No.	Ph_4Pb, g.	Pb, g.	*t*, °C.	Time, hrs.	Lead, g.	Yield of diphenyl	% of decomp.	Remain. Ph_4Pb
1	1	...	255°	1	0.011	Trace	2.7	0.94
2	1	...	255°	1	Trace	None	...	.98
3	1	...	255°	2	0.0277	0.03	6.9	.92
4	1	1	245°	1	.0310	.02	7.72	.91
5	1	1	250°	1	.0580	.06	17.46	.80
6	1	1	255°	1	.2626	.38	65.48	.33

The experiment being over, the tube was opened, the diphenyl extracted with ether and after removal of the latter recrystallized from alcohol. The melting point was in all cases 69–70°.

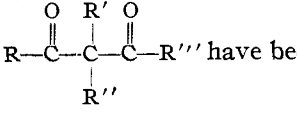
The remaining lead tetraphenyl was extracted with a mixture of benzene and xylene. After having been washed with ether, lead was determined by usual methods.

LENINGRAD, U. S. S. R. RECEIVED JANUARY 29, 1934

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

Polarity and Alcoholysis of 1,3-Diketones and β-Keto Esters

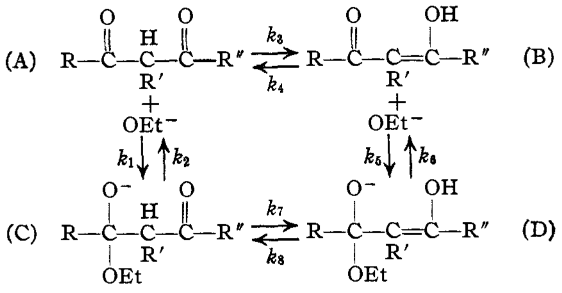
BY LELAND J. BECKHAM AND HOMER ADKINS

The experimental findings with respect to the cleavage by alcohol of a number of compounds of the type  $R—\overset{O}{\overset{\|}{C}}—\underset{R''}{\overset{R'}{C}}—\overset{O}{\overset{\|}{C}}—R'''$ have been presented in a series of papers.[1,2,3,4,5] It is now possible to rationalize many of these findings upon the basis of the polarization (I effects) and polarizability (T effects) of R, R′, R″, and R‴, due consideration being given to the number and position of the substituents and to the conditions of reaction. The discussion in this paper is based upon the ideas developed by Ingold, Robinson, Watson, Shoppee, Lapworth, Kon, Linstead, Farmer and others.[6] The terminology adopted is that originally due to Ingold.

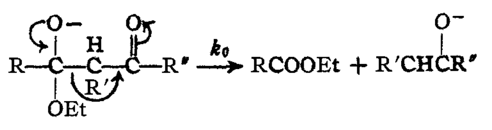
The alcoholysis of the 1,3-diketones or the β-keto esters may involve the cleavage of the dicarbonyl compounds, or of the corresponding enols which are more or less chelated. Therefore it is necessary to distinguish between the effect of substituents upon the two types of cleavage as well as upon the extent and position of enolization.

In the ensuing discussion it will be necessary to refer to the three distinctly different conditions under which the experimental results were obtained, *i. e.*, "basic alcoholysis" which occurred in the presence of a considerable quantity of sodium ethoxide at 60°; "acid alcoholysis" which took place at 60° in the presence of considerable quantities of hydrogen chloride;[1] and "high temperature alcoholysis" which occurred at 150–250° in the presence of traces of water or aluminum ethoxide.[4]

Mechanisms for the cleavage and the competitive enolization of a diketone may be outlined as follows.[7] It is suggested that A, B, C and D occur in basic solutions.[8]



(C) is presumed to be the compound which undergoes cleavage, *i. e.*,



In the presence of acid the following equilibria are established

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[1] Adkins, Kutz and Coffman, THIS JOURNAL, **52**, 3213 (1930).

[2] Kutz and Adkins, *ibid.*, **52**, 4036 (1930).

[3] Kutz and Adkins, *ibid.*, **52**, 4391 (1930).

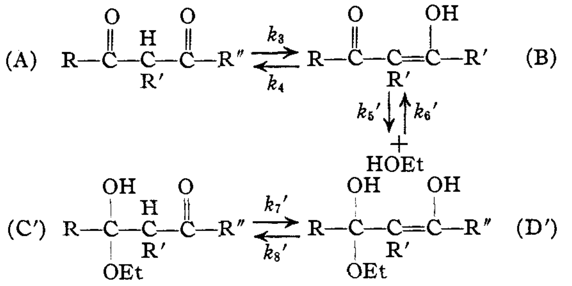
[4] Connor and Adkins, *ibid.*, **54**, 3420 (1932).

[5] Isbell, Wojcik and Adkins, *ibid.*, **54**, 3678 (1932).

[6] (a) Ingold and Ingold, *J. Chem. Soc.*, 2359 (1931); (b) Ingold, *ibid.*, 1120 (1933); (c) Watson and Yates, *ibid.*, 220 (1933); (d) Shoppee, *ibid.*, 968 (1930); (e) *ibid.*, 1117 (1933); (f) Robinson, *ibid.*, 1114 (1933); (g) "Outline of an Electrochemical Theory of the Course of Organic Reactions," The Institute of Chemistry, Great Britain and Ireland, London, 1932.

[7] *Cf.* Bradley and Robinson, *J. Chem. Soc.*, **129**, 2359 (1926).

[8] Compounds B and D as here employed are intended to cover not only the enol form shown but also the corresponding ions and sodium salts, which are present in basic solution. Addition is assumed to take place in every case on the unenolized side of the diketone and is consequently more or less independent of the condition at the other end of the molecule. The fact that alcohol does not add to ketones to any considerable extent indicates that the addition product D is present in much lower concentrations than B (including of course ion and sodium salt). A and C are present in small concentration as would be expected from the concentration of D and the high tendency to enolize in the presence of NaOEt. Consequently the species B may be taken as the predominant species, equal approximately to the total concentration of all forms present.

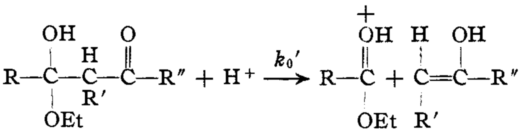


$$\text{(A)}\ R-\overset{O}{\overset{\|}{C}}-\underset{R'}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-R'' \underset{k_4}{\overset{k_3}{\rightleftarrows}} R-\overset{O}{\overset{\|}{C}}-\underset{R'}{C}=\overset{OH}{\overset{|}{C}}-R'\ \text{(B)}$$

$$k_5' \downarrow \uparrow k_6' \quad + \text{HOEt}$$

$$\text{(C}')\ R-\underset{OEt}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{R'}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-R'' \underset{k_8'}{\overset{k_7'}{\rightleftarrows}} R-\underset{OEt}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{R'}{C}=\overset{OH}{\overset{|}{C}}-R''\ \text{(D}')$$

Equilibrium is established between A and C′ through B and D′ as intermediates and not directly as is the case in the presence of a base. This is presumably due to the difficulty of rapid direct addition of the comparatively neutral ethanol without some additional activating influence furnished by the enol form, supposedly its chelation.[9] C′ is the form undergoing cleavage, and this reaction is the master reaction



$$R-\underset{OEt}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\underset{R'}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-R'' + H^+ \xrightarrow{k_0'} R-\underset{OEt}{\underset{|}{\overset{\overset{+}{OH}}{\overset{\|}{C}}}} + \underset{R'}{\underset{|}{\overset{H}{\overset{|}{C}}}}=\overset{OH}{\overset{|}{C}}-R''$$

The "high temperature cleavage" involves a combination of the basic and acidic mechanism, and since it is more complicated and does not involve any new concepts is not treated in detail in this paper. The conclusions are very similar to those discussed for the other two, however.

The question now arises as to the effect of a given substituent having a ±I or a ±T effect upon the rates (actual or relative) of the transformations suggested above. This question is most simply answered by a mathematical analysis of the rates of change in the schemes suggested. Three assumptions are introduced in the analysis: 1. The speed of the cleavage reaction is slow as compared to the enolization and addition so that an equilibrium is established between each adjacent pair of compounds. 2. A variation of substituents, R, R′, R″ will have a proportionate effect on (a) the rate of addition to, and the interconversion of, the keto and enol forms; (b) the rates of enolization and cleavage.[10] 3. A variation of substituents, R, R′ and R″ will have but little effect upon coördination of the proton, as compared to the addition of OEt^-.[11]

The rate of cleavage of unsubstituted and monosubstituted 1,3-dicarbonyl compounds in the basic cleavage: by assumption 2:

$$k_5 = c_1k_1$$
$$k_6 = c_2k_2$$
$$k_7 = c_0k_0$$

$$\text{Velocity of basic cleavage } k_0\ (C) = \frac{k_0k_8}{k_7}\ (D) = \frac{k_0k_8k_5}{k_7k_6}$$
$$(B)\ (OEt) = \frac{c_1k_1k_8}{c_0c_2k_2}\ (B)\ (OEt^-) = \alpha\ \frac{k_1k_8}{k_2}\ (\text{ketone})\ (OEt^-)$$

where α = a constant = c_1/c_0c_2

B ≅ concentration of predominant molecular species in basic solution.

k_1 is dependent upon the electrical positivity of carbonyl carbon and consequently is favored by −I, −T and hindered by +I; k_2 upon the electrical negativity of carbonyl carbon, favored by +I, +T, and hindered by −I; k_8 upon the negativity of methylene carbon, favored by +I and hindered by −I; and k_0 upon the positivity of methylene carbon, favored by −I and hindered by +I.

The rate of cleavage of disubstituted 1,3-dicarbonyl compounds in the basic cleavage: for the special case of disubstitution an entirely different situation exists. In this case A is the predominant molecular species present in the solution.

$$\text{Velocity of cleavage} = k_0c = \frac{k_0k_1}{k_2}\ (AOEt^-) = \frac{k_0k_1}{k_2}\ (\text{ketone})\ (OEt^-)$$

A ≅ concentration of predominant molecular species.

The rate of cleavage of 1,3-dicarbonyl compounds in the acidic cleavage: in the case of the acidic cleavage, it is not possible to express the rate in terms of a predominant species for in most cases none exist, but both keto and enol forms are

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[9] The assumed mechanism of the addition of HOEt to B is first the coördination of a H^+ at carbonyl carbon followed by the reaction of this active complex with HOEt to give D with the elimination of H^+. D′ and C′ are present in small concentration as compared to A and B which are both present in large amounts. B (including B itself and the corresponding coördination complex with H^+) represents thus approximately the total concentration of the enolized part of the diketone which is present in solution.

[10] These follow from the similarity of the reactions and the nature of the I effects. It seems reasonable to assume that two reactions involving similar displacements of electrons and consequently affected by substituents exhibiting the same influence should both be changed in a similar manner by a variation in the magnitude of the influence exerted by the substituent. Consequently when these two reaction rates occur in both numerator and denominator of an expression they must compensate each other to a great degree. For convenience in the mathematical analysis they are set as directly proportional, although obviously this is not strictly true.

[11] This assumption which applies only to the acid alcoholysis is justified because addition of OEt occurs at carbonyl carbon to which the substituent group is attached and is consequently more influenced by the nature of this substituent than the addition of H^+ which occurs at carbonyl oxygen, one atom further removed. This is merely an assumption regarding the lesser magnitude of the I effects after transmission through an intervening atom and not of the influence of a group in attracting or repelling a given reactant. On the basis of this assumption then the rate of the addition of alcohol to the diketone (the mechanism of which involves first the addition of hydrogen, and second reaction with ethanol) will, with a variation of substituents, depend upon the effect which the substituents exert upon the addition of ethanol to the complex and not with their effect on the preliminary coördination of the proton.

present in large amounts. In this case the rate is expressed in terms of the per cent. enol (B). As B is not equal to the total concentration of all forms present, it changes with a variation of R, R′ and R″. This change is, however, experimentally available as a result of the knowledge of the extent of enolization.

By assumption 2:

$$k_7' = c_0'k_0'$$

$$\text{Velocity of cleavage} = k_0'(\text{H}^+)(\text{C}') = \frac{k_0'k_8'}{k_7'}(\text{H}^+)(\text{D}')$$

$$= \frac{k_0'k_8'k_5'}{k_7'k_6'}(\text{H}^+)(\text{B})(\text{HOEt}) = \frac{k_8'k_5'}{c_0'k_6'}(\text{H}^+)(\text{B})(\text{HOEt})$$

$$= \alpha'\frac{k_8'k_5'}{k_6'}(\%\ \text{enol})\ (\text{H}^+)(\text{HOEt})$$

$\alpha' = 1/c_0'$ = a constant

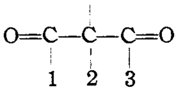
B $\cong$ concentration of all enolized forms present.

k_6' and k_8' are influenced by the same factors as k_2 and k_8, respectively. k_5' in this case is dependent primarily on the permanent positivity of the carbonyl carbon[12] and consequently favored by −I and hindered by +I and +T effects, the +T effects being especially harmful.

The conclusions with respect to the influence of groups of various polarities upon the cleavage of the system under consideration are listed in Table I, due consideration being given to the number of factors into which a given effect enters, its relative importance in that factor and the relation of the position of the substituent with respect to the point of reaction.

TABLE I

I AND T EFFECTS IN ACCELERATING (+) OR RETARDING (−) CLEAVAGE BETWEEN CARBONS 1 AND 2 IN THE SYSTEM



$$\text{O=C—C—C=O}$$

Substituent → Location → ↓ Polarity	C_1	C_2 (R and H)	C_2 (2R)	C_3
Basic cleavage				
−I	+	−	+	+[a]
+I	−	+	−	−[a]
+T	−[a]			−[a]
−T	+			+[a]
Acidic cleavage				
−I	+[c]	−		+[a]
+I	−[c]	+		−[a]
+T	−[b]			−
−T	+			+[a]

[a] Relatively less important; [b] most important of the effects; [c] more important in enol than in keto cleavage.

Upon the basis of the mechanism discussed and the conclusions recorded in Table I, it will be necessary in order to predict the course of the reactions to know the electrical effects of R, R′, R″ and R‴, and the extent and direction of enolization. A series of groups arranged in order of decreasing I effects is: t-C$_4$H$_9$, 2.2; s-C$_4$H$_9$, 2.1; n-C$_4$H$_9$, 2.0; CH$_3$, 1.5; C$_6$H$_5$CH$_2$, 0.0; H, 0.0; C$_6$H$_5$, 0.0; —CH$_2$CH$_2$COOEt (?); —CH$_2$CO$_2$Et (?); COO$^-$, −0.9; —OCH$_3$, −1.2; —OH, −1.7; —CO$_2$Et, −1.3; —CHO, −2.7; CH$_3$CO, −2.9.[13] Shoppee[6] gives a similar series for T effects where groups before CH$_3$ are +T and those after it are —T, *e. g.*, —O$^-$, —NR$_2$, —OR, —CH$_3$, —COO$^-$, —CONR$_2$, —COOEt, CH$_3$CO. The C$_6$H$_5$— group has both ±T effects.

The conclusions reached as above will now be applied to the experimental observations on the alcoholysis of 1,3-diketones and β-keto esters. The experimental results will be stated, followed by the rationalization.

1. The substitution of an alkyl group for H on the methylene carbon atom increased the rate of cleavage of the diketone or keto ester in basic solution or in the high temperature cleavage.[3,4,5] For example, under similar conditions, diacetylmethane underwent 8% reaction, whereas the monoethyl derivative underwent 19% reaction. The direction and extent of enolization is immaterial in the alkaline cleavage for symmetrical compounds. By a reference to Table I it is observed that one alkyl group should favor cleavage by virtue of its +I effect.

2. The substitution of two alkyl groups on the methylene carbon atom increased the rate of basic cleavage as compared to the monosubstitution product.[3] In this case the competing side reaction (enolization) is entirely eliminated, so that the basic cleavage will occur more rapidly.

3. The substitution of one alkyl group for a H of the methylene carbon atom decreased the rate of acidic split.[1] As a particular example, diacetylmethane underwent 58% reaction under conditions where the mono ethyl derivative underwent 37% cleavage. In acid solution the extent

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[12] By assumption 3, substituents influence k_5' by their influence on the addition of ethanol to the complex. This reaction only takes place readily when there is sufficient activation to give a large permanent charge to the carbonyl atom to which the ethanol is to add. Consequently any groups allowing a dissipation of this charge are especially harmful.

[13] These values (10^{-18} E. S. U.) are values for the corresponding dipole moments. They are taken from Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Company, New York, 1931. The values for the alkyl groups are the values of the bromides and the others from substituted benzenes.

of enolization is one of the factors in the rate of cleavage. Diacetylmethane contains 83% enol, and ethyldiacetylmethane 28%. Thus, if we calculate to a constant enol basis, we find that ethyldiacetylmethane underwent reaction 1.9 as fast as diacetylmethane. On the basis of the mechanism postulated, the results calculated to a constant enol content for the acid mechanism should correspond with the basic results. Thus the 1.9 ratio is approximately in accord with the 2.4 ratio of rates in basic solution.

4. Dialkyl derivatives cleaved more slowly in acid or high temperature alcoholysis than did unsubstituted or monosubstituted diketones and keto esters.[1,4] This corresponds to the fact that enolization upon which acid cleavage depends is impossible under such conditions.

The analysis in sections 1 to 4 above makes it clear why *if a series of diketones is arranged in the order of decreasing ease of acid alcoholysis, it will be found that they have been arranged in general in the order of increasing ease of alkaline alcoholysis.*

5. Acetoacetic ester did not undergo acid alcoholysis under conditions which cleaved diacetylmethane rapidly,[1] and malonic ester was more stable to high temperature alcoholysis than was acetoacetic ester. In the presence of sodium ethoxide diacetylmethane underwent alkaline alcoholysis two to three times as rapidly as acetoacetic ester and considerably higher temperatures were necessary for the cleavage of acetoacetic ester in the absence of a catalyst.[4]

Acetoacetic ester is only slightly enolized and the OEt group dissipates the charge due to its +T effect. Therefore it should cleave with difficulty as compared to diacetylmethane in acid solution or at moderate temperatures without a catalyst. The retarding effect of a +T group is less important in basic solution and the rate does not depend upon the percentage enol (Table I). Therefore it should slow the rate of alkaline alcoholysis but not nearly as much as the relative effect in acid, and should require a higher temperature for cleavage without a catalyst. The same explanation may be offered for the greater stability of malonic as contrasted with acetoacetic ester since the malonic has two rather than one OEt group with its stabilizing +T effect.

6. Substitution of C_6H_5 for CH_3 in diacetylmethane to form acetylbenzoylmethane lowered the rate of acidic cleavage,[1] but did not affect relative basic rate.[3] The two phenyl groups in dibenzoylmethane stopped acidic cleavage and increased basic cleavage. The methyl group exerts a weak (+I) effect and the phenyl group both +T and −T effects. Notwithstanding the fact that the introduction of a phenyl group raises the extent of enolization from 80 to 100% the introduction of the +T effect which this group may exhibit will be more important than the −T effect in the acid mechanism (see Table I) and thus slow the rate of acid split. Two such groups should have a correspondingly greater effect. The relative rates of the basic alcoholysis of acetylbenzoylmethane and diacetylmethane cannot be predicted, the relative magnitude of the + and −T effects being unknown in the basic mechanism. But as effects at carbon 3 are small, and if they are approximately equal, no great change would be expected in the cleavage rate. On the other hand, the introduction of the second phenyl group at carbon 1 will facilitate cleavage by virtue of its −T effect, which is of greater importance than the +T effect in this position. Thus the rate of alcoholysis of dibenzoylmethane should be greater than acetylbenzoylmethane in alkaline solution.

The direction and extent of enolization[14] apparently accounts for the cleavage of CH_3–CO–CH_2–CO–R (R equals phenyl, furyl, or a higher alkyl) entirely or primarily at the bond on the acetyl group, the cleavage occurring on the unenolized side of the diketone. The compounds where R is a primary group cleave more rapidly in acid than those with a secondary or tertiary alkyl because the former are more enolized.

7. α-Ethylacetoacetic ester underwent alkaline alcoholysis more rapidly than α-benzylacetoacetic ester, but the α,α-dibenzylacetoacetic ester underwent cleavage more rapidly than the α,α-diethylacetoacetic ester.[3] Ethyl has a greater +I effect than benzyl. Application of the conclusions in Table I shows that the ester possessing the substituent with greater +I should cleave more rapidly in the case of monosubstitution and less rapidly in the case of disubstitution. *Thus is verified a surprising conclusion recorded in Table I, i. e., that one +I group on the middle carbon is more favorable to cleavage while −I groups are more favorable if there are two substituents.* The conclusion is also verified by a comparison of the rates of alcoholysis of mono- and diacylsuccinic and glutaric esters.

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(14) Weygand and Baumgartel, *Ber.*, **62B**, 574 (1929).

8. The I effects discussed in the preceding sections are greater the longer the chain or the more branched the alkyl. Thus on a constant enol basis the order of rates of acid alcoholysis for a series of diacetylmethane derivatives is: i-C_3H_7, n-C_4H_9, n-C_3H_7, C_2H_5, $C_6H_5CH_2$. This is also the order of polarity (+I). The cyclohexyl group has a +I effect like the alkyl groups and so has a similar effect, very different from the ±T of the phenyl group.

9. Monoacylglutaric esters underwent acid alcoholysis more rapidly than the corresponding succinates.[5] This is presumably due to the greater −I of the —CH_2COOEt in the succinate as compared to the —CH_3CH_2COOEt in the glutarate.

10. Acetyl trimethylacetylglutaric ester was more resistant to alcoholysis than the acetyl n-butyrylglutaric ester for the stronger +I effect of the t-butyl group decreased the rate of cleavage. The ratio of the cleavage products was more favorable to acetyl cleavage in the case of the normal compound, the actual amount of the acetyl cleavage being almost the same. This is due to the +I effect of the branched chain slowing the cleavage adjacent to that group but having only a slight slowing effect on the cleavage at the other end.

11. The proportion of acetyl cleavage was lower for the diacylglutarates than for the diacylsuccinates. The comparison is between the addition reactions (1) to the acetyl carbonyl carbon, and (2) to the other acyl carbonyl carbon. (1) is a faster reaction than (2); therefore if the product is removed faster, the disturbing influence will be greatest on the equilibrium which is maintained most slowly (2), thus the concentration of the addition product in this case is lowered and the reaction slowed relative to the competing reaction. Therefore the succinic ester which cleaves faster should have the greater percentage of acetyl cleavage.

Summary

Mechanisms have been suggested for the alcoholysis of 1,3-dicarbonyl compounds in acid and basic solutions. The polarization and the polarizability of different groups have been discussed in relation to the suggested mechanism. A correlation of the experimental work on the alcoholysis of 1,3-dicarbonyl compounds in this Laboratory has been made upon the basis of these concepts.

MADISON, WISCONSIN RECEIVED NOVEMBER 1, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Aromaticities. IV. Furyl-Alkali Compounds[1]

BY HENRY GILMAN AND FRITZ BREUER[2]

Introduction

The pronounced tendency of furan to undergo α-nuclear substitution reactions[3] has been advanced as one of a number of reactions in support of the thesis that furan has super-aromatic properties. The facility of such substitution is not confined to the use of acidic reagents, for it is now shown that furan undergoes nuclear substitution by metals under conditions where benzene, a typical aromatic compound, is unaffected.

Schorigin[4] showed that simple saturated aliphatic hydrocarbons underwent no reaction with sodium and that ethylsodium reacted with benzene to give phenylsodium and ethane. Inasmuch as both ethylsodium and phenylsodium react with furan to give 2-furylsodium, the order of decreasing ease of substitution by sodium is: $C_4H_4O > C_6H_6 > C_2H_6$. This order of relative aromaticities is also shown by other studies such as the electronegativities of the radicals as determined by hydrogen chloride scission of organolead compounds and the ionization constants of the corresponding carboxylic acids. The correlation of organo-alkali formation (by replacement of hydrogen by sodium or potassium) with negativity series has not been settled. For example, triphenylmethane with potassium gives triphenylmethylpotassium [$(C_6H_5)_3CK$] under conditions where benzene undergoes no reaction.[5] On such a basis, the triphenylmethyl radical may be considered more negative than the phenyl radical. However, this reaction has been interpreted

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[1] The preceding paper in this series, THIS JOURNAL, **56**, 464 (1934).

[2] Austro-American Exchange Fellow.

[3] Gilman and Wright, *Chem. Reviews*, **11**, 323 (1932).

[4] Schorigin, *Ber.*, **41**, 2711, 2723 (1908); **43**, 1938 (1910).

[5] Wooster and Mitchell, THIS JOURNAL, **52**, 688 (1930).