Recrystallization from absolute ethanol yielded pure *p*-nitrobenzylamine hydrochloride, m.p. 225–227°, a yield of 79%.

Similarly, 0.20 mole of adiponitrile, b.p. 154–156° at 8 mm., was treated with 0.16 mole of diborane. After 4 hours, the product was treated with hydrogen chloride and isolated as in the above procedure in the form of the dihydrochloride: 32.2 g., m.p. 245–247°, 85% yield. Recrystallization from absolute ethanol–benzene gave 28.0 g., 74% yield, of 1,6-hexamethylenediamine dihydrochloride, m.p. 246–248°.

p-Chlorobenzoic acid, m.p. 237–239°, 31.3 g., 0.20 mole, was cautiously added to 0.18 mole of sodium borohydride (180 ml. of 1.0 *M* solution in diglyme) in a 500-ml. round-bottom flask, fitted with a magnetic stirrer and a separatory funnel. When the acid had gone into solution, evolving hydrogen, 0.24 mole of boron trifluoride etherate, in 50 ml. of diglyme, was added over a period of 1 hour through the separatory funnel to the stirred solution. After 3 additional hours at room temperature, the reaction mixture was poured onto crushed ice, the precipitated solid collected on a filter, washed with ice-water and dried. The crude product, 27.7 g., m.p. 73–75°, 92% yield, was recrystallized from hot aqueous ethanol to give *p*-chlorobenzyl alcohol, m.p. 74–75°, in 81% yield.

In a similar manner, 0.20 mole of *p*-nitrobenzoic acid, 33.4 g., m.p. 240–242°, was reduced with sodium borohydride–boron trifluoride etherate, and the product poured onto crushed ice and dilute hydrochloric acid. The precipitated alcohol was separated, and the aqueous filtrate extracted with ethyl ether. The ether extract was washed with small quantities of ice-water to remove diglyme. There was obtained a total of 24.1 g. of product, m.p. 91–93°, a yield of 79%. After treatment with active carbon and recrystallization from hot water, pure *p*-nitrobenzyl alcohol, white crystals, m.p. 92–93°, was obtained in a yield of 72%.

Using essentially the same procedure, 41.3 g., 0.4 mole, of benzonitrile, b.p. 189° at 743 mm., was treated with 0.27 mole of sodium borohydride (30% excess) and 0.36 mole of boron trifluoride etherate. After a reaction time of 2 hours (1 hour addition of the boron trifluoride etherate, followed by 1 hour standing at room temperature), the excess hydride in the reaction mixture was destroyed by adding concentrated hydrochloric acid. The solvent and excess acid was removed under reduced pressure, leaving a residue of inorganic salts and benzylamine hydrochloride. Strong aqueous alkali was added, the amine extracted with ether, dried and distilled. There was obtained 35.7 g. of benzylamine, b.p. 181–183° at 734 mm., a yield of 83%.

Similarly, 0.20 mole of phenylacetonitrile, b.p. 107–108° at 10 mm., yielded 20.3 g. of β-phenylethylamine, b.p. 196–198° at 748 mm., a yield of 84%.

Styrene oxide, 0.40 mole, 48.0 g., b.p. 190–191° at 749 mm., was treated with 0.11 mole of sodium borohydride and 0.13 mole of boron trifluoride etherate. After a reaction time of 1 hour, the product was hydrolyzed and the alcohol recovered with ether. There was obtained 36.6 g. of mixed alcohols, a yield of 75%. On distillation there was obtained 25.1 g. of 2-phenylethanol, b.p. 103–105° at 14 mm., and 9.3 g. of 1-phenylethanol, b.p. 91–92° at 14 mm.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Rates of Reaction of Some Substituted Diarylmercury Compounds with Hydrogen Chloride

BY RAYMOND E. DESSY AND JIN-YOUNG KIM[1]

RECEIVED JUNE 15, 1959

The rates of reaction of a series of substituted aromatic organomercury compounds with HCl in DMSO–dioxane have been investigated (eq. 2). It is found that the series Z = *p*-CH_3O, Cl, F, C_6H_5 and *m*-NO_2 obeys the Hammett plot log $k = (\sigma + \sigma^+/2)\ \rho$, with $\rho = -2.8$. E^* is a linear function of ΔS^* and the isokinetic temperature is 500°K. It is suggested that the linear relationship between E^* and ΔS^* is the result of changes in the ground state solvation of the organomercury and consequent changes in the C–Hg–C angle.

In a previous paper in this series[2] the rates of reaction of some dialkymercury compounds with hydrogen chloride in dimethyl sulfoxide–dioxane solution were reported, and a mechanism for the reaction proposed.

$$R_2Hg + HCl \xrightarrow[10:1]{\text{DMSO–dioxane}} RHgCl + RH \quad (1)$$

In light of the increased interest in the reactions of organomercury compounds, it was felt that an investigation of the reaction rates of a series of substituted aromatic mercury compounds would prove valuable

$$(Z\text{–}C_6H_4)_2Hg + HCl \xrightarrow[10:1]{\text{DMSO–dioxane}} Z\text{–}C_6H_4HgCl + Z\text{–}C_6H_5 \quad (2)$$

Although considerable experimental evidence has accumulated concerning electrophilic substitution at an aromatic carbon involving proton expulsion, and nucleophilic substitution at a saturated carbon center, little work has been done on electrophilic substitution at such centers which involve the expulsion of a group other than hydrogen.

Experimental

Organomercury Compounds.—The organomercury compounds were prepared by standard techniques.[3]

Diphenylmercury was prepared by treating phenylmagnesium bromide with mercuric chloride in ether–benzene.[3] The product was recrystallized from chloroform, m.p. 122–124°.

Bis-*p*-chlorophenylmercury.—*p*-Chlorobromobenzene was converted to the Grignard reagent, and treated with $HgCl_2$ in ether. The product crystallized from chloroform, m.p. 249–252° (lit.[4] 242–243°).

Anal. Calcd. for $C_{12}H_8Cl_2Hg$: C, 34.01; H, 1.90. Found: C, 34.31; H, 2.05.

Bis-*p*-fluorophenylmercury.—*p*-Fluorobromobenzene was converted to the Grignard reagent and treated with $HgCl_2$ in ether. The product was recrystallized from ligroin–benzene, m.p. 151–154° (lit.[5] 151–155°).

Anal. Calcd. for $C_{12}H_8F_2Hg$: C, 36.87; H, 2.06. Found: C, 36.30; H, 2.61.

Bis-*p*-diphenylmercury.—4-Bromodiphenyl was converted to the Grignard reagent, and treated with $HgCl_2$ in ether,

---

(1) National Science Foundation Research Fellow.

(2) Raymond E. Dessy, G. F. Reynolds and Jin-Young Kim, THIS JOURNAL, **81**, 2683 (1959).

(3) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalogue Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1921.

(4) Fr. Hein and K. Wagler, *Ber.*, **58**, 1499 (1925).

(5) G. C. Hampson, *Trans. Faraday Soc.*, **30**, 877 (1934).

TABLE I

$$(Z\text{–}C_6H_4)_2Hg + HCl \xrightarrow[\text{dioxane}]{\text{DMSO}} Z\text{–}C_6H_4HgCl + Z\text{–}C_6H_5$$

Z				k, l./mole-sec. × 10^3					
	t, °C. 12.8	19.0	25.0	32.0	40.0	50.0	57.0	65.0	75.0
p-CH_3O	172	242		460[a]					
p-C_6H_5				26.1	44.5	77.6			
p-H			9.30	16.2	25.0				
p-F				13.6	23.7	50.8			
p-Cl				4.78	9.48	1.89			
m-NO				0.140[a]			1.67	3.39	8.21
Et_2Hg			0.82						
i-Pr_2Hg			.56						
n-Pr_2Hg			.51						

[a] Values obtained by extrapolating the log k vs. 1/T curve.

TABLE II

$$(Z\text{–}C_6H_4)_2Hg + HCl \xrightarrow[\substack{\text{dioxane}\\ 32°}]{\text{DMSO}} Z\text{–}C_6H_4HgCl + Z\text{–}C_6H_5$$

Z	k, l./mole-sec. × 10^3	$E^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
p-CH_3O	460	9.2	—32
p-C_6H_5	26.1	11.9	—30
p-H	16.2	12.2	—29
p-F	13.6	11.4	—31
p-Cl	4.78	15.0	—22
m-NO_2	0.14	20.8	—10
Et_2Hg		15.5	—27
i-Pr_2Hg		15.4	—28
n-Pr_2Hg		16.5	—25

benzene. The product was recrystallized from benzene, p-xylene and finally chloroform, m.p. 216–220° (lit.[6] 216°).

Anal. Calcd. for $C_{24}H_{18}Hg$: C, 56.85; H, 3.58. Found: C, 56.12; H, 3.71.

Bis-m-nitrophenylmercury.—The mercuration of nitrobenzene was adapted from the method of Klapproth and Westheimer.[7] Red HgO (5.4 g., 0.025 mole) and nitrobenzene (12.3 g., 0.10 mole) were allowed to react in 250 ml. of 70% perchloric acid for 5 days at room temperature. The reaction mixture was poured onto an excess of salt water, and the product, m-nitrophenylmercuric chloride, when recrystallized from alcohol, had a m.p. 240–242°. Reaction with sodium iodide in acetone gave bis-m-nitrophenylmercury, m.p. 300–302°.

Anal. Calcd. for $C_{12}H_8HgN_2O_4$: C, 32.38; H, 1.81. Found: C, 32.75; H, 1.60.

Dianisylmercury.—The preparation was a modification of that described by Michaelis and Rabinerson[6] using sodium amalgam. Mercury, 388 g., and xylene, 30 g., were placed in a three-necked reaction vessel, and heated to 100°. Nine grams of sodium metal (0.4 g.-atom) was added, followed by p-bromoanisole (37 g., 0.2 mole) dissolved in 6 ml. of ethyl acetate and 100 ml. of xylene. The mixture was refluxed for 24 hours at 160°, and the reaction mixture hydrolyzed with water and dried. Removal of the solvent and recrystallization from methanol gave dianisylmercury, m.p. 202–204° (lit.[6] 202°).

Kinetic Method.—The conductivity method used to follow the kinetics has been described in a previous paper.[2] A mineral oil thermostat operating at temperatures from 12° to 75° was used. Dimethyl sulfoxide (DMSO) was purified by redistillation of commercial material (b.p. 54–56° (4 mm.)). The acid solution was made by passing the hydrogen chloride through phosphorus pentoxide, and dissolving in dioxane. A calculated amount of organomercury compound was weighed directly into the conductivity cell, and 10 ml. of DMSO was added. This was allowed to equilibrate with the bath temperature. Then 1.0 ml. of dioxane-HCl solution was added. The readings of the resistance of the solution were taken for well over 75% of the reaction. The initial acid concentration used for the reactions ranged from 0.035 to 0.07 N, and the initial concentration of organomercury compound was usually equal to or twice that of the acid concentration.

Results and Discussion

Table I lists the rate data found for a series of substituted aromatic mercury compounds reacting with hydrogen chloride under the conditions stated. Table II lists the thermodynamic data obtained from the kinetic data. The aliphatic compounds are included for comparison purposes. Figure 1 shows a Hammett plot[8] for the kinetic data at 32°.

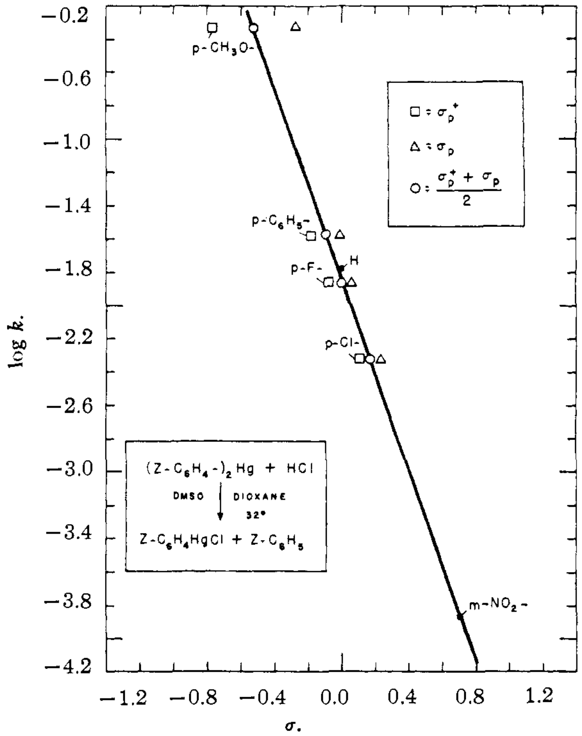


Fig. 1.

It is evident from the kinetic data that electron-withdrawing substituents decrease the reaction rate, while electron-donating groups increase the

---

[6] A. Michaelis and J. Rabinerson, *Ber.*, **23**, 2343 (1890).

[7] Wm. J. Klapproth and F. H. Westheimer, THIS JOURNAL, **72**, 4461 (1950).

[8] Values for σ are taken from the review by H. H. Jaffé (*Chem. Revs.*, **53**, 191 (1953)). Values for σ^+ are taken from the work of H. C. Brown and Y. Okamoto (THIS JOURNAL, **79**, 1913 (1957)).

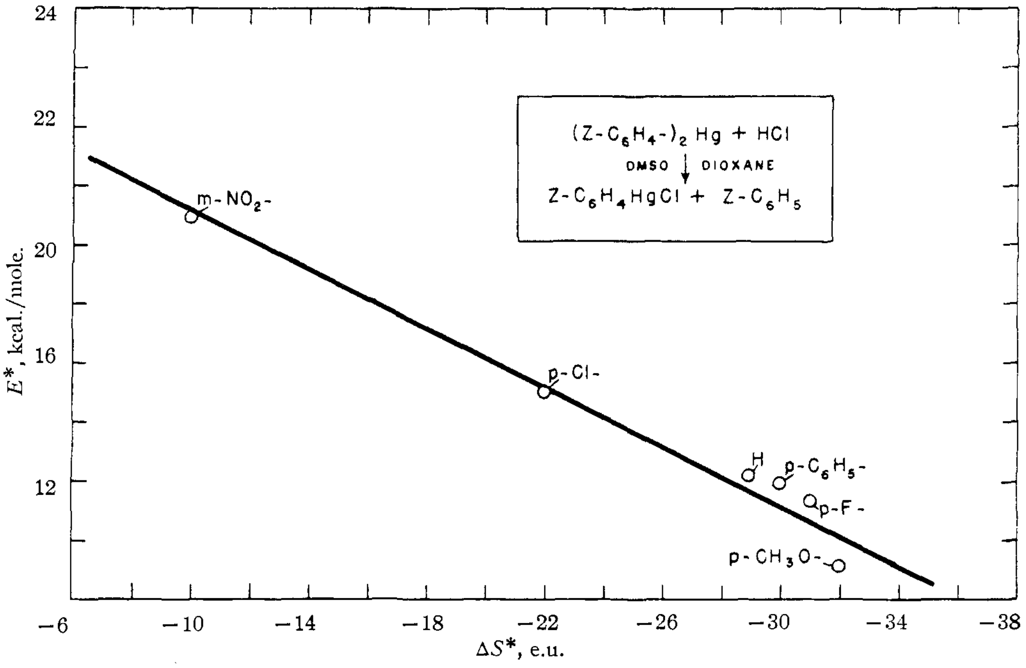
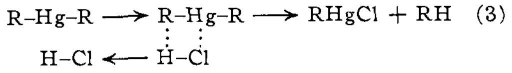


Fig. 2.

reaction rate. This supports the mechanism previously proposed for the reaction[2]



$$\begin{matrix} \text{R–Hg–R} & \longrightarrow & \text{R–Hg–R} & \longrightarrow & \text{RHgCl} + \text{RH} \quad (3) \\ & & \vdots \quad \vdots & & \\ \text{H–Cl} & \longleftarrow & \text{H–Cl} & & \end{matrix}$$

in which electrophilic attack by molecular or ion-pair HCl was proposed. It is obvious that the important rate-determining attack lies with the H, and not with Cl. This is of course in line with the fact that Cl$^\ominus$ ion does not materially affect the rate.[2] It must be emphasized that the present data do not distinguish between ion-pair or molecular attack.

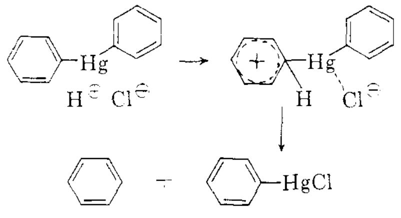
It is interesting to note that in going from aliphatic to aromatic mercury compounds the change in rate appears to be due to the change in the activation energy term.

Within the aromatic series several interesting relationships may be noted: a. A plot of log k_2^{32} *vs.* σ or σ^+ is not linear, but a plot *versus* $(\sigma + \sigma^+)/2$ does give a good linear fit ($\rho = -2.8$). b. A plot of E^* *vs.* ΔS^* is approximately linear, with a slope of 500 (Fig. 2).

With substituents in both rings it is possible that the Hammett relationship could be expressed as

$$\log k/k_0 = \sigma\rho + \sigma^+\rho'$$

but only coincidence of a high degree would result in $\rho = \rho'$. It is likely that the Hg atom serves as a very effective block or sink for electrical effects, just as a phenyl group can, or that the hybridization of the Hg prevents interaction of the rings. The observed correlation could represent the action of one substituent on the electron density at the attacked position, the use of both σ and σ^+ giving a better fit because of the introduction of another parameter. Alternatively a more appealing picture lies in a transition state which takes into account the ability of H$^+$ and phenyl groups to interact in phenonium ion formation, a process that undoubtedly occurs in four-center attack by H–Cl or H$^\oplus$Cl$^\ominus$ ion pairs.



Such a picture would require the use of both σ and σ^+ to express the *actual and potential* electron density at the attacked site.

According to the isokinetic relationships developed by Leffler[9]

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (4)$$

$$\text{if } \Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta\Delta S^{\ddagger} \quad (5)$$

$$\text{then } \Delta F^{\ddagger} = \Delta H_0^{\ddagger} - (T - \beta)\Delta S^{\ddagger} \quad (6)$$

$$\text{and } \Delta F^{\ddagger} = T/\beta\ \Delta H_0^{\ddagger} + (1 - T/\beta)\Delta H^{\ddagger} \quad (7)$$

where β is the isokinetic temperature. Approximating $E^{\ddagger}$ with $\Delta H^{\ddagger}$, the isokinetic temperature for the reaction under investigation is *ca.* 500°K. Since we are operating well below the isokinetic temperature, positive changes in $\Delta H^{\ddagger}$ are reflected in positive changes in $\Delta F^{\ddagger}$, and the present reaction can be said to be enthalpy controlled, rather than entropy controlled.

The linear relationship observed between $E^{\ddagger}$ and $\Delta S^{\ddagger}$ indicates also a single mechanism for the series.

The change in the entropy term throughout the series seems surprising, in light of the distance of the substituent from the reaction site. One interesting and thought provoking possibility presents itself.

It is well known that the C–Hg–C bond angle in the organomercury compounds is a function of

---

[9] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

solvent. Absolute values are not known, but dipole moment measurements[10] indicate that in solvents such as dioxane, benzene or CCl_4 the angle may be of the order or 120–150°, and that it is highly dependent upon solvent and temperature.

The change in dipole moment is believed to be the result of changes in solvation around the mercury—changes which cause the normal sp-hybrid, which yields a 180° C–Hg–C bond angle, to rehybridize to something which, in a sufficiently solvating media, would approximate the tetrahedral.

Complex mercuric ions of the type HgI_3^-–$HgI_4^{=}$- are stable and the latter have been shown to be tetrahedral.[11] Mercuric iodide dissolved in dioxane also has been reported to be tetrahedral in structure. All the information seems to indicate that divalent mercury compounds have a strong tendency to accept one or two pairs of electrons, a conclusion which might be expected from the fact that Hg is one of the so-called electron-deficient elements and has 2 vacant p-orbitals.

A tetrahedral configuration would mean that mesomeric effects cannot be transmitted from one benzene ring to the other, whereas an sp- or sp^2-hybrid in a substituted diphenyl mercury would at least permit certain interaction. It has been found[12] that there is little interaction of the π-electrons of the two benzene rings of diphenylmercury in ethanol as determined by ultraviolet spectroscopy. The spectrum resembles that of $(C_6H_5)_2CH_2$, which is tetrahedral. This seems to support the solvation concept, with the hybridization of the Hg somewhere between sp^2 and sp^3.

In a polar media such as DMSO, solvation is likely to be important in determining the over-all entropy term. The solvation of $(Z{-}C_6H_4)_2Hg$ in the highly polar transition state is probably independent of the substituent, but in the ground state large differences in solvation around Hg and consequent changes in the C–Hg–C angle could be expected. The largest solvation would be expected for those molecules having electron-withdrawing groups attached–solvation in the ground and transition state would not be appreciably different, and $\Delta S^{\ddagger}$ would be fairly high: in those compounds having electron donors attached to the ring the solvation in the ground state would be low, and the amount of solvent "frozen-out" in the transition state would be large leading to a very low entropy term. Such behavior is indeed noted in the present series investigated, the highest entropy term being associated with the *m*-NO_2 substituent, the lowest with *p*-CH_3O. The effect upon the activation energy term would of course be in the opposite direction, because of the positive nature of the attacking species.

It is possible that the changing molecular geometry also affects both energy terms. One would expect the ground states of those compounds containing electron-withdrawing groups to be more "tetrahedral" around Hg than those possessing electron donors attached to the ring. The effect of changing molecular geometry on reaction rates is a subject that has not been explored to date. It seems obvious that solvation can influence hybridization., *e.g.*, there seems to be little hesitation in thinking of R_2Mg compounds as being tetrahedral in diethyl ether. It is hoped that this suggestion will lead to further investigation in the area.

Acknowledgment.—The authors wish to acknowledge support of this work by a National Science Foundation Grant NSF G-5911.

CINCINNATI, OHIO

[10] *Cf.* H. Sawatzky and G. F. Wright, *Can. J. Chem.*, **36**, 1555 (1958).

[11] M. L. Delwaulle, F. Fraveois and J. Wiemann, *Compt. rend.*, **207**, 340 (1938).

[12] B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, 1454 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

The Mechanism of the Reaction of Mercuric Halides with Dialkyl and Diarylmercury Compounds

BY RAYMOND E. DESSY AND Y. K. LEE[1]

RECEIVED JUNE 15, 1959

The rates of reaction of a series of aliphatic and substituted aromatic organomercury compounds with mercuric halides have been measured by a convenient spectrophotometric technique in dioxane: $R_2Hg + HgX_2 \rightarrow 2RHgX$; $(Z{-}C_6H_4)_2Hg + HgX_2 \rightarrow 2Z{-}C_6H_4HgX$. In the aliphatic series (R = Me, Et, *n*-Pr, *i*-Pr) the reaction rate appears to be largely independent of R. In the aromatic series (Z = *p*-CH_3O, CH_3, Cl, F, C_6H_5) the Hammett equation is obeyed, $\rho = -5.87$. The addition of H_2O and $X^{\ominus}$ has little or no effect upon rate, and the observed rate sequence upon changing X is $HgCl_2 > HgBr_2 > HgI_2$. Activation energies and entropies have been measured, and in conjunction with other data indicate a four-center transition state arising from molecular or ion pair attack.

Although the reaction of a dialkyl- or diarylmercury compound with mercuric halides

$$\left.\begin{matrix}R_2Hg\\ Ar_2Hg\end{matrix}\right\} + HgX_2 \longrightarrow \left\{\begin{matrix}2RHgX\\ 2ArHgX\end{matrix}\right. \qquad (1)$$

has been known and used synthetically for a number of years,[2] very little is known about the mechanism of this reaction.

Winstein[3] has reported that the cleavage of *cis*-2-methoxycyclohexylneophylmercury by Hg^*Cl_2 pro-

[1] National Science Foundation Research Fellow.

[2] F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalogue Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1921.

[3] S. Winstein, T. G. Traylor and C. S. Gainer, THIS JOURNAL, **77**, 3741 (1955).