lationship. Furthermore, it is noteworthy that all of the *ortho* derivatives esterify at rates greater than those to be expected from the magnitude of the ionization constants of the corresponding *o*-substituted phenylpropiolic acids. A steric effect is undoubtedly at the root of this behavior since the sigma values for the *ortho* derivatives are derived from the ionization constants of the corresponding phenylpropiolic acids. A convincing explanation for this example of steric assistance is not apparent to the authors.

The selection of a proper rho value for the esterification of benzoic acids with methanol is difficult because the experimental values for the rate constants for all of the *m*- and *p*-substituted benzoic acids do not yield a good Hammett plot. Considerable variation in the rho value can be obtained if certain acids are included or excluded. All of the recorded data come from two papers[9] and in these a rho value of -0.56 is derived. On the other hand Jaffe[1] gives a rho value of -0.23, obtained by recalculation according to certain standardized procedures. For the esterification of the phenylpropiolic acids herein reported a rho value of -0.44 was obtained at 25 and at 35°. This fact indicates that transmission of polar effects from substituent to carboxyl groups is about the same when either a $-C_6H_4-$ or a $-C_6H_4C\equiv C-$ group intervenes. The above findings are of interest in view of the fact that as a class the phenylpropiolic acids are about 6–10 times stronger than the corresponding benzoic acids (see Table I).[10] The spread in esterification rates was insufficient to permit accurate evaluation of the *E* and *PZ* terms. However, they are recorded in Table II.

Table III

Ultraviolet Absorption Maxima of Ethyl Esters of Phenylpropiolic Acids

Substituent	Principal mμ	E_{max} $\times 10^{-3}$	Secondary mμ	E_{max} $\times 10^{-3}$
H	258	15.2		
o-Cl	259	12.6		
m-Cl	256	14.4		
p-Cl	266	18.7		
o-NO_2	232	20.2	307	4.0
m-NO_2	250	22.3		
p-NO_2	286	19.6		
o-OCH_3	268	9.3	310	6.7
m-OCH_3	262	12.7	301	4.3
p-OCH_3	286	19.0		

Infrared and Ultraviolet Spectra.—The position of the principal maxima and intensities in the ultraviolet absorption spectra of the ethyl esters of the phenylpropiolic esters studied are given in Table III. The spectra were taken in the hope that some light might be shed on the abnormal *ortho* effect noted in the section above.

No significant shifts in the position of the 4.5–4.6 μ band characteristic for the $-C\equiv C-$ grouping were found in the spectra of the ethyl esters.

Columbus 10, Ohio

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[9] R. J. Hartman and A. M. Borders, This Journal, **59**, 2107 (1937); R. J. Hartman and A. G. Gassman, *ibid.*, **62**, 1559 (1940).

[10] It should be pointed out, however, that the ionization constants for the benzoic acids are for water whereas the constants of the phenylpropiolic acids were taken in 35% dioxane.

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

Electrical Effects of Substituent Groups. Reactivities of Substituted Phenylpropiolic Acids

By John D. Roberts[1a] and Rudolph A. Carboni[1b]

Received January 27, 1955

Measurements have been made of the reactivities of some substituted phenylpropiolic acids. It is concluded that the inductive and field effects are of comparable importance in the transmission of the electrical influences of dipolar substituents to a reactive center.

In a previous study[2] of the reactivities of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids, the magnitudes of the polar effects of the 4-substituents were found to be comparable to those of the corresponding *m*- and *p*-substituted benzoic acids. It was deduced that the π-electron systems in aromatic compounds play a relatively minor role in the transmission of electrical effects from dipolar substituents to other parts of the molecule in the absence of direct and important conjugation between the substituent and ring. The magnitudes of the relative reactivities of the 4-substituted bicyclo-[2.2.2]octane-1-carboxylic acids were about twice as large as predicted from the Kirkwood–Westheimer equations[3] which only take into account the effect on the reaction center of direct electrostatic influences of substituents and might be regarded as giving a first approximation of the field effect.[2] The saturated nature of the bicyclo[2.2.2]octane ring system clearly precluded resonance effects involving conjugated unsaturation but no experimental information was obtained concerning the importance, relative to the field effect, of the *inductive effect* which was taken as transmission of polarity through a chain of atoms by displacement of binding electrons between successive atoms. With all of the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids which were studied, the field and inductive effects might be expected to operate in the same direction to influence the reactivity of the carboxyl group.

It should be clear that any attempt to separate quantitatively electrical influences of dipolar substituent groups into field and inductive effects must ultimately run afoul of the formidable difficulty of evaluation of dielectric constants in very electrically inhomogeneous systems at the molecular level. As a result, it is not surprising that the field and inductive effects have been often regarded as even qualitatively indistinguishable and have been treated practically as a composite influence. Nonetheless, the effects can be regarded as differing fundamentally because, while the efficiency of

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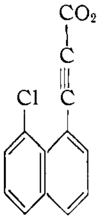
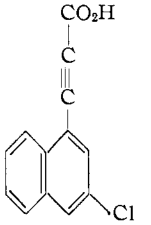
[1] (a) Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4; (b) United States Rubber Company Fellow, 1952–1953.

[2] J. D. Roberts and W. T. Moreland, Jr., This Journal, **75**, 2167 (1953).

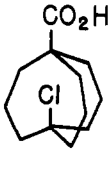
[3] (a) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); (b) F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

the direct electrostatic effect of a dipolar substituent should depend on the orientation of the dipole and its distance (*r*) from the reactive center, the inductive effect should depend on the number and kind of atoms in the chain (or chains) connecting the dipolar group to the reactive center. In principle, the relative magnitudes of the field and inductive effects of dipolar substituents could be determined through the use of compounds with similar or identical linkages for transmission of the inductive effect but widely different angles between the substituent and the reactive groups. For example, in a compound like (8-chloro-1-naphthyl)-propiolic acid (I), the angle of the dipolar substituents with respect to the carboxyl group is such that the field effect of the C–Cl dipole should act to reduce the $-CO_2H$ acid strength while, in (3-chloro-1-naphthyl)-propiolic acid (II), the field effect would be expected to operate so as to increase the acid strength as it does in *m*-chlorobenzoic acid. With both I and II, the inductive effect would be acting over the same number of carbon atoms (for the shortest paths) and would be expected to be roughly the same.


I


II

Thus, if I were found to be just as strong an acid[4] as II, then it might be concluded qualitatively that the field effect was of negligible importance relative to the inductive effect provided no specific resonance interactions were important with one compound and not the other. If I were a stronger acid than the 1-naphthylpropiolic acid (III) but weaker than II then the operation of both effects would be indicated but the inductive effect would be more important. In the event that I was much weaker than III, the field effect could be said to be more important than the inductive effect. While it is easy to design many "horseshoe" compounds like I, where the field and inductive effects of a dipolar substituent can be regarded as operating in opposition to one another, consideration of convenience of preparation and solubility probably make impractical comparisons between "ideal" molecules like IV and V.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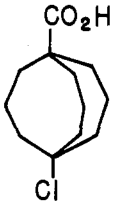
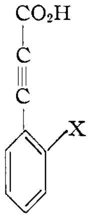
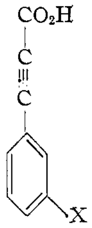
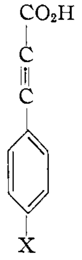

V

In the present research, an attempt was made to evaluate qualitatively the relative importance of the field and inductive effects through studies of reactivities of substituted phenylpropiolic acids (VI–VIII).


VI


VII


VIII

X = –Cl or $-NO_2$

The physical properties of the phenylpropiolic acids and esters used in the reactivity studies are given in Table I. The acids were prepared by dehydrobromination of the corresponding cinnamic acid or ester dibromides with alcoholic potassium hydroxide. The relative reactivities of the phenylpropiolic derivatives were determined by three methods each of which has been employed in previous studies. The apparent dissociation constants K_A of the acids were determined in 50% ethanol-water (by volume) at 25.0°[5] and are listed in Table I. The reactivities of the acids toward diphenyldiazomethane were determined in absolute ethanol and dioxane at 30.0° as described previously.[5,6]. The rate data are summarized in Table I. Finally, the rates of alkaline hydrolysis of the ethyl esters of the phenylpropiolic acids were measured in 87.83% ethanol (by weight) at 20.0° by the procedure of Kindler.[7] The saponification rate constants are given in Table I. The reactions were quite fast and it is not considered that the rate constants are accurate to better than ±15%.

Plots of the reactivity data for the *m*- and *p*-substituted phenylpropiolic acids against the appropriate σ-constants[8] indicate the expected approximately linear relationship (see Fig. 1). The $\log k^0$ and ρ-values corresponding to these plots are listed in Table II. Figure 2 shows the relationship between the logarithms of the ionization constants of the various phenylpropiolic acids and the other reactivity data. The lines in Fig. 2 are drawn to represent least-squares, fits of the *m*- and *p*-points only. The diphenyldiazomethane rates for the *o*-substituents are related to the ionization constants in almost the same way as with the *m,p*-substituted acids. This parallelism indicates that the usual *ortho* or proximity effects[8] are probably not very important with the *o*-substituted phenylpropiolic acids. The saponification rates of the *o*-esters are rather faster than would be expected from the relationship between the rates and ionization constants of *m,p*-substituted acids. Similar observations

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[4] To eliminate specific solvent effects, it would be particularly appropriate to have acidities referred to the vapor state. This does not appear to be practical but, as will be shown later, a crude approximation is probably achieved by working in solvents of low dielectric constants.

[5] J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

[6] J. D. Roberts, W. H. Watanabe and R. E. McMahon, *ibid.*, **73**, 760 (1951).

[7] K. Kindler, *Ann.*, **450**, 1 (1926).

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

TABLE I

PHYSICAL CONSTANTS, APPARENT IONIZATION CONSTANTS (25.0 ± 0.1°) AND DIPHENYLDIAZOMETHANE REACTION RATE CONSTANTS (30 ± 0.1°) OF SUBSTITUTED PHENYLPROPIOLIC ACIDS AND ALKALINE SAPONIFICATION RATE CONSTANTS (20.0 ± 0.1°) OF SUBSTITUTED ETHYL PHENYLPROPIOLATES

Substituent	M.p., °C. Acid	Lit.	M.p., °C. Ethyl ester	Lit.	Half point[a]	Av. dev.	Av. $K \times 10^4$ [b]	Av. k_2, l./mole-min., ethanol[c]	Av. dev.	Av. k_2, l./mole-min., dioxane[d]	Av. dev.	k_2, l./mole-min. ester hydrolysis[e]
None	137.5	135–136[f]	102–105 (3–4 mm.)[g] (1.5521)[h]	....	3.58	0.02	2.63	19.6	0.5	3.32	0.05	0.48
2-Cl	133–135	131–132[i] 132.7–133.8[j]	121–126 (4–5 mm.)[g] (1.5599)[h]	....	3.51	.01	3.09	23.4	.3	5.64	.05	3.4
3-Cl	148–149	140–141[k] 144.3–145.1[j]	153 (7 mm.)[g] (1.5600)[h]	....	3.43	.01	3.64	25.6	.4	6.34	.02	3.3
4-Cl	193–195[l]	147[i] 192–193[j]	43–44[m]	....	3.47	.01	3.39	21.8	.4	5.25	.02	3.6
2-NO_2	163–164	166 dec.[n] 160.5–161.0[j]	60–62	60–61[o] 57.3–58.1[j]	3.39	.01	4.08	29.7	.4	10.5	.15	12
3-NO_2	143–143.5	143[p] 143.7–144.4[j]	.....	....	3.28	.01	5.25	33.3	.5	14.0	.05	...
4-NO_2	206–208	200–201[q] 204–205 dec.[j]	125–126	126[r] 123.0–123.8[j]	3.26	.02	5.50	32.5	.5	18.9	.33	19

[a] Reading on *p*H scale of *p*H meter calibrated for aqueous buffer solutions at half-neutralization point in 50% ethanol–50% water (by volume), using glass and saturated calomel electrodes without correction for liquid junction potentials. [b] Calculated assuming unit activities and readings of *p*H meter scale to be equal to reciprocal of hydrogen ion concentration. [c] Reaction rate constants for acids with diphenyldiazomethane in 100% ethanol by procedure of Ref. 5 and 6. [d] Same in 100% dioxane. [e] Ester saponification rate constants in 87.83% ethanol–12.17% water (by weight) using the procedure of Kindler.[7] The starting NaOH and ester concentrations were equal and about 0.022 *M*. At least ten points were taken in each run and each compound was run in duplicate. The rate constants were obtained by least-squares fits to plots of $(a - x)^{-1}$ against *t*. [f] T. W. Abbott, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 515. [g] Boiling point at indicated pressure. [h] $n^{25}D$ [i] C. J. Wilson and H. H. Wenzke, THIS JOURNAL, **57**, 1265 (1935). [j] Newman and Merrill.[9] [k] M. M. Otto, THIS JOURNAL, **56**, 1393 (1934). [l] In view of the discrepancy in lit. m.p., the assigned structure was established by analysis (*Anal.* Calcd. for $C_9H_5O_2Cl$: C, 60.00; H, 2.79. Found: C, 60.12; H, 2.98) and decarboxylation through heating with 5% aqueous cupric acetate in a sealed tube at 130° for four hours. The resulting *p*-chlorophenylacetylene had m.p. 44.8–45.4° (lit. 45.3–46.1°; T. H. Vaughan and J. A. Nieuwland, *ibid.*, **56**, 1207 (1934)). [m] *Anal.* Calcd. for $C_{11}H_9O_2Cl$: C, 63.32; H, 4.35; Cl, 17.0. Found: C, 63.12; H, 4.40; Cl, 17.09. [n] K. Schofield and J. C. E. Simpson, *J. Chem. Soc.*, 512 (1945). [o] A. Baeyer, *Ber.*, **13**, 2254 (1880). [p] S. Reich and S. Koehler, *Ber.*, **46**, 3727 (1913). [q] S. Reich, *Compt. rend.*, **162**, 129 (1916). [r] V. B. Drewson, *Ann.*, **212**, 150 (1882).

have been made by Newman and Merrill[9] for acid-catalyzed esterifications of *o*-substituted phenylpropiolic acids.

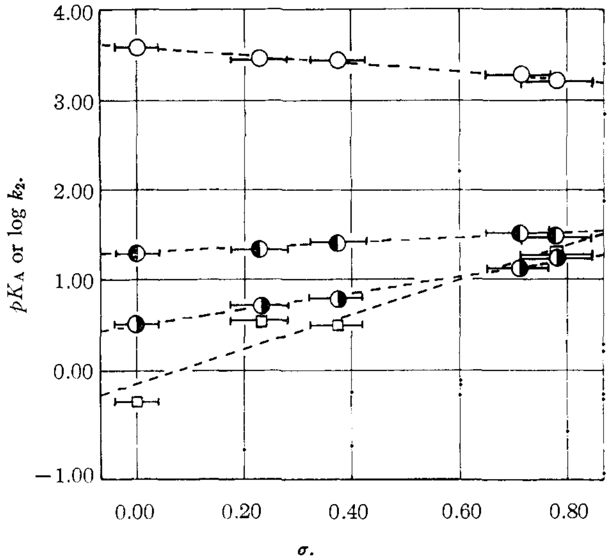

Fig. 1.—Relationship between reactivity data for *m*- and *p*-substituted phenylpropiolic acids and Hammett's σ-constants: ○, apparent pK_A (50% ethanol–water); ◐, log k_2 (diphenyldiazomethane, ethanol); ◑, log k_2 (diphenyldiazomethane, dioxane); □, log k_2 (ester hydrolysis, aqueous ethanol).

TABLE II

REACTION CONSTANTS FOR SUBSTITUTED PHENYLPROPIOLIC ACIDS AND ESTERS[a]

Reaction	log k° [b]	ρ	r	n
1. E. Ionization of phenylpropiolic acids, 50% ethanol–water, 25°	−3.57	+0.41	0.02	5
2. R. Diphenyldiazomethane with phenylpropiolic acids, ethanol, 30°	1.286	+ .31	.05	5
3. R. Diphenyldiazomethane with phenylpropiolic acids, dioxane, 30°	0.498	+ .95	.03	5
4. R. Alkaline hydrolysis of ethyl phenylpropiolates, 87.83% ethanol, 20°	−0.149	+1.91	.07	4

[a] The data are presented in the form used by Hammett.[8] [b] The log k° values are those obtained from the least-squares fits of the data in Fig. 1.

The order of acidities or reactivities of the nitro- and chloro-substituted phenylpropiolic acids would be $o > m > p > H$ if only the inductive effect were operating. If the field effect were the only important electrical effect of a dipolar substituent, then one would expect $m \sim p > H > o$. In connection with the latter order it is considered that the larger value of θ for a substituent at the *m*-position tends to partly compensate for the larger *r* of a similar substituent at the *p*-position. A small resonance influence also can be postulated which would be acid-enhancing for the nitro group and acid-weak-

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(9) M. S. Newman and S. H. Merrill, THIS JOURNAL, **76**, 5552 (1955).

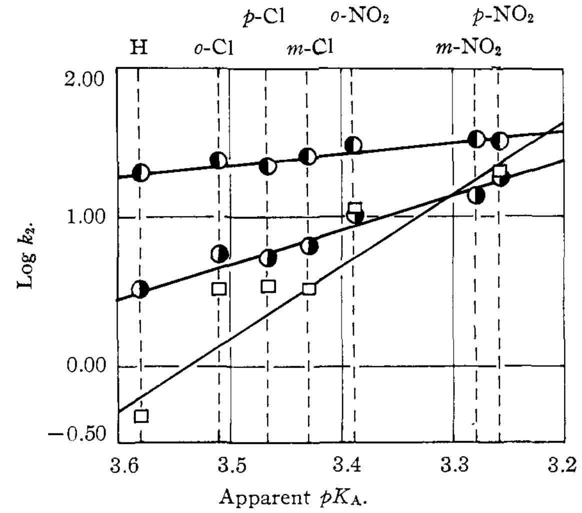

Fig. 2.—Relationship between apparent pK_A values of o-, m- and p-substituted phenylpropiolic acids and other reactivity data: ◐, log k_2 (diphenyldiazomethane, ethanol); ◑, log k_2 (diphenyldiazomethane, dioxane); □, log k_2 (ester hydrolysis, aqueous ethanol).

ening for chlorine in the order $o \sim p^{10} > m$. Steric inhibition of resonance of the o-nitro group appears unlikely for o-nitrophenylpropiolic acid since Fisher–Hirschfelder models indicate no interference between the $-NO_2$ group and the acetylene side-chain (Fig. 3). The previous comparison[2] between reactivities in aromatic and saturated systems indicates that resonance effects with nitro and chlorine substituents should be much smaller than the combined inductive and field effects, but sufficient to produce the acidity order $p > m$ for nitro-substituted acids and sufficient to accentuate the order $m > p$ expected for chlorine-substituted acids.

The experimental orders of acidities and diphenyldiazomethane reactivities are $m > p > o >$ H for chlorine and $p > m > o >$ H for $-NO_2$. In the first approximation, these orders clearly indicate that the inductive effect is of comparable importance to the field effect. The exact balance between the two influences cannot be readily assessed because of uncertainties regarding the location in space of the proton of the carboxyl group with concomitant uncertainty in θ and r. It would not be fair to take the order $o >$ H to indicate a general greater importance of the inductive effect because θ in the compounds investigated is only slightly greater than 90°. With a substance like I, where θ would be almost 180°, a much better evaluation should be possible.

It has been pointed out to us by Professor F. H. Westheimer that the magnitudes of the electrostatic effects for the m,p-substituted acids relative to those for the o-substituted acids might be quite different than expected from considerations of θ alone. This possibility arises because the electrostatic potentials produced by the outer ends of o-substituent dipoles are expected to operate more through the solvent with its higher dielectric constant than the potentials of the inner ends which are buried in the low-dielectric cavities defined by the hydrocarbon portion of the molecules. With m,p-substituted acids, both ends of the substituent dipoles should operate more along the axes of the molecules. This complication with o-substituents may not be very important in practice since the data of Table I show that the diphenyldiazomethane reactivity sequences are not greatly altered by the solvent change from ethanol (D = 24) to dioxane (D = 2). In dioxane, the internal and external dielectric constants should be nearly the same and the relative magnitudes of the field and inductive effects should crudely approximate those for the vapor state.

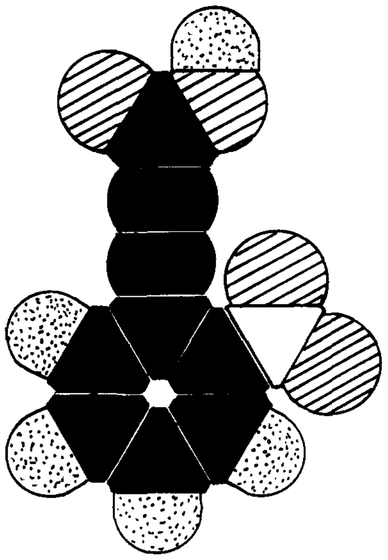

Fig. 3.—Fisher–Hirschfelder model of planar o-nitrophenylpropiolic acid.

As mentioned earlier, the reactivities of the o-chloro and o-nitro derivatives in esterification of phenylpropiolic acids[9] and hydrolysis of ethyl phenylpropiolates are greater than expected from the acid ionization constants (*cf.* Table II and Newman and Merrill[9]). This is easily accounted for if the field effect is considered to be reasonably important. In the first place, Hammett's relationship necessarily depends on a relatively constant balance between the field and inductive effects for different kinds of reaction centers. An approximately constant balance of these effects will be most easily achieved when the substituents are in the m- and p-positions since the values of cos θ for m,p-substituents are nearly unity and the field and inductive effects operate in the *same* direction. With a dipolar o-substituent such as chlorine, cos θ will change from about +0.7 for a reaction directly on the ring to about −0.2 for ionization of a phenylpropiolic acid. Clearly, the σ-value of an o-substituent should vary markedly as the reaction site-ring distance is increased and the balance shifts between the inductive and field effects. In esterification and hydrolysis of phenylpropiolic acid derivatives, the rate-determining steps involve attack of a nucleophilic agent at the carbonyl carbon and each will be speeded by electron-attracting groups (ir-

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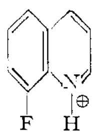
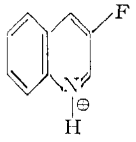
(10) The assignment of roughly equal resonance effects to the o- and p-positions is supported by simple molecular orbital calculations of charge distributions in benzene derivatives. See J. D. Roberts and D. Semenow, THIS JOURNAL, **77**, 3152 (1955) for some recent examples and references.

respective of ρ for the over-all reactions). The effect of *o*-substituents will be larger than expected on the basis of acid ionization constants because the reactive centers involved in the rate-determining steps are one carbon atom along the chains closer to the ring and cos θ for a group like *o*-Cl will have a value of about -0.1 as compared to about -0.2 for the acid ionizations. It is possible that part of the proximity effect discussed by Hammett[8] for *o*-substituents may be regarded as the result of changing balances between field and inductive effects.

A comparable influence of field and inductive effects can be employed to explain reactivities in some other systems. Thus the conjugate acid of 8-fluoroquinoline (IX, $pK_a = 3.08$) is a stronger acid than the conjugate acid of quinoline ($pK_A = 4.69$) but substantially weaker than the conjugate acid of 3-fluoroquinoline (X, $pK_A = 2.36$).[11] The value of cos θ for IX should be almost 0 and about $+0.8$ for X.


IX


X

Studies of the reactivities of some other "horseshoe"-type compounds are in progress.

ADDED IN PROOF.—In a recent paper, D. H. McDaniel and H. C. Brown, THIS JOURNAL, **77**, 3756 (1955), approach the effect of *o*-substituents in aromatic systems by an attempted calibration of *o*-electrical effects from studies of basicities of 2-substituted pyridines. The procedure would seem invalid because of (1) the large difference in θ in the change from a 2-substituted pyridine to an *o*-substituted benzoic acid and (2) the concomitant attenuation of the short-range inductive effect which appears to operate strongly only at the position immediately adjacent to the substituent; *cf.* also G. E. Hall, R. Piccolini and J. D. Roberts, *ibid.*, **77**, 4540 (1955).

CAMBRIDGE 39, MASS.

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[11] W. K. Miller, S. B. Knight and A. Roe, *ibid.*, **72**, 4763 (1950).

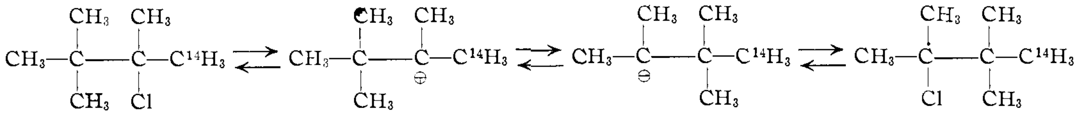
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Rearrangements in Carbonium-ion Type Reactions of C^{14}-Labeled Pentamethylethanol (2,3,3-Trimethyl-2-butanol-1-C^{14})[1]

BY JOHN D. ROBERTS[2] AND JOEL A. YANCEY

RECEIVED MAY 9, 1955

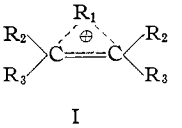
Treatment of 2,3,3-trimethyl-2-butanol-1-C^{14} with concentrated hydrochloric acid and zinc chloride (Lucas reagent) yielded 2-chloro-2,3,3-trimethylbutane with the C^{14} distributed essentially equally among the five methyl groups. Under the conditions used, the aliphatic chloride equilibrated completely with Lucas reagent containing radioactive chloride ion. The rearrangement and chloride exchange may be accounted for by the following equilibria involving solvated carbonium ions.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{Cl}{C}}-C^{14}H_3 \rightleftarrows CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{\oplus}{C}}-C^{14}H_3 \rightleftarrows CH_3-\overset{CH_3}{\underset{\oplus}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-C^{14}H_3 \rightleftarrows CH_3-\overset{CH_3}{\underset{Cl}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-C^{14}H_3$$

Treatment of 2,3,3-trimethyl-2-butanol-1-C^{14} with concentrated hydrochloric acid at 25° for 20 minutes and 0° for one minute gave 36% and 12–16% of methyl group rearrangement, respectively. At 0° and one minute, the reaction was essentially irreversible since chloride exchange between the aliphatic chloride and radioactive concentrated hydrochloric acid was negligible. Hydrolysis of 2-chloro-2,3,3-trimethyl-2-butane by shaking with water at room temperature gave no additional methyl group rearrangement. It is concluded that the non-classical cationic intermediate VIII is not an important intermediate in *irreversible* carbonium ion type reactions of pentamethylethyl derivatives ina queous solution and that such an intermediate is unlikely to be as stable as the classical cations shown in the equations above.

A large part of our program of research[3] on carbonium-ion type reactions has been devoted to elucidation of the structural and environmental factors which are important for the occurrence of non-classical cationic intermediates of the "ethyleneonium" variety I. Very substantial progress toward similar objectives has been made, principally by Winstein,[4] Cram,[5] Collins[6] and their co-workers, using reaction rate and stereochemical techniques. Non-classical cationic intermediates of one variety


I

II, $R_1 = C_6H_5$; $R_2 = H$; $R_3 = CH_3$
IV,[3f] $R_1 = H$; $R_2, R_3 = H$
V,[3d] $R_1 = H$; $R_2 = CH_3$; $R_3 = H$
VI,[3g] $R_1 = C_6H_5$; $R_2, R_3 = H$
VII,[3i] $R_1 = CH_3$: $R_2, R_3 = H$
VIII, $R_1 = CH_3$; $R_2, R_3 = CH_3$

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[1] Supported in part by the joint program of research of the Office of Naval Research and the U. S. Atomic Energy Commission. Presented at the Symposium on Reaction Mechanisms at the 75th Anniversary of the American Chemical Society, September 13, 1951.

[2] Gates and Crellin Laboratories, California Insitute of Technology, Pasadena 4, Calif.

[3] (a) J. D. Roberts, R. E. McMahon and J. S. Hine, THIS JOURNAL, **72**, 4237 (1950); (b) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951); (c) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); (d) J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., *ibid.*, **74**, 4283 (1952); (e) J. D. Roberts and G. R. Coraor, *ibid.*, **74**, 3586 (1952); (f) J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5943 (1952); (g) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953); (h) J. D. Roberts and J. A. Yancey, *ibid.*, **75**, 3165 (1953); (i) J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953); (j) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); **77**, 3034 (1955).

[4] (a) As a leading reference to a number of papers see S. Winstein, C. R. Lindgren, H. Marshall and L. L. Ingraham, *ibid.*, **75**, 147 (1953); (b) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1950); **74**, 1147, 1154 (1952).

[5] *Cf.* D. J. Cram, *ibid.*, **71**, 3863 (1949); **74**, 2129, 2159 (1952); and later papers.

[6] C. J. Collins and W. Bonner, *ibid.*, **75**, 5372 (1953); **77**, 72, 99 (1955).