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Application of Linear Free Energy Relationships to Some Reactions of Triarylmethane Derivatives

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Several acid–base and oxidation–reduction reactions of a series of 3''- and 4''- substituted derivatives of malachite green (4,4'-bis-(dimethylamino)-triphenylmethyl chloride) have been studied. The various rate and equilibrium constants are correlated by the Hammett equation, and the ρ-values obtained are compared with those calculated by the methods proposed in several recent theoretical studies. Reasonable agreement is found. The constants obtained for this series are combined with data for a broader series of triarylmethane derivatives in order to investigate the effects of multiple variations in structure. It is found that Miller's equation for multiple variation in structure–reactivity correlations gives excellent agreement with the data.

Introduction

A series of 3''- and 4''-substituted derivatives of malachite green (4,4'-bis (dimethylamino)-triphenylmethyl chloride) provide the opportunity to study a number of acid–base and oxidation–reduction reactions in which the basic skeletal structure of the substrate is unchanged from one reaction series to another. Thus, these reaction series furnish an interesting set in which to investigate the applicability of structure–reactivity correlations.

The base strengths of a wide series of substituted triarylmethanols have been previously investigated,[2] and the data can be combined to provide a test of multiple variations in structure–reactivity correlations.[3]

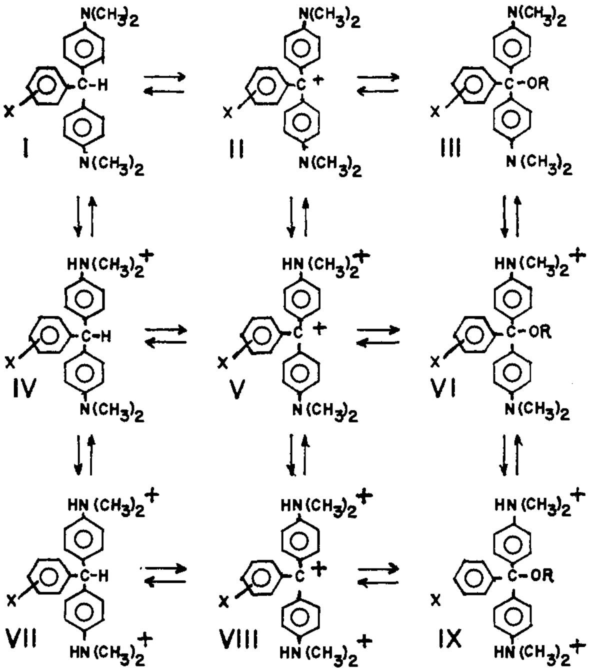
In this paper, we shall be concerned with the various transformations indicated in Scheme I, with R = H or CH_3.

Methods and Results

A series of 3''- and 4''-substituted leuco bases of malachite green (I) were prepared by the condensation of the appropriately substituted benzaldehyde with dimethylaniline in aqueous sulfuric acid. The carbinol bases III were prepared by oxidation of the leuco bases with excess chloranil (tetrachloro-*p*-benzoquinone). Fluoborate salts of the dyes II were prepared by dissolving the carbinol bases in dilute aqueous acid and adding sodium fluoborate to precipitate the salts.

The carbinol bases proved to be exceedingly difficult to purify. The final compounds used in this study showed extinction coefficients which were generally higher than any previously reported. The melting points of the carbinol bases were also generally higher than those which have been reported in the literature.

Physical data and elemental analyses of these compounds are shown in Table I. The elemental analyses are poorest for those compounds which we have found hardest to purify. The extinction coefficients obtained by dissolving the carbinol bases in aqueous solution buffered at *p*H 4.0 agree with those obtained by oxidizing a known amount of the leuco base with an excess of chloranil and adding several lambda of the resulting solution to an aqueous solution buffered at *p*H 4.0.



SCHEME 1.—R is H or CH_3.

A rather disturbing feature of the carbinol bases is that we have been unable to observe an OH stretching band in the infrared spectra. That the absence of the OH band in the infrared is not due to hydrogen bonding is indicated by the fact that a band fails to appear when a dilute solution of the carbinol base in carbon tetrachloride is examined in a 1- cm. path length cell. An examination of the n.m.r. spectrum of the carbinol base of crystal violet, (III, X = *p*-dimethylamino), also failed to show a band corresponding to a proton of an OH group. The presence of oxygen is shown, however, by the results of the elemental analyses, and by a qualitative test for oxygen described in the Experimental section. Molecular weight determinations, both by depression of the melting point of camphor and by the isopiestic method for benzene solution, show that the carbinol bases are monomeric. There can be little doubt,

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[2] (a) N. C. Deno, *et al.*, *J. Org. Chem.*, **19**, 155 (1954); *J. Am. Chem. Soc.*, **77**, 3044 (1955); **77**, 3051 (1955); **79**, 5805 (1957). (b) O. F. Ginsberg and N. S. Mel'nkova, *J. Gen. Chem.*, *U. S. S. R.*, **25**, 1109 (1955); *C. A.*, **51**, 16368 (1957). (c) M. Gillois and P. Rumpf, *Compt. rend.*, **238**, 591 (1954).

[3] S. I. Miller, *J. Am. Chem. Soc.*, **81**, 101 (1959).

TABLE I

PHYSICAL CONSTANTS OF MALACHITE GREEN DERIVATIVES

	Leuco bases				Dyes			Carbinol bases					
Subst.	M.p., °C. Obsd.	M.p., °C. Lit.	λ_{max}, mμ	ϵ_{max}[a]	λ_{max}, mμ	ϵ_{max},[a] H_2O	ϵ_{max},[a] MeOH	M.p., °C. Obsd.	M.p., °C. Lit.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	99	94	263	3.24	623	8.35	10.7	163	117	79.7	78.1	7.52	7.85
m''-Cl	110	112	265	3.24	632	8.13	11.1	140	..	72.5	70.9	6.58	6.21
p''-Cl	97	98	264	3.29	627	8.47	...	160	..	72.5	72.7	6.58	6.62
m''-CH_3	86	85	264	3.24	622	...	11.5	..	..	..	..	..	..
p''-CH_3	100	94	262	3.30	620	9.39	...	151	..	80.0	79.7	7.78	7.44
m''-NO_2	152	152	266	4.12	639	7.51	9.17	165	..	70.7	69.9	6.40	6.10
p''-NO_2	179	177	267	4.10	648	5.59	8.20	190	..	70.7	71.3	6.40	6.61
m''-OCH_3	124	123	263	3.27	626	8.65	...	151	140	76.7	77.0	7.45	7.37
p''-OCH_3	105	105	263	3.36	615	9.21	11.5	154	..	76.7	76.6	7.45	7.52
p''-DMA[b]	175	173	265	4.86	592	11.0	11.5	190	180	77.2	77.2	7.98	7.92

[a] 1-cm.$^{-1}$-mole^{-1} × 10^{-4}. [b] Dimethylamino.

TABLE II

EQUILIBRIUM AND RATE CONSTANTS FOR MALACHITE GREEN DERIVATIVES[h]

Subst.	σ[a]	σ^+[b]	pK_{eq}[d] IV $\rightleftarrows$ I	pK_{eq}[d] II $\rightleftarrows$ III, R = CH_3	pK_{eq}[d] IX $\rightleftarrows$ II	$-\log k_1$[d,e] II → III	$\log k_2$[f,d] I → II	$pK(H_2O)$[c] II $\rightleftarrows$ III, R = H
H	0	0	6.06	2.40	0.761	2.94	0.67	6.84
m''-Cl	0.373	0.399	5.86	1.35	1.44	2.58	0.34	6.23
m''-CH_3	− .069	− .066	..	..	..	..	..	7.21
p''-CH_3	− .170	− .311	..	..	..	..	..	7.27
m''-NO_2	.710	.710	5.73	0.442	1.80	2.17	0.10	5.84
p''-NO_2	.778	.778	..	0.392	1.77	2.28	0.03	5.50
m''-OCH_3	.115	.047	..	..	..	..	..	6.95
p''-OCH_3	− .268	− .778	..	..	..	..	..	7.18
p''-DMA[g]	− .83	−2.00	..	..	..	..	..	9.36
p''-Br	.232	0.150	..	..	..	..	..	6.38

[a] H. C. Brown and D. McDaniel, *J. Org. Chem.*, **23**, 420 (1958). [b] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4978 (1958). [c] Ref. 2; aqueous solution. [d] Relative values, see text, methanol solution. [e] *k*, sec.$^{-1}$. [f] *k*, l.-mole^{-1}-min.$^{-1}$. [g] Dimethylamino. [h] Temperature 25°.

then, that we have indeed obtained the carbinol bases (III, R = H).

Because of the solubility limitations of the carbinol bases and leuco bases in water, we have examined all of the reactions in methanol solution. Buffer solutions were prepared by partial neutralization of various tertiary amines with *p*-toluenesulfonic acid. The inertness of the amine toward the dyes was established in each case by the use of different buffer concentrations.

Spectrophotometric measurements have been employed throughout, and the procedures are described in detail in the Experimental section.

Conversion of Dyes to Methyl Ethers (II $\rightleftarrows$ III, R = CH_3).—The relative equilibrium constants for the transformation of the methyl ethers to the dyes were measured in anhydrous methanol using tribenzylamine–tribenzylammonium *p*-toluenesulfonate buffers. The results are reported in Table II as pK_a–$pK_{\text{tribenzylamine}}$.

The relative rates of reaction of the dyes with methoxide were measured in triethylamine–triethylammonium *p*-toluenesulfonate buffers. The rates, in each case, were measured at two different buffer ratios. The ratio of pseudo-first-order rate constants obtained agreed with those calculated assuming that the rate of reaction of the dye with methanol was negligible. The results are reported in Table II as the log of the pseudo-first-order rate constants, $\log k_1 = \log k_2 + \log K_b$ (triethylamine).

Conversion of Dyes to Protonated Methyl Ethers (IX (R=CH_3) $\rightleftarrows$ II).—When acid is added to a solution of one of the dyes, there is an immediate change in the color of the solution, followed by a slow fading of the color. When equilibrium is reached, the visible spectrum of the solution is identical to the original spectrum except for diminished intensity. No absorbance corresponding to that expected of the monoprotonated dye is observable except in the case of crystal violet.

From the changes observed it may be deduced that the monoprotonated dye reacts with solvent to form the diprotonated methyl ether. The same behavior is noted in water, and Hantzsch[4] was able to isolate the triprotonated carbinol base in the case of crystal violet.

The equilibrium constants for the conversion (II $\rightleftarrows$ IX, R=CH_3) were measured by adding known amounts of *p*-toluenesulfonic acid to *ca.* 10^{-5} molar solutions of the dyes in methanol. The results are shown in Table II.

Basicity of Leuco Bases (IV $\rightleftarrows$ I).—The basicities of the leuco bases were measured in dichloroacetic acid-dichloroacetate buffers in which the extent of protonation of the leuco bases is small. The second ionization of the leuco bases has, therefore, been neglected. The values of the first ionization constant are reported in Table II, and are calculated using the value of pK_a = 6.4 for the ionization of dichloroacetic acid.[5]

The Reaction of the Leuco Base of Malachite Green (I, X = H) with Chloranil (I → II).—The stoichiometry of the reaction of the leuco base of

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(4) A. Hantzsch, *Ber.*, **33**, 752 (1900).

(5) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p. 44.

malachite green with chloranil[6] to produce the corresponding dye in methanol solution degassed with nitrogen was found to be accurately represented by eq. 1 to about 50% completion. After this

$$\mathrm{Ar_3CH} + \mathrm{Q} + \mathrm{H^+} \rightleftarrows \mathrm{Ar_3C^+} + \mathrm{H_2Q} \qquad (1)$$

point, the amount of dihydrochloranil present became progressively greater than the amount of dye. Since the concentration of dye plus unreacted leuco base was always equal to the initial concentration of leuco base, it appears that the complication is caused by a slow reaction of chloranil with solvent.

The rate of oxidation of the leuco base followed second-order kinetics accurately to about 50% completion. If air was not removed from the solutions, the kinetics were second order to only about 25% completion, and the rate constant determined was about 20% higher than that determined in degassed solutions.

A tenfold change in the hydrogen ion concentration of the reaction solution caused no change in the rate constant.

If the reaction was carried out in solution buffered at a *p*H where the carbinol was the stable species, the concentration of dye initially rose, and then declined as the reaction proceeded. Although no quantitative measurements were made, this observation indicates that the dye is the initially produced species in the reaction.

The second-order rate constants, calculated from initial rates of reaction in 0.1 *M* acetic acid in methanol, are reported in Table II.

Evidence for the Existence of Monoprotonated Carbinol Base in Aqueous Solution.—It was noted that the extinction coefficient of malachite green is considerably greater in methanol than in water (*ca.* 25%). The integrated intensities of the visible bands differ by only 7%. When a solution of the dye in methanol is rapidly diluted with water, buffered at *p*H 4.0, the absorbance of the dye is *ca.* 7% greater than that normally measured. The absorbance of the solution slowly decreases to the normal value.

These observations are simply explained if one assumes that the dye is in equilibrium with the monoprotonated carbinol base (II ⇄ VI) in aqueous solution.[7] The position of this equilibrium is independent of *p*H and would be exceedingly difficult to determine in studies with aqueous solutions alone.

The integrated intensities of solutions of the dyes in acetonitrile are the same as those in methanol, and we take this as evidence that practically no monoprotonated methyl ether exists in the methanol solutions.

Discussion

Application of the Hammett equation[8] to the data of Table II, using only *m*″- and "+R" *p*″-substituted compounds in the correlation[9] gives the results shown in Table III.

TABLE III

HAMMETT EQUATION CORRELATIONS

Reaction	ρ	$-\log K_0$
IV ⇄ I equil. MeOH, 25°	0.466	6.05
II ⇄ III (R = CH_3) equil. MeOH, 25°	2.64	2.37
II → III (R = CH_3) rate, MeOH, 25°	0.940	2.93
IX ⇄ II (R = CH_3) equil. MeOH, 25°	−1.33	0.824
I → II, rate MeOH, 25°	−0.81	−0.66
II ⇄ III (R = H)[a] equil. H_2O, 20°	1.83	7.01
ν_{max}, of dyes H_2O, 25°, cm.$^{-1}$	−559	16,040

[a] Data taken from ref. 2b.

Also shown in Table III are the results of the application of the Hammett equation to the correlation of the wave lengths of maximum absorbance of the dyes, and to the data for the basicity of the carbinol bases in water. Plots of the data are shown in Figs. 1–7.

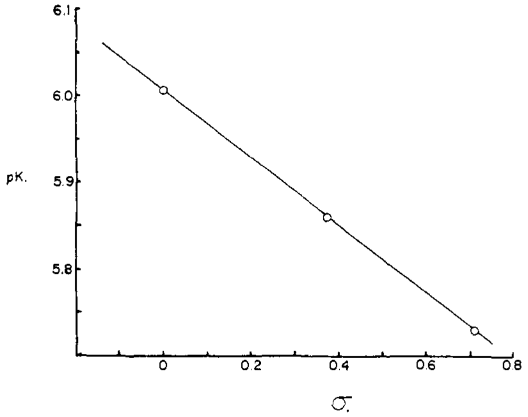

Fig. 1.—Hammett plot of basicities of leuco bases.

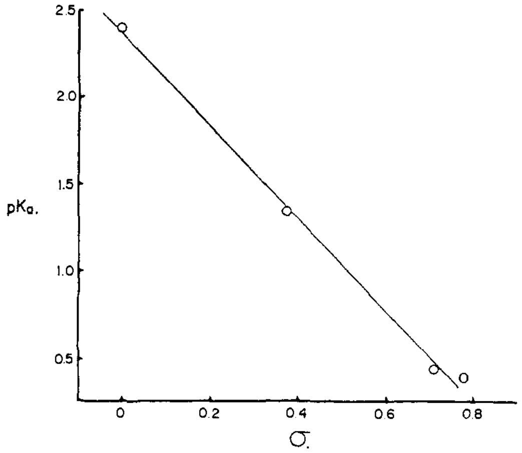

Fig. 2.—Hammett plot of basicities of methyl ethers.

One other ρ-value may be determined from the present data by noting that ρ for the reaction of the dyes to form the diprotonated methyl ethers (II ⇄ IX, R=CH_3) must be the sum of ρ for the diprotonation of the methyl ethers (III ⇄ IX,

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[6] J. H. Jones, *et al.*, *J. Assoc. Off. Agric. Chem.*, **38**, 977 (1955).

[7] The possibility of monoprotonated carbinol base in certain cases has been suggested by: C. C. Barker, G. Hallas and A. Stamp, *J. Chem. Soc.*, 3791 (1960).

[8] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chap. VII.

[9] Procedure recommended by: R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

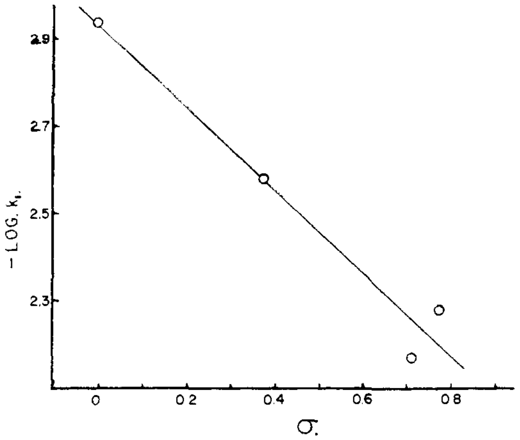

Fig. 3.—Hammett plot of rate constants for reaction of dyes with methoxide.

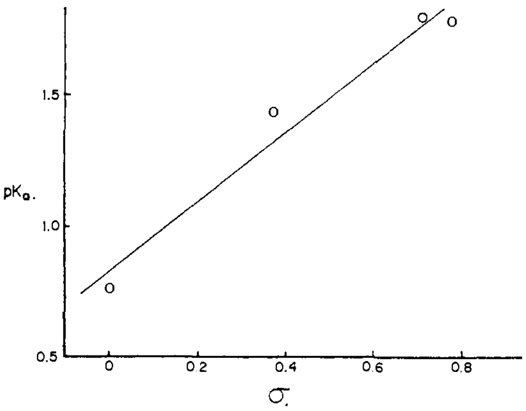

Fig. 4.—Hammett plot of equilibrium constants for conversion of dyes to diprotonated methyl ethers.

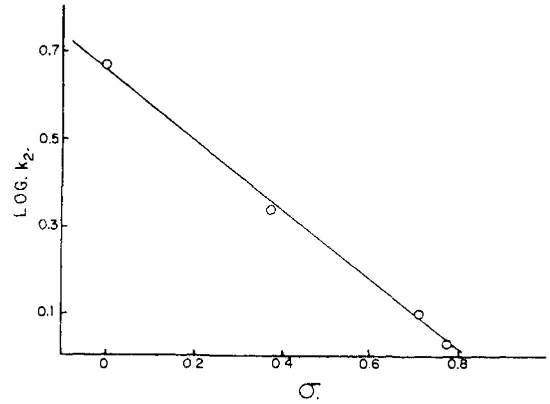

Fig. 5.—Hammett plot of rate constants for reaction of leucos with chloranil.

R = CH_3) and that for the formation of the methyl ether from the dyes (II $\rightleftarrows$ III, R=CH_3). Thus, ρ for the diprotonation of the methyl ethers is −1.31.

The Reaction of Chloranil with the Leuco Bases.—Any mechanism proposed for the oxidation must be in accord with the observed second-order kinetics, and the observation that the dye is the initially produced species. The simplest mechanism that is in accord with these observations,

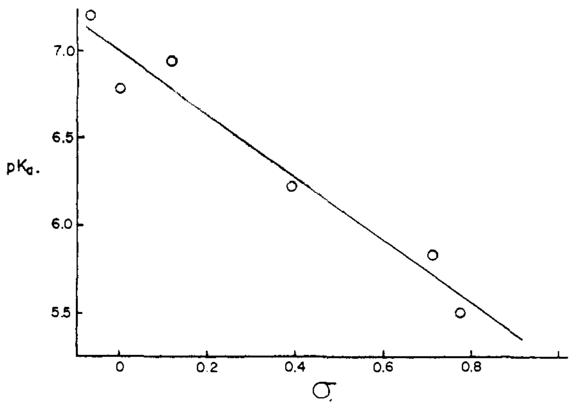

Fig. 6.—Hammett plot of basicities of carbinol bases in aqueous solution.

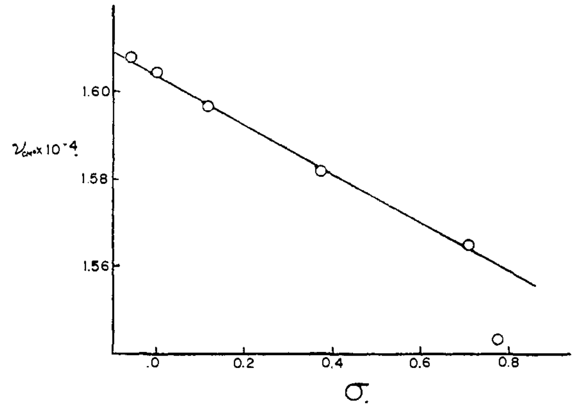

Fig. 7.—Hammett plot of frequencies of absorption of dyes.

and which appears reasonable from the mechanism of other triphenylmethane oxidations,[10] is a hydride transfer

$$\mathrm{Ar_3CH} + \mathrm{Q} \xrightarrow{\text{r.d.}} \mathrm{Ar_3C^+} + \mathrm{HQ^-}$$
$$\mathrm{HQ^-} + \mathrm{H^+} \xrightarrow{\text{fast}} \mathrm{H_2Q} \qquad (2)$$

Obviously, however, our data do not rule out other mechanisms in which a slow second-order reaction is followed by a fast step producing the dye. Nor can we rule out a mechanism similar to that proposed by Swain and Hedberg[11] for the oxidation of leuco malachite green by ceric sulfate. Assuming mechanism 2, if the charge on the carbonium ion were fully developed in the transition state of the rate-determining step, we should expect a ρ of nearly the same magnitude as that for the equilibrium conversion of the methyl ether to the dye (−2.6). Since the observed ρ is only −0.81, very little charge has developed in the transition state.

Basicity of the Amino Groups in the Leucos and Methyl Ethers.—The ρ for the basicity of the amino group in the leuco bases (−0.47) is very close to that which one would predict from the basicity of anilines in methanol (−3.02[12]), and the fall-off factor for a benzene ring (0.303[13]) and a saturated

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[10] R. Stewart, *Can. J. Chem.*, **35**, 766 (1957).

[11] C. G. Swain and K. Hedberg, *J. Am. Chem. Soc.*, **72**, 3375 (1950).

[12] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[13] H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953).

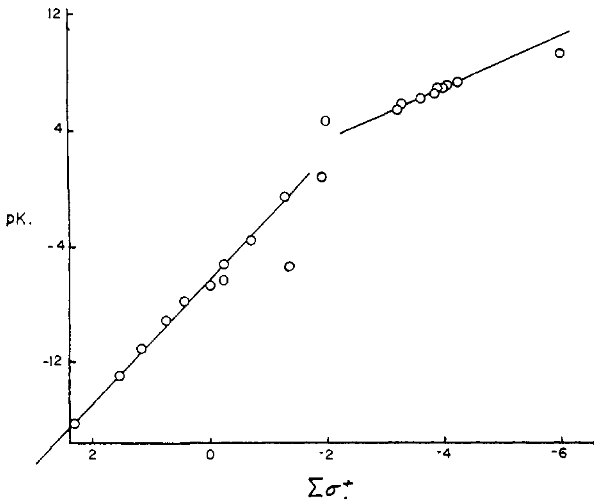

Fig. 8.—Hammett plot of basicities of triarylmethanols in water.

carbon atom (0.358[14]). Thus one predicts $\rho = -0.33$ (*i.e.*, $-3.02 \times 0.303 \times 0.358$).

Rho for the reaction III $\rightleftarrows$ VI, R = CH_3, may be estimated as one-half that for reaction III $\rightleftarrows$ IX, R = CH_3, if we assume that the protonated amino group of VI does not appreciably change the effect of the X group on the second amino group.

The value estimated in this manner (-0.655) is higher than expected by a significant amount when compared with ρ for the reaction I $\rightleftarrows$ IV of the leuco bases.

Since the only change from the leuco base situation is that a hydrogen has been replaced by a methoxyl on the central carbon, we must ascribe the differences in ρ values to an increased transmission by the central carbon when H is replaced by OCH_3.

Qualitatively, this observation is in agreement with the prediction that the transmission properties of groups are changed by substitution.[15]

It should be noted that this change is in the opposite direction to that found in the aliphatic series,[15] however. In the aliphatic system, an electron-withdrawing substituent attached to carbon diminishes the transmission properties of the carbon, while in the present system, the substitution of OCH_3, an electron - withdrawing substituent, for hydrogen has increased the transmission properties of the carbon.

From the arguments presented in the earlier paper,[15] this result requires a value of q[16] which is of the same sign as ρ, rather than of opposite sign as in the aliphatic series. We shall proceed to show that this result is consistent with other properties of the system.

Basicity of the Methyl Ethers.—From the value of ρ for the basicity of the methyl ethers found in this work, we predict a ρ of -1.95 in aqueous solution, using the equation

$$(1.8 + 67/D)\Delta\sigma_r = \rho^{17} \qquad (3)$$

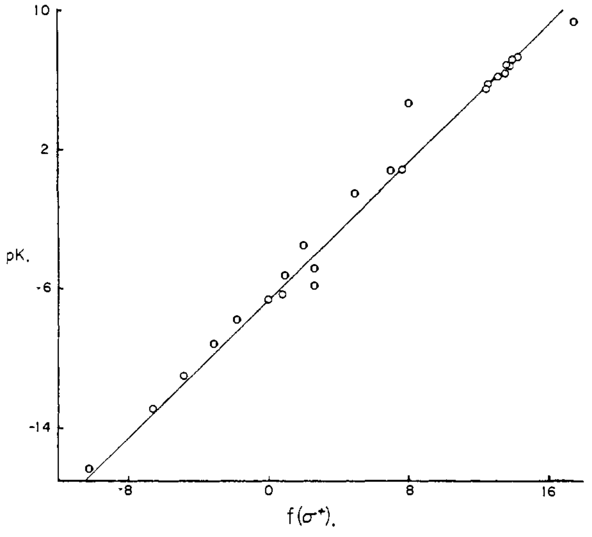

Fig. 9.—Plot of basicities of triarylmethanols according to eq. 4.

where D is the dielectric constant of the solvent, and $\Delta\sigma_r$ is the difference in the σ constant of the reaction site in the reactants and products.

If one assumes that the effect of an OH group is very nearly that of an OCH_3 group, this value may be compared with that found for the basicity of the carbinol bases in water (-1.83). The agreement is excellent.

Multiple Variations in Structure–Reactivity Correlation.—Deno[2a] has determined the basicity of a large number of mono-, di- and trisubstituted triphenylmethanols in aqueous solution, and has calculated a ρ for this series of -4.0. A plot of Deno's pK values and the values for the malachite green series *versus* the sum of the σ values of the substituents is shown in Fig. 8. The plot is certainly not linear.

Plotting only the monosubstituted derivatives *versus* σ gives a ρ of -4.0. If one then examines the eq. 4 for multiple variations in structure,[15] it is seen that the difference between this value

$$\log K = (\sigma_1 + \sigma_2 + \sigma_3)\rho_0 + (\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3)q + \log K_0 \qquad (4)$$

and that for the malachite green series is due to the term q (*i.e.*, $\rho - \rho_0 = +(\sigma_2 + \sigma_3)q$). Assigning a σ value of -2.00 to the dimethylamino group,[18] we then find $q = -0.55$.[19]

The sign of q is the same as that of ρ as required from the previous section.

Figure 9 shows a plot of the first two terms on the right of eq. 4 *versus* the experimental pK values for all of the experimental data available. The line drawn is the line of unit slope predicted by the equation.

We feel that this correlation, involving a range in K of over twenty powers of ten, is a striking con-

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[14] R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

[15] C. D. Ritchie, *J. Phys. Chem.*, **65**, 2091 (1961).

[16] q is the constant in the equation: $\log K = \sum_{1}\sigma_1\rho^\circ + \sum_{i,j}\sigma_1\sigma_j q + \log K_0$, which was derived by Miller (*cf.* ref. 3).

[17] W. F. Sager and C. D. Ritchie, *J. Am. Chem. Soc.*, **83**, 3498 (1961).

[18] H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958); the extreme value of σ was chosen because of the nature of the present system.

[19] This treatment implicitly assumes the propeller model for the triarylcarbonium ions. *Cf.* N. N. Lichtin and M. J. Vignoli, *J. Am. Chem. Soc.*, **79**, 579 (1957).

firmation of the utility of multiple variations in structure–reactivity correlations.

Experimental

Materials.—Eastman Kodak Co. *p*-toluenesulfonic acid was recrystallized from methanol and dried at 100° for several hours.

Dichloroacetic acid was distilled at atmospheric pressure through a 50-cm. Vigreux column. The fraction boiling between 193.5 and 194.5° was collected and used for the preparation of buffers.

Practical grade chloranil was recrystallized from benzene to constant melting point. Dihydrochloranil was recrystallized from ethanol.

Reagent grade anhydrous methanol was used without further purification.

Tribenzylamine and triethylamine were Eastman Kodak Co. white label reagents.

Temperature Control.—The Cary model 14 spectrophotometer was equipped with a thermostated cell compartment which was kept at 25 ± 0.5° by means of water circulated from a constant temperature bath. All solutions were thermostated in the bath prior to mixing or measuring.

Preparation of Leuco Bases.—The leuco bases used in this study were prepared by condensation of the appropriately substituted benzaldehyde with dimethylaniline using standard procedures.[6] The melting points of these compounds agree well with previously reported values as shown in Table I.

Preparation of Carbinol Bases.—The carbinol bases were prepared by the oxidation of the corresponding leuco bases with excess chloranil.

The leuco base (2 g.) was dissolved in 150 ml. of ethanol and 4 g. of chloranil was added in one portion. The resulting mixture was refluxed for 1 hour. At this time, 200 ml. of hot 10% sodium hydroxide solution was added. The solution was immediately extracted with several 100 ml. portions of hot *n*-heptane. The *n*-heptane extract was washed with hot 10% sodium hydroxide, dried with sodium sulfate, and set aside to cool slowly. The sides of the flask were scratched vigorously to initiate crystallization.

The precipitate thus obtained was repeatedly recrystallized from *n*-heptane until constant melting point and molar absorbance in the visible spectrum of the derived dyes were obtained.

The absorbances of the compounds in the visible range were obtained by adding several lambda of an acetone solution of the carbinol bases to an aqueous solution buffered at *p*H 4.0. Spectra were obtained with a Cary model 14 spectrophotometer.

Physical constants for the compounds are shown in Table I.

Fluoroborate salts of the dyes were prepared by adding sodium fluoroborate to aqueous solutions of the dyes buffered at *p*H 4.0. The fluoroborates were recrystallized from water.

Basicity of Methyl Ethers in Methanol.—Buffers prepared by adding *p*-toluenesulfonic acid to methanol solutions of tribenzylamine were found to be in the proper range for measurement of the equilibria between the dyes and the methyl ethers.

A typical experiment was performed by adding an aliquot portion of a solution of the dye, or carbinol, in methanol to a buffered portion of methanol, waiting for establishment of the equilibrium, and measuring the absorbance of the resulting solution in the visible range with a Cary model 14 spectrophotometer.

A second aliquot of the dye solution was added to methanol buffered at $pH = pK_{\text{tribenzylamine}} - 1.00$ in order to determine the absorbance of the dye. It was found that at this *p*H the dissociation of the methyl ethers was complete.

The various buffers were prepared by adding known amounts of tribenzylamine to a methanolic solution 1.08×10^{-3} *M* in *p*-toluenesulfonic acid, which had been standardized against standard sodium hydroxide.

The inertness of the amine toward the dye was established by repeating the measurement using a solution having a different buffer concentration but the same ratio as previously used.

The final concentration of dye plus ether was in each case about 10^{-5} *M*.

The equilibrium constants were calculated from the equation

$$pK_a - pK_{\text{tribenzylamine}} = \log[A/(A_{\max} - A)] + \log[(R_3N)/(R_3NH^+)] \quad (5)$$

where A is the absorbance of a solution with buffer ratio $(R_3N)/(R_3NH^+)$, $A_{\max}$ is the absorbance of a solution containing the same amount of added dye, but buffered at $pH = pK_{\text{amine}} - 1.00$, and K_a is the equilibrium constant for the reaction

$$Ar_3C^+ + CH_3OH \rightleftarrows Ar_3OCH_3 + H^+$$

Table IV shows a series of typical experimental data.

TABLE IV

DETERMINATION OF EQUILIBRIUM CONSTANTS

$Ar_3C^+ + CH_3OH \rightleftarrows Ar_3COCH_3 + H^+$; p''-NO_2 derivative

Buffer ratio[a]	Absorbance	$pK - pK_{\text{amine}}$	Buffer ratio[a]	Absorbance	$pK - pK_{\text{amine}}$
0.10[b]	1.220	...	2.00[b]	0.707	0.397
.30[b]	1.138	0.403	4.00[b]	.486	.392
.50[b]	1.057	.388	9.00[b]	.280	.405
1.00[b]	0.891	.368	9.00[c]	.281	.405

[a] Buffer ratio = $(R_3N)/(R_3NH^+)$. [b] $(R_3NH^+) = 1.08 \times 10^{-3}$ *M*. [c] $(R_3NH^+) = 2.02 \times 10^{-4}$ *M*.

Basicity of Leuco Bases.—The basicities of the leuco bases were measured by an analogous method using the absorbance at about 260 mμ.

The buffer solutions were prepared by adding known concentrations of dichloroacetic acid to a methanolic solution 3.78×10^{-3} *M* in sodium methoxide which had been standardized against standard hydrochloric acid.

The buffers were such that only a small extent of protonation occurred, so that it was possible to neglect the second ionization of the leuco bases.

In order to calculate equilibrium constants from the observed absorbances, it was necessary to know the absorbance of the monoprotonated leuco bases. It was found that for those leuco bases which did not have chromophoric groups on the third ring, the diprotonated leuco base had a negligible absorbance at 260 mμ. It was also noted that the absorbance of leuco crystal violet was three-halves that for leuco malachite green. From these observations it appeared reasonable to assume that the absorbance of the leuco bases was the sum of the absorbances of the individual chromophore groups present. Thus, the molar absorbances may be expressed

$$E_1 = {}^1/_2(E_0 + E_2)$$

where E_1 is the molar absorbance of the monoprotonated leuco base, E_0 that for the free base and E_2 that for the diprotonated leuco base.

E_2 was determined by measuring the absorbance of the leuco base in a methanolic solution 10^{-1} *M* in *p*-toluenesulfonic acid, and E_0 by measuring the absorbance of the leuco base in pure methanol.

The equilibrium constants were then calculated using an equation analogous to 5. Typical experimental data are shown in Table V.

TABLE V

DETERMINATION OF EQUILIBRIUM CONSTANTS

$IV \rightleftarrows I + H^+$; m''-Cl Substituent

Buffer[a] ratio	Absorbance	$pK - pK_{\text{DCA}}$
...	1.874[b]	.....
0.291	1.799	−0.525
0.962	1.670	− .538
1.625	1.580	− .542
2.23	1.519	− .564

[a] Buffer ratio = $(HA)/(A^-)$. [b] Absorbance in pure methanol.

Conversion of Dyes to Diprotonated Methyl Ethers.—Carefully measured volumes of standardized *p*-toluenesulfonic acid in methanol were added to 10^{-5} *M* solutions of the dyes in methanol (prepared by adding the fluoroborate salt to methanol). After equilibrium had been established,

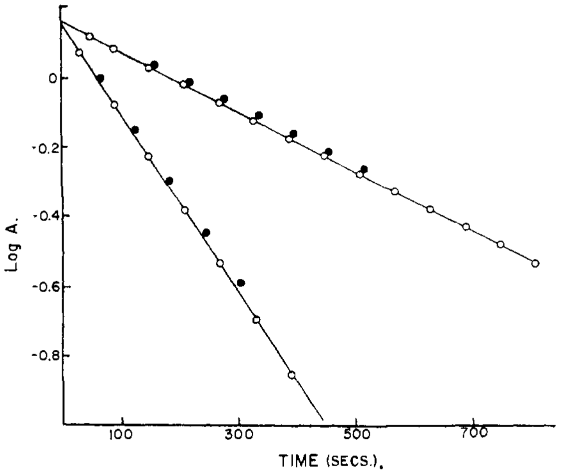

Fig. 10.—Pseudo-first-order rate plot for reaction of malachite green with methoxide: I, buffer ratio = 1.64; II, buffer ratio = 5.57; ○, (R_3NH^+) = 5.41 × 10^{-3} *M*; ●, (R_3NH^+) = 1.08 × 10^{-3} *M*.

the absorbances of the solutions in the visible region were measured. Calculations were analogous to those described above.

Some typical data are shown in Table VI.

TABLE VI

DETERMINATION OF EQUILIBRIUM CONSTANTS

IX, (R = CH_3) $\rightleftarrows$ II + $CH_3OH_2^+$; X = H(A_{max} = 1.502)

Concn. of *p*-toluenesulfonic acid	Absorbance	*pK*
1.67 × 10^{-2}	1.370	0.761
3.34 × 10^{-2}	1.314	.631
6.68 × 10^{-2}	1.131	.691
1.34 × 10^{-1}	0.860	.747
1.67 × 10^{-1}	.760	.772
3.34 × 10^{-1}	.491	.790

Reaction of Dyes with Methoxide.—Buffer solutions prepared by adding *p*-toluenesulfonic acid to solutions of triethylamine in methanol were found to give a range of *p*H in which the dyes are completely converted to the methyl ethers.

The reactions were followed by adding an aliquot portion of a solution of the dye fluoroborate in methanol to a quantity of the buffer, placing the resulting solution in a 1-cm. path length cell and measuring the absorbance *vs.* time by placing the cell in the thermostated compartment of a Cary model 14 spectrophotometer set to record absorbance at the wave length of maximum absorbance of the dye, at a known chart speed.

First-order plots of the data gave the pseudo-first-order rate constants, k_1. Runs at two different buffer ratios established that the reactions are first order with respect to methoxide, and that the rate of reaction with methanol is negligible. Runs at different buffer concentrations established the inertness of triethylamine toward the dye.

Some typical first-order plots are shown in Fig. 10.

Reaction of Leuco Bases with Chloranil.—In order to establish the stoichiometry of the reaction of chloranil with the leuco bases, the complete ultraviolet and visible spectra of chloranil, dihydrochloranil, leuco malachite green and malachite green fluoroborate were measured on carefully purified materials in methanol solution. Solutions containing mixtures of any two of the above components were observed to give spectra exactly corresponding to the sum of the spectra of the individual components.

The spectra obtained were used to analyze the spectra of reaction mixtures prepared from known amounts of chloranil and leuco base at various reaction times.

A typical experiment was performed by preparing master solutions of the leuco base and of chloranil of equal concentrations (*ca.* 5 × 10^{-4} *M*) in 1% acetic acid in methanol (the amount of acid determined to give complete conversion of the methyl ether to the dye, and only a small extent of protonation of the leuco base), and then mixing equal volumes of the solutions.

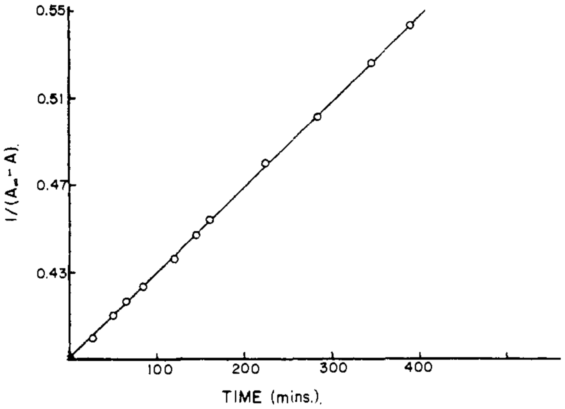

Fig. 11.—Second-order rate plot for reaction of leuco malachite green with chloranil; $(Ar_3CH)_0$ = $(Q)_0$ = 2.39 × 10^{-4} *M*; absorbance measured in 1-mm. path length cell.

Complete ultraviolet and visible spectra were obtained at 18 and 24 hours reaction time.

The absorbance of the solution at 620 mμ was used to calculate the amount of dye present. Assuming 1:1 stoichiometry, and using the spectra of the pure components, a theoretical spectrum was calculated and compared with the experimental. Nearly perfect agreement was obtained in both cases.

After 48 hours reaction time, the experimental and theoretical spectra did not agree. Analysis of the experimental spectrum revealed that more dihydrochloranil than dye was present. The spectrum of the master solution of chloranil also revealed the presence of dihydrochloranil after 48 hours.

Second-order plots of absorbance data for more concentrated reaction mixtures were accurately linear to about 50% completion. The presence of air resulted in deviations from linearity much sooner, and the calculated rate constants were higher than those obtained from degassed solutions by about 20%.

Because of the complicating factors, initial rates were used to calculate rate constants for the reaction. The constants obtained in this manner agreed reasonably well with those obtained from second-order plots of degassed solutions, and were more reproducible.

A typical second-order plot is shown in Fig. 11.

Runs using various concentrations of acetic acid were made to establish the independence of rate constant on acid concentration over a tenfold range of hydrogen ion concentration, (*i.e.*, 100-fold range of concentrations of acetic acid).

When the reactions were carried out in the absence of acetic acid, the color of the solution increased in intensity, and then decreased until no color remained after several hours. Addition of acid to the solution resulted in the immediate appearance of color.

Infrared Spectra.—Infrared spectra of the carbinol bases were measured in CS_2 and CCl_4 solutions with a Perkin-Elmer model 21 spectrophotometer.

Molecular weight determinations were performed on crystal violet carbinol using standard techniques.

Qualitative Test for Oxygen in Malachite Green Carbinol.—Anhydrous hydrochloric acid was passed through a solution of 75 mg. of malachite green carbinol in 20 ml. of carbon tetrachloride until precipitation was complete.

The lightly colored solvent was carefully decanted, and the gummy precipitate was dissolved in 0.10 ml. of absolute ethanol. The resulting ethanol solution was then analyzed for water by gas chromatography on an 8′ polyethylene glycol column. The presence of water was clearly shown by the chromatogram.

A blank of the alcohol, treated in the same manner, did not show the presence of water.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY[1] OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, IND., AND THE DEPARTMENT OF CHEMISTRY OF PROVIDENCE COLLEGE, PROVIDENCE, R. I.]

Reduction with Metal Hydrides. IX. Reaction Paths in the Reduction of Epoxides with Lithium Aluminum Hydride and Aluminum Chloride[2]

BY MARK N. RERICK AND ERNEST L. ELIEL

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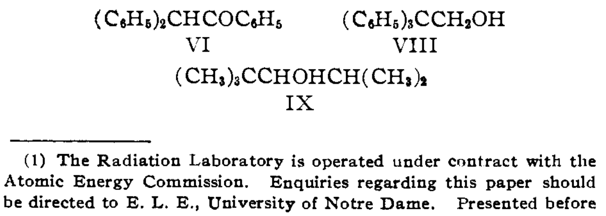
The nature of the reduction products of triphenylethylene oxide with "mixed hydride" (lithium aluminum hydride–aluminum chloride) has been found to depend on the proportions of $LiAlH_4$ and $AlCl_3$ in the reagent. With a 1:3 ($AlCl_3$:$LiAlH_4$) reagent, presumably containing AlH_3 as the active reducing agent, the product is the previously observed phenylbenzhydrylcarbinol, $Ph_2CHCHOHPh$, probably formed by direct, electrophilically assisted reductive ring opening of the epoxide. With a 4:1 reagent, presumably $AlHCl_2$ and excess $AlCl_3$, the main product is Ph_3CCH_2OH, accompanied by hydrogenolysis products of $Ph_2CHCHOHPh$. With this reagent, reduction seems to be preceded by rearrangement of the epoxide to the aldehyde Ph_3CCHO (phenyl shift) as the major product and the ketone $Ph_2CHCOPh$ (hydride shift) as the minor product. Treatment of the epoxide with $AlCl_3$ gave the aldehyde and ketone in a 3:1 ratio, as distinct from treatment with BF_3 which gives almost entirely the aldehyde. The reaction of the epoxide with $AlCl_3$ seems to involve a complex of the chlorohydrin $Ph_2CClCHOHPh$ as the first intermediate. This unstable chlorohydrin was prepared by treatment of the epoxide with hydrogen chloride. Upon treatment with a limited amount of $LiAlH_4$ (<0.25 mole) it also gave a mixture of Ph_3CCHO and $Ph_2CHCOPh$ with the aldehyde predominating, and upon reduction with mixed (4:1) hydride it gave Ph_3CCH_2OH, whereas with excess $LiAlH_4$ alone it gave mainly $Ph_2CHCHOHPh$. In this latter reduction, the ketone $Ph_2CHCOPh$ is not an intermediate, since deuteride reduction gave $Ph_2CDCHOHPh$, as shown by n.m.r. spectrum, rather than $Ph_2CHCDOHPh$. Similar results are obtained with β-diisobutylene oxide which gives mainly $Me_3CCMe_2CH_2OH$ with the 4:1 reagent but mainly $Me_3CCHOHCHMe_2$ with the 1:3 reagent.

In previous publications[3,4] from this Laboratory, the reduction of epoxides with lithium aluminum hydride–aluminum halide mixtures ("mixed hydrides"[5]) has been described. Of particular interest in connection with the present investigation is the reduction of triphenylethylene oxide (I) and of β-diisobutylene oxide (II). The former gave rise to phenylbenzhydrylcarbinol (III) and the latter to 2,2,3,3-tetramethylbutanol-1 (IV). It was postulated that the reduction of I to III involved a hydride shift in the acidic reaction medium producing phenyl benzhydryl ketone (VI) as an intermediate. This postulate was based on the demonstration[3] that reduction of styrene oxide with lithium aluminum deuteride–aluminum chloride gave 2-phenylethanol-1-*d*, evidently *via* phenylacetaldehyde, and that similar reduction of isobutylene oxide gave isobutyl-1-*d* alcohol *via* isobutyraldehyde. The mechanism of reduction of I to III was inferred by analogy, passing over the fact that in this reduction lithium aluminum hydride pre-treated with allyl bromide was used rather than lithium aluminum chloride-aluminum halide. At the time, this did not seem to matter, since allyl bromide (believed to be a generator of inorganic bromide *in situ*) had been employed interchangeably with aluminum halides in other reductions.[3] The reduction of II to IV was similarly postulated to involve shift of a *t*-butyl group to give tetramethylbutyraldehyde (VII) as an intermediate.[4] In this case the reality of the intermediate was demonstrated by isolating it from the reaction of II with aluminum chloride in the absence of hydride.[4]



$(C_6H_5)_2CHCOC_6H_5$ VI $\qquad$ $(C_6H_5)_3CCH_2OH$ VIII

$(CH_3)_3CCHOHCH(CH_3)_2$ IX

The postulated rearrangement of I to VI became a matter of concern in the light of a recent survey[6] which suggests that phenyl usually migrates in preference to hydrogen and especially in view of the demonstration[7] that treatment of triphenylethylene oxide (I) with boron trifluoride etherate gives triphenylacetaldehyde (V) by a phenyl shift rather

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(1) The Radiation Laboratory is operated under contract with the Atomic Energy Commission. Enquiries regarding this paper should be directed to E. L. E., University of Notre Dame. Presented before the Division of Organic Chemistry at the meeting of the American Chemical Society at New York, N. Y., September 12, 1960.

(2) Paper VIII, E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

(3) E. L. Eliel and D. W. Delmonte, *ibid.*, **80**, 1744 (1958).

(4) E. L. Eliel and M. N. Rerick, *ibid.*, **82**, 1362 (1960).

(5) For a review of mixed hydride reductions *cf.* M. N. Rerick, "Selective Reduction of Organic Compounds with Complex Metal Hydrides," Metal Hydrides, Inc., 33 Congress Street, Beverly, Mass., 1959, and E. L. Eliel, *Rec. Chem. Progr.*, **22**, 129 (1961).

(6) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).

(7) A. C. Cope, P. A. Trumbull and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).