TABLE I
GRIGNARD COMPOUNDS PREPARED IN BENZENE SOLVENT

Compd	Complexing agent	Yield, %	Calcd, %			Found, %			Ratio
			Mg	X	N	Mg	X	N	Mg:X:N
C_2H_5MgCl	$(C_2H_5)_3N$	97	12.8	18.7	7.4	13.0	18.6	7.1	1.05:1.03:1.00
C_2H_5MgBr	$(C_2H_5)_3N$	88	10.3	34.1	6.0	11.3	33.2	6.4	1.07:1.00:1.10
C_2H_5MgI	$(C_2H_5)_3N$	97	8.6	45.1	5.0	8.5	44.2	4.9	1.00:1.00:1.00
n-C_4H_9MgCl	$(C_2H_5)_3N$	93	11.2	16.3	6.4	11.0	16.0	5.9	1.09:1.08:1.00
C_6H_5MgBr	$(C_2H_5)_3N$	77	8.9	28.3	5.0	8.5	30.0	5.0	1.00:1.03:1.07

also has been reported;[5] however, once again the resulting magnesium product is insoluble.

We wish to report the preparation of typical Grignard compounds in hydrocarbon solvents such as benzene and toluene resulting in the production of true solutions. The method involves the reaction of an alkyl or aryl halide and magnesium turnings in benzene solvent in the presence of an equimolar amount of a tertiary amine. The preparation of true solutions by this method is somewhat unusual in that the same reaction using diethyl ether as the complexing agent results in the precipitation of solids of nonstoichiometric composition. The use of a tertiary amine as the complexing agent appears to be successful owing to the nondisproportionation tendency of the RMgX species when complexed to a tertiary amine.[6] This new method eliminates the use of the more expensive and hazardous diethyl ether and makes available Grignard compounds in hydrocarbon solution which should be of both academic and commercial value.

The results reported in Table I show that typical aliphatic and aromatic magnesium chlorides, bromides, and iodides are produced in good yield. The reactions are slightly more difficult to initiate than the corresponding reaction in diethyl ether. The reaction is normally started at room temperature to 50° and the reaction temperature is maintained no higher than 50° during reaction.

Triethylamine appears to be a good choice as the complexing agent, although other tertiary amines (such as tri-n-propylamine or tri-n-butylamine) should work as well. Trimethylamine has the disadvantage of low boiling point which makes the reaction difficult to start, and dimethylaniline has the disadvantage that not all Grignard compounds complexed with this amine are soluble in benzene. Our results using triethylamine in large excess as the solvent for the Grignard preparation indicates that quaternary salt formation ($R'X + R_3N \rightarrow R_3R'NX$) and dehydrohalogenation ($R'X + R_3N \rightarrow$ olefin $+ R_3NHX$) can be a problem. These results will be reported elsewhere. However, in benzene solvent, under the conditions employed, these side reactions were not detected.

Experimental Section

Although most of the Grignard compounds were prepared to produce a 1 M solution in benzene, ethylmagnesium bromide and n-butylmagnesium chloride have been prepared in concentrations approaching 2 and 3 M, respectively.

The general procedure for preparing Grignard compounds in benzene solvent is as follows. An alkyl halide (0.5 mole) dissolved in 400 ml of dry benzene was added to magnesium turnings (0.6 g-atom) diluted with 30 ml of benzene and 0.5 mole of triethylamine. Approximately 30 ml of the alkyl halide–benzene solution was added and the reaction was started by gentle warming. The remainder of the alkyl halide–benzene solution was added slowly over a 2-hr period keeping the reaction temperature at 40–50°. The resulting solution was clear and often colorless. It was separated from the excess magnesium turnings by filtration through a medium sintered-glass funnel. Yields were determined by isolation of the reaction product as a solid by removal of the solvent under vacuum followed by elemental analysis. Magnesium and halogen content were determined by EDTA analysis and nitrogen by titration of the tertiary amine.

(5) R. Barré and J. De Repentigny, *Can. J. Res.*, **B27**, 716 (1949).
(6) E. C. Ashby, *J. Am. Chem. Soc.*, **87**, 2509 (1965).

Spectral Solvent Shifts. Substituent Effects. II[1]

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It has been known for many years that polar solvents cause displacements of the ultraviolet absorption maxima of aromatic compounds as compared to nonpolar solvents. There have been many attempts to explain these effects. Ungnada,[3] Nagakura and Baba,[4] Baba and Suzuki,[5] Utley,[6] Lees and Burawoy,[7] and Dearden and Forbes[8] have emphasized hydrogen bonding of the types solvent H→solute and solute H→solvent. Ungnade[3] and Schubert, *et al.*,[9] have shown the importance of ground-state solvation and excited-state solvation, red shifts being caused by greater solvation of excited states than ground states and blue shifts being due to highly solvated ground states that hinder excitation.

Bayliss and McRae[10] have considered the importance of the dipole moment transitions of the solute molecule in going from ground to excited state with the resultant greater solvation of the polar excited state. McRae,[11] Sembe,[12] and others believe that solvent shifts are related to the dielectric constant and refractive index of the solvent. West and Geddes[13] have recently con-

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(2) In part from the M.S. Thesis of J. Olguin.
(3) H. E. Ungnade, *J. Am. Chem. Soc.*, **75**, 432 (1953).
(4) S. Nagakura and H. Baba, *ibid.*, **74**, 5693 (1952).
(5) H. Baba and S. Suzuki, *J. Chem. Phys.*, **35**, 1118 (1961).
(6) J. H. P. Utley, *J. Chem. Soc.*, 3252 (1963).
(7) W. A. Lees and A. Burawoy, *Tetrahedron*, **19**, 419 (1963).
(8) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).
(9) (a) W. M. Schubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957); (b) W. M. Schubert, H. Steadley, and J. M. Craven, *ibid.*, **82**, 1353 (1960); (c) W. M. Schubert and J. M. Craven, *ibid.*, **82**, 1357 (1960).
(10) N. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).
(11) E. G. McRae, *ibid.*, **61**, 562 (1957).
(12) K. Sembe, *Bull. Chem. Soc. Japan*, **34**, 722 (1961).
(13) W. West and A. L. Geddes, *J. Phys. Chem.*, **68**, 837 (1964).

TABLE I[a]

ΔE VALUES FOR *p*-ANILINES

	Dioxane		Methanol		Propanol-1		Propanol-2		*t*-Butyl alcohol			
	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	σ_p	M
OCH_3	−2.0	−0.92	+1.00	+1.50	+1.00	+1.50	+0.70	+0.8	+0.7	+1.3	−0.27	−2.58
CH_3	−2.3	−1.46	+0.7	+1.10	+0.7	+1.10	+0.50	+0.51	+0.2	+0.9	−0.17	−0.77
OPh	−2.4	−1.60	+0.49	+1.97	−0.5	0	0	+0.7	−0.5	−1.0	−0.32	−3.78
OH	−2.5	−2.1	−3.00	...	+0.4	+1.1	+0.40	+0.8	+0.40	+0.5	−0.36	−3.36
Br	−2.7	−0.8	−0.90	+0.14	−1.2	+0.1	−1.20	−0.3	−1.2	+0.1	+0.23	−0.77
H	−3.0	−1.4	+0.26	+0.34	0	+1.1	0	−0.34	+0.4	+0.5	0	0
COOH	−3.1	...	+1.60	...	−5.8	...	−5.7	...	−4.6	...	+0.41	+0.91
CN	−3.4	...	−4.8	...	−6.0	...	−5.7	...	−5.7	...	+0.66	+1.23
COOEt	−3.9	...	−7.4	...	−8.5	...	−8.6	...	−8.0	...	+0.45	+0.91
$-C(=O)-CH_3$	−5.0	...	−9.4	...	−10.5	...	−9.8	...	−9.5	...	+0.502	+1.24

[a] The wavelength maxima in millimicrons may be obtained from the senior author on request.

TABLE II

ΔE VALUES FOR *m*-ANILINES

	Dioxane		Methanol		Propanol-1		Propanol-2		*t*-Butyl alcohol				
	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	σ_m	σ_I	F
CH_3	−3.5	−1.2	−0.5	−0.8	−1.8	+0.7	−0.5	+0.8	−0.8	+0.8	−0.069	−0.05	−0.12
OH	−3.0	−1.5	−0.5	−0.4	−0.5	0	+0.4	+0.4	+0.4	+0.4	+0.12	+0.25	+0.21
OCH_3	−2.9	−1.2	+2.3	+0.6	−1.4	−0.5	−0.8	+0.3	−0.8	−0.1	+0.115	+0.25	+0.20
COOEt	−3.0	−2.7	−1.8	−1.1	−3.2	−2.7	−2.4	−1.7	−2.4	−1.8	+0.37	+0.32	+0.64
COOH	−2.9	−1.4	+0.5	+3.8	−2.0	−0.2	−0.5	−0.2	−0.7	−0.6	+0.35		+0.64
Br	−2.5	−1.0	−1.5	−0.2	−0.5	−0.3	−1.0	−0.3	0	−0.1	+0.39	+0.45	+0.68

TABLE III

ΔE VALUES FOR *o*-ANILINES

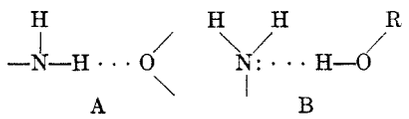
	Dioxane		Methanol		Propanol-1		Propanol-2		*t*-Butyl alcohol			
	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	^1L_a	^1L_b	σ_I	F
CH_3	−3.2	−1.3	0	+0.7	−1.2	0	−1.0	−0.2	−0.5	−0.5	−0.05	−0.12
OH	−3.0	−1.4	−0.6	−0.3	−2.0	−0.4	0	−0.4	0	−0.3	+0.25	+0.21
OCH_3	−2.1	−0.7	+1.3	+1.2	−0.7	−0.6	+1.0	+0.8	+0.8	+1.0	+0.25	+0.20
Br	−2.0	−1.3	−0.5	0	−2.3	−1.0	−1.0	−0.6	−1.0	−0.7	+0.45	+0.68
COOEt	−1.1	−0.4	−0.3	−0.1	−0.8	−0.7	0	−0.8	−0.3	−0.8	+0.32	+0.64
COOH	−1.0	−0.2	+0.7	+5.4	−0.2	−0.2	0	+0.2	0	+0.4		+0.64

cluded that the red shifts of cyanine dyes are related only to the refractive index of the solvent.

In a previous report from this laboratory,[1] we observed that solvent shifts for a series of *ortho*-, *meta*-, and *para*-substituted nitrobenzenes were related to the electron-releasing properties of the substituent group. For a series of *para*-substituted nitrobenzenes, the red shifts for cyclohexane to polar solvent were related linearly with σ_p, while those for the *meta* isomers were linear with σ_I for dioxane. Further, it was observed that substituent groups with hydrogens available for hydrogen bonding gave larger red shifts than those groups which could not enter into hydrogen bonding.

Results and Discussion

In the present investigation a series of *ortho*-, *meta*-, and *para*-substituted anilines and *para*-substituted benzoic acids have been studied in various polar solvents with the object in mind of studying three factors: (1) the effects of hydrogen bonding of the type A *vs.* B on the shifts of the absorption maxima; (2) the effects of the electron donor–acceptor properties of the substituent group on which of the above types of bonding



may take place; and (3) the relationship of the solvent shifts on the high-intensity band (^1L_a)[14] and the low-intensity band (^1L_b)[14] of substituted anilines.

The polar solvents were chosen on the basis of their potential hydrogen-bonding ability and acidity,[15] dielectric constant, and index of refraction, and include dioxane, methanol, propanol-1, propanol-2, and *t*-butyl alcohol. Of these dioxane can act only as a proton acceptor while the alcohols would be expected to serve as proton donors in the order methanol > propanol-1 > *t*-butyl alcohol > propanol-2. The absorption maxima for the ^1L_a and ^1L_b bands were determined in these solvents and the energy differences (ΔE) from cyclohexane to polar solvents were calculated and are listed in Tables I, II, and III.

(14) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).
(15) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

TABLE IV

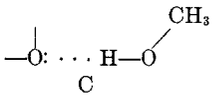
ΔE VALUES FOR THE ^1L_a BAND OF *p*-BENZOIC ACIDS

	Dioxane	Methanol	Propanol-1	Propanol-2	*t*-Butyl alcohol
CH_3	+1.0	+2.5	+0.2	+2.0	+1.0
OCH_3	+0.5	+1.4	−0.4	+0.7	−0.4
OH	−1.6	−1.9	−3.4	−3.3	−2.5
Br	+1.3	+4.3	+1.3	+2.6	+1.8
$N(CH_3)_2$	+0.8	+6.6	+0.2	+1.4	+0.6

Most of the anilines showed two structureless bands in the region 220–350 mμ, the high-intensity (log ε 3.8–4.2) ^1L_a band and the longer wavelength low-intensity (log ε 3.1–3.6) ^1L_b band. In those cases where strong electron-withdrawing groups were *para* to the amino group, the ^1L_a band tended to obscure the ^1L_b band. The intensities of both the ^1L_a and ^1L_b bands increased somewhat in going from cyclohexane to polar solvents, but there was no significant difference in intensities between the various polar solvents. A careful examination of the ΔE values show several factors. Dioxane gives a decrease in excitation energy (red shifts) for all of the anilines as compared to cyclohexane. These red shifts increase as the electron-withdrawing properties of the *para* substituent increase. The reverse order is observed for *meta* and *ortho* groups. Attempts to correlate the results with various electronic effects of the group, such as σ constants and M and F values,[16] were not completely successful, the carbethoxyl and acetyl groups giving larger red shifts than would be expected from the σ_p constants. This is probably due to the formation of quinoid-like substituent-to-substituent charge-transfer states for the *para* isomers of these groups.[17] These charge-transfer states can be more highly solvated than excited forms involving substituent states.[17] In addition, the substituent groups may themselves be solvated. However, there is a relationship between the ability of the amino group to undergo hydrogen bonding of type A with the solvent and the electron donor–acceptor properties of the *para* substituent. This type of solvation stabilizes the excited state.

Alcohols in which hydrogen bonding of type B could occur show blue shifts for anilines having electron-donor groups in the *para* position and large red shifts for *para* electron-acceptor groups. The red shifts are not related to index of refraction and dielectric constant but apparently to the ability of the solvent oxygen to act as a proton acceptor toward the amino hydrogen. Blue shifts of the type solvent H→solute stabilize the ground state at the expense of the excited states and hinder charge-transfer states of the amino group.

Substituent groups in the *meta* position of aniline have less effect than for *para* groups. In dioxane the largest red shift is observed for the electron donor methyl group, while the other groups show little or no deviation from aniline itself. In methanol the large blue shift for *m*-anisidine is probably the result of the solvation of OCH_3 as well as NH_2 by hydrogen bonding of type C, which would hinder charge-transfer states.



Propanol-1, propanol-2, and *t*-butyl alcohol show slight blue shifts or slight red shifts for the *m*-anilines. There appears to be competition between solute H→solvent and solvent H→solute in *meta* isomers.

The group order in the *ortho* position, which is the reverse of that for *para* groups, is probably a reflection of group size as well as electronic repulsions by the *ortho* group to the approach of the solvent to the amino group, the red shifts being less or the same as that for aniline. Again OCH_3 appears to be solvated by methanol.

A comparison of the four alcohols shows that methanol gives the largest blue shifts and appears to be the strongest hydrogen-bond donor, while propanol-1, which in general provides the largest red shifts, is acting predominately as a proton acceptor except with the very nucleophilic *p*-anisidine and *p*-toluidine. Propanol-2 and *t*-butyl alcohol show some steric inhibition of the approach of the solvent to the site of solvation. This is especially true for the *o*-anilines where relatively small shifts are observed. The results we obtained with propanol-1 show a close agreement with the results Forbes[8] has obtained for ethanol, suggesting that primary alcohols other than methanol act predominately as proton acceptors.

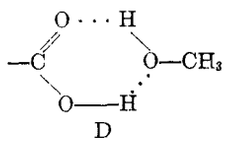
For red shifts, the ^1L_a band is affected to a greater extent than the ^1L_b band, while for blue shifts, the reverse is true except for *o*- and *m*-anisidines in methanol. Greater solvation of the excited state for the ^1L_a than for the ^1L_b band can account for this and is probably related to the fact that the charge-transfer state of the amino mixes more readily with the ^1L_a upper state ($^1B_{1u}$) than for the ^1L_b upper state ($^1B_{2u}$),[17] and would thus effect the benzene carbon framework state to a greater extent. The reverse was observed for nitrobenzenes[1] and may involve different excited-state structures for nitrobenzene systems.

The large blue shifts obtained with the aminobenzoic acids in methanol as opposed to red shifts in dioxane suggest that a different type of solvation may occur for the carboxyl group. Accordingly, a series of *para*-substituted benzoic acids was studied. The results are given in Table IV. Blue shifts were obtained for CH_3, OCH_3, Br, and $N(CH_3)_2$ in dioxane, methanol and propanol-2. *p*-Hydroxybenzoic acid undergoes red shifts in all solvents, with propanol-1 again showing the largest red shift. Whenever phenolic hydroxyls are present on the solute molecule, hydrogen bonding of the type —O—H· · ·O< can occur and explains the

(16) M. J. S. Dewar and P. J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

(17) J. Petruska, *J. Chem. Phys.*, **34**, 1111 (1961).

large red shifts obtained for nitrophenols[1] and aminophenols. For the other groups the order, Br > CH_3 > $N(CH_3)_2$ > OCH_3, for blue shifts suggests that the acidity of the acid and hence the hydrogen-donor properties of the COOH may in part be involved. The largest blue shifts were obtained for methanol with *p*-bromobenzoic and *p*-N,N-dimethylaminobenzoic acids. For the latter, solvation of the dimethylamino group could explain this effect. However, the results for bromo must be considered on the basis of solvation of the carboxyl only. This may involve a hydrogen-bonding structure of type D, in which the bonding be-



D

tween the alcohol hydrogen and the carboxyl carbonyl acts to bring the alcohol oxygen in close proximity to the carboxyl hydrogen. The latter type of bonding builds up the electron density at the substituent carbon and hinders charge-transfer states of the carboxyl. Ito[18] has observed a similar effect for benzoic acid in ether.

In summary, a study of the solvent shifts for anilines, benzoic acids, and (previously) nitrobenzenes suggest that (a) hydrogen bonding from solute to solvent in which substituent atom contains filled orbitals (*i.e.*, NH_2 and OH) leads to red shifts, (b) hydrogen bonding from solute to solvent in which a substituent atom contains an empty orbital or electron-deficient atom (*i.e.*, COOH) leads to blue shifts, (c) hydrogen bonding from solvent to solute which prevents substituent orbitals from overlapping ring orbitals (*i.e.*, NH_2 and OCH_3) leads to blue shifts, and (d) strong hydrogen-bonding effects tend to cover up other effects such as dielectric constant and index of refraction.

Experimental Section

Absorption spectra in the region 220–350 mμ were obtained using a Bausch and Lomb automatic recording ultraviolet spectrophotometer, Model 505, with a constant 5-A band width and 1-cm matched silica cells. After each determination the instrument was calibrated against the 253.7- and 313.1-mμ lines of mercury. Cyclohexane, dioxane, methanol, and propanol-2 were obtained as Spectraquality solvents (Matheson Scientific Co.). Propanol-1 and *t*-butyl alcohol were purchased as highest purity reagents, dried, and distilled through a 24-in. spinning-band column until no impurity bands were obtained when the solvent was passed through a 10-ft Carbowax column in a Wilkens Aerograph gas chromatograph. Concentrations used were 2×10^{-5} to 7×10^{-5} *M* with a scan time of 10 min.

The anilines were purchased as the highest purity compounds available and in most cases were recrystallized or distilled until the physical properties agreed with literature values, after which each was dried in an Abderhalden apparatus for 3 hr.

p-Aminobenzonitrile was prepared by the method of Friedman and Schecter[19] from *p*-bromoaniline. *p*-Phenoxyaniline was prepared by reduction of 4-nitrodiphenyl ether by the method of Suter.[20] The ethyl esters of *o*-, *m*-, and *p*-aminobenzoic acids were prepared by refluxing the respective acid with ethanol saturated with dry hydrogen chloride.

(18) M. Ito, *J. Am. Chem. Soc.*, **82**, 1559 (1960).
(19) L. Friedman and H. Schecter, *J. Org. Chem.*, **26**, 2522 (1961).
(20) C. M. Suter, *J. Am. Chem. Soc.*, **51**, 2581 (1929).

On the Supposed Resolution of 2-Bromobutane

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It has been claimed that racemic 2-bromobutane has been successfully resolved by gas chromatography on an optically active substrate.[1] In an attempt to repeat this work, we have observed dehydrohalogenation of 2-bromobutane to mixed butenes in the injection port of the chromatograph.

1-Butene and *cis*- and *trans*-2-butene have been identified by comparison of retention time and of infrared spectrum (*trans* only) with those of authentic samples. The extent of decomposition varies with the temperature of the injection port (Figure 1).

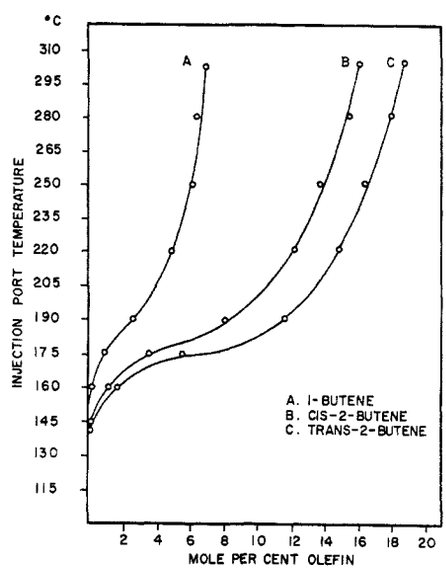

Figure 1.—Plot of temperature *vs.* amount of each decomposition product for *sec*-butyl bromide

Since other workers[2,3] have failed in attempts to resolve 2-bromobutane by gas chromatography, we feel that our results may explain Karagounis' apparent success. The similarity of our chromatograms of the butenes to Karagounis' published separation (note *three* peaks) confirms this conclusion.

Two further observations, we believe, led to Karagounis' claim for resolution. The comparative study using an optically inactive substrate [polyglycol on firebrick] led to a single "unresolved" peak. This single peak resulted from the failure of this column to resolve olefins. The second observation concerned the area of the major peaks (*cis*- and *trans*-2-butene). These were, unfortunately, of approximately equal area as one would expect in a successful resolution.

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(2) G. Goldberg and W. A. Ross, *Chem. Ind.* (London), 657 (1962).
(3) N. A. Goeckner, *Dissertation Abstr.*, **19**, 3127 (1959).