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Determination of the Donor Sites in Lewis Acid Adducts of Anisole and Thioanisole

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In solution the donors anisole and thioanisole each form two distinct 1:1 complexes with the acid phenol. For each donor-phenol system two distinct O-H stretching vibrations assignable to the complex are observed in the infrared spectrum. For one of these bands, the frequency shift of the phenol upon complexation, $\Delta\nu_{\text{O-H}}$, is found to lie on a linear plot of $\Delta\nu_{\text{O-H}}$ vs. the Hammett substituent constant for a series of donors consisting of substituted phenyl compounds. This result is interpreted to indicate that one of the donor sites in anisole and thioanisole is the phenyl ring. Arguments are presented to substantiate the assignment of the donor site in the second complex to the lone pair n-electrons of sulfur or oxygen. Symmetry arguments are presented which indicate that prior conclusions proposing the existence of two complexes because two charge-transfer bands were found in some anisole and thioanisole adducts are not valid. An alternate interpretation exists. Conditions which can lead to the simultaneous existence of two distinct complexes are outlined.

Introduction

In the course of extending previous studies¹⁻³ on the formation of 1:1 hydrogen-bonded adducts of phenol with various donors, we have observed the existence of two shifted O-H stretching frequencies in the adducts of phenol with the donors anisole and thioanisole. It is concluded that this effect is caused by the existence of two distinct complexes. A given donor molecule with two donor sites forms two different 1:1 complexes each involving a different donor site. This paper presents the most detailed study yet reported on the competitive formation of two 1:1 complexes of an acid with a base having two donor sites. In the donors anisole and thioanisole, one of the shifted infrared peaks of coordinated phenol is attributed to an adduct involving the π -electron system of the ring as a donor and the other peak to the adduct involving essentially an oxygen or sulfur lone pair (n) orbital. The correlation of the Hammett substituent constant with the frequency shift of phenol adducts involving the π -electron system of a series of substituted benzenes supports the contention that the two observed peaks are caused by two distinct complexes and not to a double minimum in the potential well of the hydrogen bond.^{4,5}

The discovery of two different complexes for the donors anisole and thioanisole with phenol led us to investigate earlier reports^{6,7} that two charge-transfer bands in the spectra of several complexes with aromatic donors of C_{2v} symmetry; e.g., C_6H_5X indicated two separate π -complexes. Invariably when the group X contains an effective donor atom (O, S, N, etc.) attached to phenyl, two widely separated charge-transfer bands are observed. Multiple charge-transfer bands have been reported for several systems involving the above donors and the acids iodine, chloranil, and tetracyanoethylene. In these adducts one complex reportedly involves coordination of the acid to the donor π -orbital with A_2 symmetry and the other to the π -orbital with B_2 symmetry. Although it is possible that two π -complexes exist in these systems, symmetry arguments are presented which indicate that the existence of two charge-transfer bands cannot be employed as proof for

this contention. The energy difference of the two charge-transfer bands observed when an effective donor atom is attached to phenyl has been reinterpreted in terms of the presence of both a π - and an n-bonded complex.

Experimental

Fisher Spectroanalyzed carbon tetrachloride was used without further purification. Reagent grade bases were distilled once and stored over Linde 3A Molecular Sieves. Baker and Adamson Reagent Grade phenol was distilled at atmospheric pressure; the fraction boiling at 182° was collected. Phenol was sublimed immediately before use. The preparation and purification of thioanisole are reported elsewhere.^{8,9} Stock solutions of phenol were prepared in a drybox in order to minimize contact with atmospheric moisture.

The O-H stretching frequency shifts for the phenol-base systems were measured employing a Beckman Model IR-7 double beam spectrometer with a fore-prism/grating optical system. Matched 0.20-mm. sodium chloride cells were used.

The general procedure followed in obtaining frequency shifts was to record infrared spectra of 0.15 M solutions of phenol with sufficient base added to complex about 50-75% of the phenol.¹ The frequency shift was obtained by measuring the difference in the peak maxima of the free and complexed O-H. The $\Delta\nu_{\text{O-H}}$ was recorded at several widely varying base concentrations in order to make sure that the frequency shift was concentration independent.¹⁰ In all cases studied here, a concentration dependence of $\Delta\nu_{\text{O-H}}$ was observed which was less than 3%.

Results

The phenol frequency shifts, $\Delta\nu_{\text{O-H}}$, on complexation to the π -system of a series of donors are presented in Table I along with the appropriate Hammett sub-

TABLE I

PHENOL FREQUENCY^a SHIFT AND HAMMETT SUBSTITUENT CONSTANTS FOR SOME π -DONORS^b

	$\nu_{1/2}$, cm. ⁻¹	$\Delta\nu_{\text{O-H}}$ (π), cm. ⁻¹	σ_p	$\Delta\nu_{\text{O-H}}$ (n), cm. ⁻¹
1 C_6H_5OH		62 ± 2	-0.357	129 ± 3
2 $C_6H_5OCH_3$	26 ± 5	58 ± 2	-0.260	165 ± 3
3 $C_6H_5CH_3$	26 ± 5	56 ± 1	-0.170	
4 $C_6H_5OC_6H_5$	25 ± 5	52 ± 2	-0.028	125 ± 3
5 C_6H_6	25 ± 5	49 ± 1	.00	
6 $C_6H_5SCH_3$	24 ± 5	49 ± 1	+0.003	170 ± 3
7 C_6H_5SH	23 ± 5	48 ± 2	+0.04	130 ± 3
8 $C_6H_5CH_2Cl$	25 ± 5	44 ± 1	+0.184	
9 C_6H_5Br	24 ± 5	40 ± 1	+0.232	
10 C_6H_5Cl	20 ± 5	39 ± 2	+0.237	

^a $\nu_{1/2}$ is the band width at half-intensity. ^b $\Delta\nu_{\text{O-H}}(n)$ is the phenol frequency shift for the adduct involving the donor orbital which is essentially a lone pair.

(1) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).
 (2) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 2037 (1962).
 (3) R. S. Drago, B. B. Wayland, and R. L. Carlson, *ibid.*, **85**, 3125 (1963).
 (4) C. G. Cannon, *Spectrochim. Acta*, **10**, 341 (1958).
 (5) P. McKinney and G. M. Barrow, *J. Chem. Phys.*, **31**, 294 (1959).
 (6) L. Orgel, *ibid.*, **23**, 1352 (1955).
 (7) P. A. D. DeMaine, *ibid.*, **26**, 1189 (1957).

(8) E. Bourgeois and A. Abraham, *Rec. trav. chim.*, **30**, 407 (1911).
 (9) R. J. Niedzielski, R. S. Drago, and R. L. Middaugh, *J. Am. Chem. Soc.*, **86**, 1694 (1964).
 (10) A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 371 (1963).

TABLE II
 THERMODYNAMIC DATA FOR SOME OXYGEN, SULFUR, AND π -DONORS

Donor	Donor site	I_2			C_6H_5OH			
		K_{298} , l. mole ⁻¹	$-\Delta H$, kcal./mole	Ref.	$\Delta\nu_{OH}$	K_{298} , l. mole ⁻¹	$-\Delta H$, kcal./mole	Ref.
$(C_2H_5)_2O$	O	0.97	4.3	14	279	9.73	5.41 ± 0.06	13a, 13b
CH_3OH	O	.46	1.9	14	230	...	4.3	^a
$C_6H_5OCH_3$	O	.35	...	7	165	1.20	3.3	13a, ^a
	π	59	
$(C_2H_5)_2S$	S	210	7.8	15	250	
$(n-C_4H_9)_2S$	S	255	...	4.19 ± 0.33	13a, 13b
$(C_2H_5)_2S_2$	S	5.6	4.6	15	155	...	3.1	^a
$C_6H_5SCH_3$	S	9.2 ± 0.1	6.1 ± 0.2	9	170	...	3.4	^a
	π	49	
$CH_3C(O)N(CH_3)_2$	O	6.9 ± 0.2	4.0 ± 0.1	16	342	134 ± 3	6.4 ± 0.2	2
$CH_3C(S)N(CH_3)_2$	S	1190 ± 40	9.5 ± 1.5	9	301	...	5.5	^a
$CH_3C(O)SCH_3$	O	0.73 ± 0.01	3.2 ± 0.1	17	162	...	3.2	^a
$C_6H_5C(O)N(CH_3)_2$	O	3.8 ± 0.1	4.0 ± 0.2	18	283	...	5.4	^a
C_6H_6	π	0.15	1.5	19	49	0.28	1.56 ± 0.11	13a, 13c
$p-CH_3C_6H_4CH_3$	π	0.31	2.4	20	63	0.38	2.42 ± 0.03	13a, 13c

^a ΔH is estimated from the phenol O-H stretching frequency shift (ref. 1).

stituent constants.^{11,12} These data are plotted in Fig. 1.

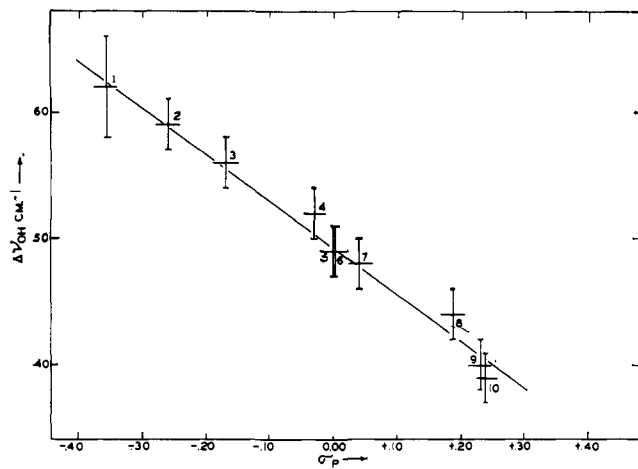


Fig. 1.—Plot of $\Delta\nu_{OH}$ for phenol vs. the Hammett substituent constant for a series of π -donors in Table I.

The phenol frequency shifts for some pertinent σ donors are summarized in Table III.

Discussion

The Assignment of the Coordination Positions in the Phenol Adducts.—The infrared spectra of free phenol and of the phenol-anisole adduct are illustrated in Fig. 4. Two bands which can be attributed to the adduct are observed at 3552 and 3447 cm^{-1} . These bands are assigned to two different adducts, one involving the ring π -orbitals of anisole as the donor site and a second involving essentially the nonbonding, n , electrons of the oxygen atom. This type of spectrum is obtained for all of the donors listed in Table I for which values for both $\Delta\nu_{OH}(\pi)$ and $\Delta\nu_{OH}(n)$ are given.

- (11) H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
 (12) P. Wells, *ibid.*, **62**, 171 (1963).
 (13) (a) D. L. Powell, Thesis, University of Wisconsin, 1962; (b) R. West, D. L. Powell, M. K. Lee, and L. S. Whatley, preprint; (c) R. West, D. L. Powell, M. K. Lee, and L. S. Whatley, *Spectrochem. Acta*, **20**, 983 (1964).
 (14) P. A. D. DeMaine, *J. Chem. Phys.*, **26**, 1192 (1957).
 (15) H. Tsubomura and R. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961).
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TABLE III
 FREQUENCY SHIFT^a AND TAFT $\Sigma\sigma^{*b}$ VALUES FOR SOME OXYGEN AND SULFUR DONORS WITH PHENOL

Base	$\Delta\nu_{OH}$, cm^{-1}	$\Sigma\sigma^*$
1 $(C_2H_5)_2S$	250 ± 10	-0.20
2 $(t-C_4H_9)_2S$	277 ± 10	- .60
3 $(n-C_4H_9)_2S$	255 ± 10	- .26
4 $(C_2H_7)SH$	175 ± 5	+ .38
5 $(C_{12}H_{25})SH$	181 ± 5	+ .38
6 $C_6H_5SCH_3$	170 ± 5	+ .60
7 $(C_2H_5)_2S_2$	155 ± 3	+1.0 ^c
8 C_6H_5SH	130 ± 3	+1.08
9 H_2S	135 ± 5	+0.98
10 $(t-C_4H_9)_2O$	329 ± 10	- .60
11 $(C_2H_5)_2O$	279 ± 7	- .20
12 $C_6H_5OCH_3$	165 ± 3	+ .60
13 C_6H_5OH	129 ± 5	+1.09
14 $C_6H_5OC_6H_5$	125 ± 5	+1.20
15 CH_3OH	230 ± 7	+0.48
16 $(C_6H_5CH_2)_2O$	230 ± 7	+ .44
17 H_2O	178 ± 7	+ .98

^a This is the lower frequency band (largest $\Delta\nu_{OH}$) for those cases where two shifted O-H bands are present. ^b R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556-675. ^c σ^* for $S-CH_3$ was estimated from σ_I .⁹

In order to substantiate the assignment of the band at 3552 cm^{-1} in the anisole-phenol adduct and the one at 3562 cm^{-1} in the thioanisole-phenol adduct to a shifted O-H stretching vibration for phenol bonded to the ring π -orbitals, the infrared spectra of the adducts formed by phenol with benzene and a series of substituted benzene donors were examined. The magnitude of $\Delta\nu_{OH}$, which has been shown to be related to the magnitude of the interaction of phenol with a series of σ -donors,¹ is linearly related to the Hammett substituent constant (Fig. 1) for the π -donors studied. Since the bands at 3552 and 3562 cm^{-1} in the anisole and thioanisole complexes fall on this plot, these bands can be assigned to an adduct in which phenol is bonded to the ring π -orbitals.

The next problem is the assignment of the low frequency peak. The proposal has previously been made⁶ that in several acceptor adducts with substituted benzene donors of C_{2v} or lower symmetry two separate π -complexes can exist. As illustrated in Fig. 5, the filled degenerate E_{1g} orbitals in benzene exist as two separate nondegenerate levels in substituted benzenes

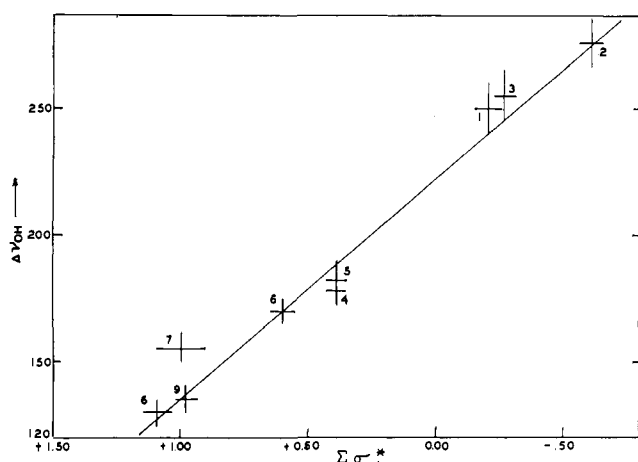


Fig. 2.—Plot of $\Delta\nu_{\text{OH}}$ vs. the sum of Taft substituent constants for the series of sulfur donors in Table III.

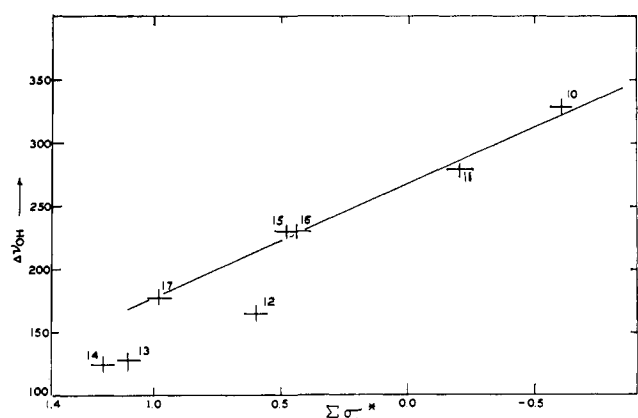


Fig. 3.—Plot of $\Delta\nu_{\text{OH}}$ for phenol vs. the sum of Taft substituent constants for oxygen donors in Table III.

of C_{2v} or lower symmetry. The two different π -complexes must involve, respectively, the two highest filled donor orbitals, *i.e.*, A_2 and B_2 in a C_{2v} donor such as C_6H_5X . There are several examples in the literature where the existence of two such π -complexes has been proposed.^{6,7,21} Consequently, the low frequency band in the anisole and the thioanisole adducts may be attributed to a second π -complex or to a complex involving n-donor electrons.

When $\Delta\nu_{\text{OH}}$ for the lower frequency band (Tables I, III) is plotted vs. the Hammett substituent constant for the substituent X, a random scattering of points results. The frequency shift of this lower energy band is not related to the perturbation of the π -system by X as was found in the case of the high frequency band. This is good evidence that the lower frequency O-H band in the adduct is not caused by a second π -complex. This band can be assigned to an n-donor site by employing the following arguments. The plot of $\Delta\nu_{\text{OH}}$ vs. the sum of the Taft substituent constants ($\Sigma\sigma^*$) for the groups attached to a series of sulfur n-donors is linear (Fig. 2). The lower frequency shifted phenol band $\Delta\nu_{\text{OH}}$ (n) in the adducts formed with thioanisole and thiophenol fall on this line. This indicates that sulfur is the donor site which gives rise to the low frequency complexed phenol peak in these adducts. It can also be inferred from the $\Sigma\sigma^*$ correlation that sulfur is not extensively π -bonded to the phenyl ring.

(21) A. Zweig, *Tetrahedron Letters*, **89**, (1964).

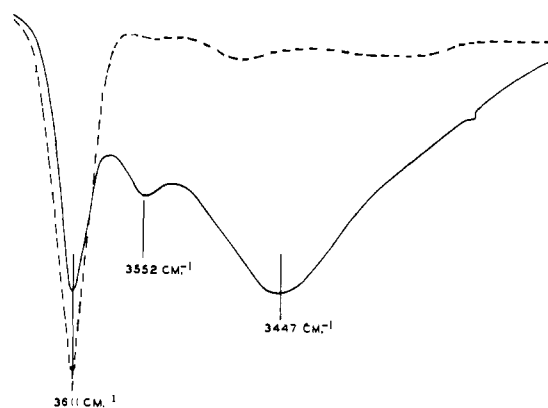


Fig. 4.—Infrared spectra: ----, 0.15 M C_6H_5OH ; —, 0.15 M C_6H_5OH + 0.5 M $C_6H_5OCH_3$.

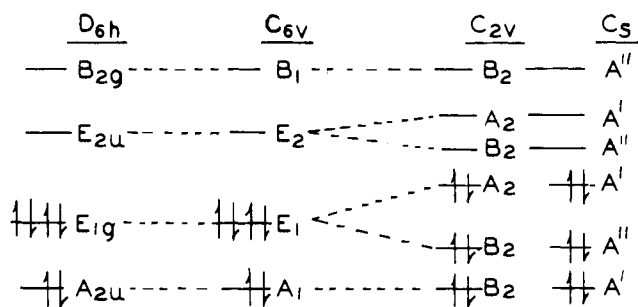


Fig. 5.—Degeneracy and symmetry of the benzene π -orbitals for different symmetries.

Plotting $\Delta\nu_{\text{OH}}$ vs. $\Sigma\sigma^*$ for a series of oxygen donors with substituents not capable of π -bonding with the oxygen lone pairs yields a straight line (Fig. 3). The corresponding data for diphenyl ether, phenol, and anisole fall below the line. This is probably caused by the fact that conjugation of oxygen with the phenyl ring reduces the oxygen donor strength.

We have found that many other donors such as thiophenol, benzaldehyde, diphenyl ether, and *o*-dimethoxybenzene yield upon complexation to phenol two O-H stretching vibrations which can be attributed to the adduct. In each case $\Delta\nu_{\text{OH}}$ for the high frequency band fits the relationship in Fig. 1 supporting its assignment to a π -complex. It is apparent from the asymmetry of the complexed O-H phenol band in the benzonitrile and nitrobenzene adducts that there are two bands, with one in the region expected for a π -complex. Accurate resolution of the π -complex band was not possible owing to the large overlap of the two complex bands. It has been proposed that two complexes exist^{22,23} in several other systems, but the lack of substituent constant data prevent their inclusion in the plot in Fig. 1.

The possibility still exists that there could be two distinct π -complexes in the anisole-phenol system giving rise to the complex absorption band at high frequency. The band widths of this complex peak at half-intensity were measured for the benzene and anisole π -complexes with phenol. If more than one different energy π -complex existed for anisole, the width of the unresolved band would be greater than that for the benzene adduct. This is not found to be the case. If two π -complexes do exist, they must be

(22) R. West, L. Whatley, and K. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).

(23) R. West and C. Kraihanzel, *ibid.*, **83**, 765 (1961).

very nearly equal in energy, giving rise to two almost identical overlapping complexed phenol bands in the infrared spectrum.

If two π -donor sites were the source of the two complexes found for both anisole and thioanisole with phenol, the following arguments predict that the interaction of phenol with anisole would be much greater than with thioanisole. The σ_I values of S-CH₃ and O-CH₃ are similar, indicating that the two substituents will have a similar effect on the σ -system. Since O-CH₃ conjugates more effectively with the ring π -orbitals than S-CH₃, anisole π -orbitals should be better donors than those in thioanisole. This prediction by use of the two π -complex model is not borne out experimentally (Tables II, III). In view of our assignment of the second complex to an n-donor site, the similarity in donor properties of anisole and thioanisole toward phenol is interesting when it is recalled that oxygen donors are generally much better bases toward phenol than are analogous sulfur donors (Table II). The oxygen basicity must be reduced below that of sulfur by its greater involvement in the π -system of the ring.

Assignment of the Coordination Position in Some Iodine Adducts.—The symmetry considerations reported by Orgel and illustrated in Fig. 5 have been referred to by several authors. The existence of two distinct π -complexes has been proposed in the interpretation of the electronic spectra of the adducts formed by anisole and thioanisole with several acids including iodine,⁷ tetracyanoethylene,²¹ and chloranil.⁶ Changes in the molar absorptivities of the charge-transfer bands of several adducts have also been interpreted to indicate the existence of two π -complexes (private communication, P. A. D. DeMaine).

It can be argued that two charge-transfer bands cannot be employed as a reliable criterion of two complexes. If the iodine molecule were located over the center of the phenyl ring of a C_{2v} donor with the I₂ bond axis perpendicular to the plane of the ring, the adduct would have C_s symmetry. The π -molecular orbitals of benzene in this point group are represented in Fig. 5. This structure contains the highest symmetry of all reasonable structures that can be considered and consequently the conclusions to be drawn are either equivalent or more stringent than those for other possible structures. As indicated in Fig. 6, two charge-transfer transitions are possible, involving an electron from either A' or A''. The character table for C_s indicates that both transitions are symmetry allowed; thus a single complex can give rise to two different charge-transfer bands. Therefore existence of two charge-transfer bands cannot be utilized to demonstrate unequivocally the existence of two π -complexes in these systems.

Recently, it was suggested that sulfur is the principal donor site in the thioanisole adduct with iodine.⁹ The enthalpy of formation of this adduct falls on a line relating the enthalpies of a series of adducts with donors of the type R-S-X to the Taft substituent constants, $\Sigma\sigma^*$, for R and X. As in the case of the phenol adducts, this correlation indicates that the sulfur atom is the donor site and sulfur is not extensively involved in the ring π -system. Furthermore, oxygen being a first row element is more intimately involved in the ring π -system than is sulfur. Using the two π -complex

model, the magnitude of the donor-acceptor interaction would depend directly upon the magnitude of the perturbation of the π -orbitals by the substituent. Use of this model for both anisole and thioanisole predicts anisole to be a better donor than thioanisole, which is not found experimentally. The magnitude of the thioanisole-I₂ interaction and the agreement with the value predicted by the $\Sigma\sigma^*$ correlation preclude the possibility of the principal donor site being a π -orbital. The interpretation of the anisole-I₂ complex is less clear cut. The extensive involvement of oxygen in the ring π -system makes the possibility of two π -complexes more feasible for anisole.

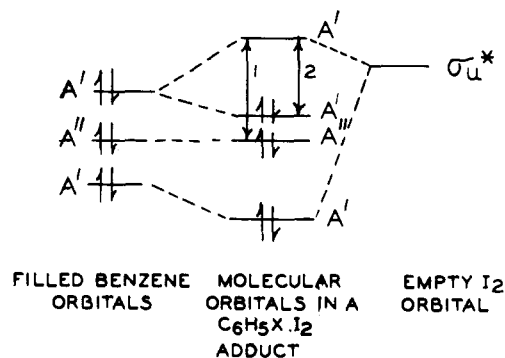


Fig. 6.—Combination of C₆H₅X π -orbitals with iodine to form a complex.

If in the anisole complex the two charge-transfer bands at 295 and 345 μ m are assigned to π - and n-complexes, the frequency (energy) for the n-donor charge-transfer band is found to be very low compared to diethyl ether. This argument has been used to eliminate the possibility of an n-donor complex in this system. However, the long wave length for this transition can be attributed to a lowering of the energy of the charge-transfer transition by stabilization of the positive charge on oxygen in the excited state by conjugation to phenyl. Consequently, the assignment of the donor sites in the anisole-iodine system is not rigorously established.

Relative Amounts of π - and n-Donor Complexes.—The ratio of π -complex to n-complex in a system is given by the ratio of the equilibrium constants for the formation of the two 1:1 adducts. The π -donors considered in this paper have equilibrium constants in the range 0.2 to 0.3 l. mole⁻¹. Since the measured equilibrium^{13a} constant of 1.2 l. mole⁻¹ for the phenol-anisole adduct can be shown to be the sum of equilibrium constants for the π - and n-complex,⁷ an equilibrium constant of approximately 0.9 l. mole⁻¹ can be estimated for the n-complex. About 20–25% of the complexed phenol is involved in the π -complex. If the n-donor site has an equilibrium constant of 30 or higher, then there would be less than 1% of the π -complex and observation of a π -complex band in the infrared would be difficult. In keeping with the expected large equilibrium constant for the oxygen donor site, no π -complex infrared band was detected in the phenol-N,N-dimethylbenzamide system.

Equilibrium constant arguments can also be used to predict the presence of both π - and n-bonded complexes in the anisole-I₂ system in solution. The I₂ equilibrium constant with diethyl ether is 0.97 l. mole⁻¹ while the benzene-I₂ equilibrium constant is 0.15 l.

mole⁻¹. In anisole the n-bonding ability of oxygen is decreased and π -complex-forming ability of the phenyl ring is enhanced. By comparison with the analogous phenol complexes it is predicted that the n- and π -complex equilibrium constants of anisole with I₂ are the same order of magnitude. Appreciable concentrations

of both π - and n-bonded complexes are thus almost certainly present in solutions of I₂ with anisole.

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The Coupling of 4-Chloro-4-methyl-2-pentyne with Alkyl and Phenyl Grignard Reagents

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4-Chloro-4-methyl-2-pentyne reacted with methylmagnesium bromide to yield 4,4-dimethyl-2-pentyne (65–72%), 2-methyl-1-penten-3-yne (11–21%), and 2,4-dimethyl-1,3-pentadiene (24–7%) contrary to an earlier report that an allene was the main product. Similarly, phenylmagnesium bromide gave 4-methyl-4-phenyl-2-pentyne, 2-methyl-1-penten-3-yne, 4-methyl-2-phenyl-1,3-pentadiene, and 2-methyl-4-phenyl-1,3-pentadiene, rather than 2-methyl-4-phenyl-2,3-pentadiene. However, isopropylmagnesium bromide gave 2,4,5-trimethyl-2,3-hexadiene and 4,4,5-trimethyl-2-hexyne. The mechanism of formation of the rearranged products is discussed.

The coupling of propargyl halides $RC\equiv CCCIR'R''$ with Grignard reagents has been used as a synthetic method for acetylenic hydrocarbons $RC\equiv CCR'R''R'''$ on several occasions.^{2–4} However, a hydrocarbon of unknown structure was reported as a by-product from reaction of 2-chloro-2,5,5-trimethyl-3-hexyne with methylmagnesium bromide³ and the hydrocarbon obtained from reaction of 2-chloro-2-methyl-3-octyne with octylmagnesium bromide was shown by g.l.c. to be a mixture of three products even though the composition was that expected for 7,7-dimethyl-5-pentadecyne and the boiling range was narrow.⁵ It has also been reported⁶ that 4-chloro-4-methyl-2-pentyne yielded 2,4-dimethyl-2,3-pentadiene as the principal product (50%) by reaction with methylmagnesium bromide; only a small amount of 4,4-dimethyl-2-pentyne or 4,4-dimethyl-1,2-butadiene was observed. With phenylmagnesium bromide the only product isolated was 2-methyl-4-phenyl-2,3-pentadiene (40%). Similar results were reported for 4-chloro-4-methyl-2-hexyne⁷ and 4-chloro-4,5,5-trimethyl-2-hexyne.⁸ Reports of coupling of Grignard reagents with less highly substituted propargyl halides are similarly conflicting, although with certain of these recent evidence for allenic products appears to be more certain.^{9–12}

A reinvestigation of the coupling reaction was undertaken in order to determine the synthetic value of the reaction and to study the acetylene-allene rearrange-

ment which is involved in formation of allenic products. It was of special interest to examine such products because aliphatic tetrasubstituted allenes are difficult to prepare. The work reported in the present paper involves only 4-chloro-4-methyl-2-pentyne (I), which was chosen because it is the simplest trisubstituted propargyl chloride and because allenes were reported as principal products.

Results and Discussion

Coupling reactions were carried out with excess methyl-, phenyl- and isopropylmagnesium bromide (1.4 to 2.4 M) in ether at room temperature. Preliminary experiments were also carried out with *tert*-butylmagnesium bromide. With methyl and phenyl Grignard reagents no allenic hydrocarbons were detected among the products. In addition to the normal acetylenic coupling products the reactions gave conjugated dienes and the enyne which would result from elimination of hydrogen chloride from 4-chloro-4-methyl-2-pentyne. However, isopropylmagnesium bromide gave no conjugated diene or enyne, but 4,4,5-trimethyl-2-hexyne (X) and 2,4,5-trimethyl-2,3-hexadiene (XI) were obtained in the ratio 64:36. Products were separated by g.l.c. and identified by n.m.r. and infrared spectra. Raman spectra were also obtained for the acetylenic hydrocarbons and ultraviolet spectra for the conjugated dienes. The products are summarized in Table I and the spectral properties in Table II or in the Experimental.

More extended investigation was made of the reaction with methylmagnesium bromide because it was easier to prepare authentic samples of the products and of the expected allene V when methyl was the substituent introduced (see Experimental). Direct comparison by g.l.c. and of spectral properties as well as other physical properties showed that II, III, and IV were the products; V was absent although it was readily detected in the presence of the other hydrocarbons. Compound V was added to a coupling run and shown to survive without rearrangement. It was also found that II was not rearranged to V or III and

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