as judged by the relatively small $\Delta\nu_{CO}$ for the complex of Ag$^+$ with acetophenone (25 cm^{-1}) compared with the range of values for other Lewis acids[35] such as HgCl$_2$, ZnCl$_2$, BF$_3$, and AlCl$_3$, which gave values in benzene of 18, 47, 107, and 120 cm^{-1}, respectively. Simple calculations[35] assuming bonding to n electrons in an sp^2 orbital show that $\Delta\nu$ is due to a lower CO force constant and not to an increase in the effective mass of oxygen. This reduction in π bond order leading to increased bonding between oxygen and the Lewis acid is lowest for HgCl$_2$ and AgBF$_4$. Of course, an isomeric π complex would also lower $\Delta\nu$.[30c] Also suggestive of relatively weak bonding is the very fast exchange of Ag$^+$ compared to H$^+$.

(31) Data from ref 7d for compelxation of silver nitrate in methanol at a 1:1 mol ratio.

(32) In aqueous media, however, LFER correlations[3,28b] indicate complexation of Ag$^+$ on the aromatic ring of acetophenone. Apparently in water the carbonyl group is preferentially bonded to solvent leaving only the aromatic ring as a site for complexation.

(33) R. G. Pearson, *J. Chem. Educ.,* **45**, 581, 643 (1968). For a precautionary note on the usual terminology, see R. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.,* **93**, 6014 (1971).

(34) G. A. Olah and M. W. Meyer in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience, New York, N. Y., 1963, p 707.

(35) B. P. Susz and P. Chalandon, *Helv. Chim. Acta,* **41**, 1332 (1958).

Summary

Simple aliphatic and aromatic ketones form complexes with AgBF$_4$ in methylene chloride. On the basis of ^{13}C chemical shifts compared with those of model complexes, it seems reasonable to conclude that the carbonyl group is acting as an n donor toward Ag$^+$. The silver–oxygen bond is probably rather weak, and, as demonstrated in the present work, its nature could best be elucidated by spectroscopic studies in nonhydroxylic solutions. Our results concerning the reactivity of ketone·Ag$^+$ complexes and the use of AgBF$_4$ in gc applications will be reported in subsequent publications.

Experimental Section

Materials. All ketones, reagent grade, were distilled prior to use and stored over magnesium sulfate. Freshly distilled cyclohexene and spectroscopic grade CH$_2$Cl$_2$ were stored over molecular sieves (Baker 4A, 4–8 mesh) prior to use. Lithium perchlorate, reagent grade, was dried at 130° for 3 hr while silver nitrate, anhydrous silver perchlorate (Alfa Inorganics), tetrabutylammonium fluoborate (Analytical Chemicals), and anhydrous silver fluoborate[36] (Alfa Inorganics) were used as supplied.

Formation of Complexes. Solutions of ketones and silver fluoborate in methylene chloride were prepared and added to ir cells or nmr tubes in a drybox flushed with nitrogen. The general procedure can be illustrated for *p*-methylacetophenone. To 1.00-g (7.5 mmol) samples of the ketone were added various amounts of AgBF$_4$ and enough methylene chloride to make a total weight of 4.00 g. Solutions of benzene, toluene, and cyclohexene complexes were made at the same donor concentrations as above with silver salt at about a 0.5 mol ratio. For low-temperature studies, solutions of ketones were *ca.* 8% by weight, and complexes were made by adding AgBF$_4$ to these solutions until saturated. On cooling to −90° negligible precipitation occurred. Though solutions of the ketone complexes exhibited various color changes with time, nmr spectra before and after color formation were identical.

A complex of *p*-methylacetophenone–AgBF$_4$ was isolated by warming *ca.* 1 g of the ketone with *ca.* 0.75 g of the silver salt. Filtering the hot solution and cooling gave white crystals whose ir (Nujol) showed a new absorption band at *ca.* 1660 cm^{-1}, mp 80–81°. For silver analysis, a 230-mg sample of the complex was dissolved in 25 ml of 50% aqueous ethanol and 5-ml aliquots were titrated with 0.0205 *M* potassium thiocyanate. To determine per cent ketone a 37.2-mg sample was dissolved in methanol containing 16.4 mg of dioxane and relative integrals for nmr signals of dioxane and acetyl methyl protons were measured.

Anal. Calcd for 2(ketone)·AgBF$_4$: Ag, 23.3; ketone, 57.9. Found: Ag, 22.4; ketone, 58.9.

Spectra. A Perkin-Elmer Model 225 grating spectrophotometer was used to measure ir spectra of CH$_2$Cl$_2$ solutions of free ketones and silver complexes. Rapid scans in the carbonyl region minimized the extent of thermal decomposition. Proton and ^{13}C spectra were measured at *ca.* 26° on a Bruker HFX-90 (90 MHz) spectrometer as described elsewhere.[26] All chemical shifts were measured relative to internal TMS, with uncertainties of ±0.01 and ±0.1 ppm for proton and ^{13}C, respectively. In some cases up to four accumulations on a Varian C-1024 time-averaging computer were necessary to obtain ^{13}C chemical shifts. Assignments of chemical shifts of complexes were made by comparison with values for uncomplexed acetophenones[37] and other donors.[38]

Possible Aldol Reactions. To test the reversibility of complex formation, a solution containing 1.90 g (0.0193 mmol) of cyclohexanone and 1.53 g (0.0078 mmol) of AgBF$_4$, which showed spectroscopic evidence for complex formation, was diluted with 100 ml of ether and extracted with water until a chloride test showed that no silver salt remained. Evaporation of ether gave an oil with an ir corresponding to cyclohexanone (83% recovery).

(36) A portion of AgBF$_4$ purified as described by K. Heyns and H. Paulsen, *Angew. Chem.,* **72**, 349 (1960), gave the same values as unpurified material.

(37) K. S. Dhami and J. B. Stothers, *Can. J. Chem.,* **43**, 497 (1965).

(38) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.

The proton nmr of 1,3-di(4-methylphenyl)-3-buten-1-one,[39] prepared by the method of Wayne and Adkins,[40] in the presence of a 0.12 mol ratio of AgBF$_4$ showed an aromatic multiplet at ca. 6.7

(39) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).
(40) W. Wayne and H. Adkins, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 367.

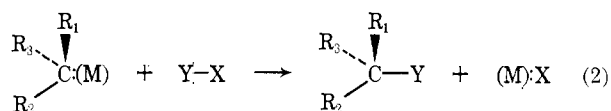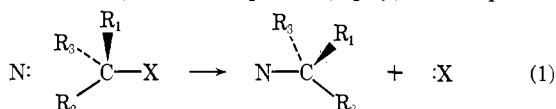which did not appear in the simple AB system of complexed *p*-methylacetophenone.

Generation and Utilization of Copper(I) Ate Complexes from Diastereomeric and Enantiomeric Alkylmercury Reagents[1]

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Abstract: Treatment of alkylmercuric halides in succession with 1 equiv of iodo(tri-*n*-butylphosphine)copper(I) and 3 equiv of *tert*-butyllithium at −78° in tetrahydrofuran results in formation of a reactive ate complex which incorporates the alkyl group originally bonded to mercury. The reactions of this alkyl group resemble those of a lithium dialkylcuprate: it can be alkylated with alkyl halides and coupled with a *tert*-butyl moiety by oxidation with nitrobenzene; it does not, however, undergo conjugate additions to α,β-unsaturated ketones. In certain instances, but not always, the overall conversion from alkylmercuric halide to product takes place with retention of configuration at the carbon originally bonded to mercury. The structure(s) of these ate complexes cannot be established from the available data, but qualitative evidence suggests that lithium, copper(I), and mercury(II) are all present in the metal core. Possible applications and limitations of these complexes in synthesis are briefly outlined.

The inversion of stereochemistry that characterizes S$_N$2 displacement at carbon is the basis for many important methods of controlling stereochemistry in organic synthesis (eq 1). In principle, it should be possible to carry out stereoselective transformations at carbon using diastereomeric carbanions (or their functional equivalents) as nucleophiles (eq 2); these species

$$N: \quad \overset{R_1}{\underset{R_2}{\overset{R_3\diagdown}{C}}}-X \quad \longrightarrow \quad N-\overset{R_1}{\underset{R_2}{\overset{R_3}{C}}} \quad + \quad :X \qquad (1)$$

$$\overset{R_1}{\underset{R_2}{\overset{R_3\diagdown}{C}}}(M) \quad + \quad Y-X \quad \longrightarrow \quad \overset{R_1}{\underset{R_2}{\overset{R_3\diagdown}{C}}}-Y \quad + \quad (M)X \qquad (2)$$

would also be useful in mechanistic studies. In practice, difficulties in generating and utilizing the required nucleophilic species have prevented common use of procedures based on this principle. General methods for the synthesis of pure diastereomers of organolithium and magnesium species are not available,[3,4] and even in

the special instances in which they have been prepared, only one of two diastereomers has been obtained.[5] Indeed, even if it were possible to generate diastereomerically pure *sec*-alkyllithium and -magnesium reagents, it is not clear that they would be more than marginally stable toward epimerization.[4–6]

In contrast, diastereomerically pure or enriched organometallic derivatives of a number of other metals—particularly mercury(II), tin(IV), and lead(IV)—have been prepared[7–9] and established not to epimerize readily once formed.[10] Unfortunately, organometallic derivatives of these metals are only weakly nucleophilic and of limited synthetic utility.

The work reported in this paper was directed toward developing methods for increasing the nucleophilic

(1) Supported in part by the National Science Foundation, Grants GP-28586X and GP-14247, and by the International Copper Research Association.
(2) Texaco Predoctoral Fellow, 1971–1973.
(3) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964); H. L. Goering and F. H. McCarron, *ibid.*, **80**, 2287 (1958), and references in each.
(4) Recent studies of the mechanism of conversion of alkyl bromides to alkylmagnesium and -lithium reagents by reaction with metal indicate that species resembling a radical in many of its properties are intermediates in these reactions: cf. H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **51**, 31 (1973); H. M. Walborsky and M. S. Aronoff, *ibid.*, **51**, 55 (1973); H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron*, **29**, 719 (1973); R. J. Rogers, H. L. Mitchell, Y. Fujiwara, and G. M. Whitesides, *J. Org. Chem.*, **39**, 857 (1974).
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(9) G. M. Whitesides and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 6611 (1970); C. L. Hill and G. M. Whitesides, *ibid.*, **96**, 870 (1974).
(10) Although alkylmercuric reagents are stable toward epimerization once prepared, our own experience and a private communication from F. R. Jensen has emphasized the possibility of their epimerization in solution during recrystallization or chromatography. This epimerization apparently reflects a radical chain reaction initiated by small amounts of peroxides present in solvents or formed on exposure of alkylmercury compounds to oxygen.