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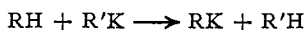
## THE STUDY OF EXTREMELY WEAK ACIDS

By J. B. CONANT AND G. W. WHELAND

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The purpose of this paper is to make a preliminary exploration of the possibility of a quantitative study of such extremely weak acids as enols, alcohols, derivatives of ammonia and phenylated hydrocarbons. It is well known that all these substances form salt-like sodium and potassium derivatives and that to some extent, at least, reactions of the following type take place in absolute ether



Following Brönsted's definition of an acid and base, we may regard the hydrogen compounds as very weak acids and the ions of the metallic derivatives as extremely strong bases. In principle there is little to distinguish the interaction of acetic acid and sodium phenolate in water from the action of triphenylmethane and  $(CH_3)_2CKC_6H_5$  in absolute ether.

Although the acidic properties of the phenylated hydrocarbons and similar substances have been often discussed, the possibility of comparing the strengths of a number of such extremely weak acids does not seem to have been considered except in the recent paper of Wooster and Mitchell<sup>1</sup> which concerns reactions in liquid ammonia. Leaving aside the possibility of applying an electrochemical method, it is clear that a scale of acids of increasing strength could be prepared by studying metathetical reactions between salts and acids provided the degree of dissociation of all the salts is approximately the same. It would only be necessary to determine whether a reaction of the type given above proceeded from right to left or *vice versa* with each pair of acid and salt. Considerable information of this sort is already available. For example, the action of sodium ethyl on toluene produces sodium benzyl, which in turn gives up its sodium to diphenylmethane;<sup>2</sup> the acid strengths are thus  $(C_6H_5)_2CH_2 > C_6H_5CH_3 > C_2H_6$ . Wooster and Mitchell<sup>1</sup> used potassium amide in liquid ammonia to divide the weakly acidic hydrocarbons into two classes, according to whether or not the potassium compound would be stable in liquid ammonia. Recently Ziegler<sup>3</sup> has greatly increased our knowledge of organo-metallic compounds and their behavior in ether. He has studied a number of metathesis reactions particularly with potassium dimethylphenylmethyl which he showed to be the salt of a weaker acid than triphenylmethane. He has also studied the conductivity in pyridine of the potassium deriva-

<sup>1</sup> Wooster and Mitchell, *THIS JOURNAL*, 52, 688 (1930).

<sup>2</sup> Schorigin, *Ber.*, 41, 2723 (1908); Schlenk and Bergmann, *Ann.*, 464, 21 (1928).

<sup>3</sup> Ziegler, Crössman, Kleiner and Schäfer, *ibid.*, 473, 1 (1929); Ziegler and Bähr, *Ber.*, 61, 253 (1928).

tives of a few triarylmethanes.<sup>4</sup> His results tend to support the assumption that underlies the present investigation—namely, that the degree of dissociation is approximately the same for the salts of a variety of very weak acids. The conductivities in pyridine of potassium triphenylmethyl and potassium trinitrotriphenylmethyl were very similar though the acid strength of the hydrogen compounds is very different. In ether the conductivities are very much less and change in an anomalous way with dilution, but there is no reason to believe that a change in solvent would affect seriously the relative degrees of dissociation of a series of related salts. Evidence pointing in the same direction has been obtained by Bent<sup>5</sup> in his study of the electron affinity of free radicals. His results indicated that the degree of dissociation of the sodium derivatives of the triarylmethanes he studied were the same within a power of ten. The quantitative study of very weak acids in such solvents as ether is undoubtedly greatly complicated by differences in the degree of dissociation of the salts, and differences may be expected in changing the solvent from ether to pyridine or liquid ammonia. The dissociation constants of the acids are thus to be interpreted with the reservation that they are somewhat uncertain due to variations in the activity of the negative ion. It should be pointed out, however, that the same situation holds, though probably to a less serious extent, in regard to the degree of dissociation of the usual weak acids determined in water solution.<sup>6</sup> Because of the variations of the constants relative to each other in going from one solvent to another, it is doubtful whether any significance can be attached to changes of two or three-fold in the dissociation constant with changes in structure.

We have chosen to use anhydrous ether as a solvent because of the high solubility in it of almost all the hydrogen compounds and nearly all the sodium or potassium derivatives. All the experiments were performed in a dry nitrogen atmosphere, of course. In Table I are collected the results of our preliminary survey of the situation. The hydrogen compounds are listed in the first vertical column and the corresponding sodium or potassium derivatives (*i. e.*, salts) across the top. Each square summarizes our experiments with a pair of compounds; the symbols used are explained in the attached key and the experimental procedure is given in the last part of this paper. Two methods were employed for determining whether or not a pair of compounds had interacted. The first method was to observe the color of the solution. The color of a number of the metallic compounds is very characteristic (top horizontal column, Table I), and the color changes therefore give definite information. The other method was to treat the reaction mixture with dry carbon dioxide and after a short

<sup>4</sup> Ziegler and Wollschitt, *Ann.*, 479, 123 (1930).

<sup>5</sup> Bent, *THIS JOURNAL*, 52, 1498 (1930); 53, 1786 (1931).

<sup>6</sup> Halford, *ibid.*, 53, 2939, 2944 (1931).

TABLE I  
SUMMARY OF REACTIONS BETWEEN METHANE DERIVATIVES RH AND ORGANO-METALLIC COMPOUNDS (OF K OR Na) RM

	1 $\begin{array}{c} \text{CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \end{array}$	2 $\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C} \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	3 $\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C} \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	4 $\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C} \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	5 $\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C} \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	6 $\begin{array}{c} (\text{C}_6\text{H}_5)_2\text{C} \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	7 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	8 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	9 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	10 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	11 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$	12 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$
1 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{CH} \\   \\ (\text{CH}_3)_2\text{C} \end{array}$	red	red brown	orange	green	orange red	purple	orange red	yellow	orange	1. yellow	colorless	colorless
2 $(\text{C}_6\text{H}_5)_2\text{C} \cdot \text{CHCH}_3$	*K +C A	(-)	(-)	K -C	K -C A	(-)	(-)	(-)	(-)	(-)	(-)	(-)
3 $(\text{C}_6\text{H}_5)_2\text{CH}_2$	K +C A	**K +C	(-)	Na -C	Na -C	Na -C	Na -C	(-)	(-)	(-)	(-)	(-)
4 $(\text{C}_6\text{H}_5)_2\text{CH}$	K +C A	**K +C	**K +C	(-)	Na -C	Na -C	Na -C	(-)	(-)	(-)	(-)	(-)
5 $(\text{C}_6\text{H}_5)_3\text{CH}$	K +C	(-)	(-)	K D Na	(-)	Na -C	(-)	(-)	(-)	(-)	(-)	(-)
6 $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{CH}$	K +C	K +C	**Na +C A	**Na +C A	**Na +C A	(-)	(-)	(-)	(-)	(-)	(-)	(-)
7 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array} \cdot \text{CH}_2$	*K +C	(-)	(-)	**Na +C	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)
8 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array} \cdot \text{CH}_2$	(-)	(-)	(-)	K +Na +C	Na +C A	Na +C A	Na +C A	Na +A	Na -A	Na -A	Na E A	Na E A
9 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array} \cdot \text{CH}_2$	K +C	(-)	(-)	K +C	Na +C A	Na +C A	Na +C A	Na +A	Na -A	Na -A	Na E A	Na E A
10 $\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C} \\   \\ \text{C}_6\text{H}_5 \end{array} \cdot \text{CH}_2$	(-)	(-)	(-)	(-)	Na +C A	Na +C A	Na +C A	Na +A	Na -A	Na -A	Na E A	Na E A
11 $\text{C}_6\text{H}_5\text{C} \cdot \text{CH}$	(-)	(-)	(-)	Na +C	Na +C A	Na +C	Na +C	Na +A	Na -A	Na -A	Na E A	Na E A
12 $\text{C}_6\text{H}_5\text{COCH}_3$	K +C	(-)	(-)	Na K +C	Na +C	Na K +C	Na +C	Na +A	Na -A	Na -A	Na E A	Na E A

## EXPLANATION OF SYMBOLS IN TABLE

In each square is summarized the information in regard to the reaction between the methane on the left and the metallic compound at the top, in absolute ether in nitrogen; K or Na signify whether the K or Na salt (or both) was tried. The other

symbols have the following meaning: +, reaction goes essentially to completion; -, no evident reaction; E, incomplete reaction judged to be an equilibrium (the two squares joined by an arrow are the same experiment); (-), no reaction between these components since they are the products in a reaction going essentially to completion; D, decomposition instead of expected reaction; the letter C, and A, indicate whether the reaction was followed colorimetrically or by isolating the corresponding acid after treatment with carbon dioxide. In the first case a five-fold excess of hydrogen compound was employed, in the second equimolecular quantities of the reactants. Unless starred the reactions were instantaneous; the time necessary for practical completion in the other cases is noted as follows: \*, a few hours; \*\*, a few days; \*\*\*, about a month.

time treat with water and isolate the carboxylic acid in the usual manner. The reaction of all the metallic compounds (except No. 12) with carbon dioxide is very rapid. The validity of this method depends on the rate of the carbonation reaction being more rapid than the rate of metathesis; in some cases where the metathesis is very slow this assumption is certainly justified even if the metathesis is a balanced reaction containing a considerable amount of both salts. In other cases the assumption might be questioned. In the reactions involving indene and phenylacetylene, in which there seemed to be a measurable amount of both salts in the final reaction mixture, the amount of the two carboxylic acids isolated is a correct measure of the composition of the equilibrium only if both salts are carbonated before any shift of the equilibrium occurs. In every case where it was possible to use both the colorimetric and carbonation methods the results obtained by the two methods agreed.

The reaction between sodium or potassium  $\alpha$ -naphthyldiphenylmethyl and triphenylmethane was the only anomalous one found. When the sodium salt was used, the solution decolorized through a dirty brown to the usual light yellow in a length of time varying erratically from a few minutes to several months. The following regularities, however, could be observed: the speed of decolorization increased with the temperature and with the concentration of triphenylmethane. When the potassium salt was used, decolorization was invariably almost instantaneous. In no case was the orange-red color of sodium or potassium triphenylmethyl formed, even momentarily. The source of the triphenylmethane apparently made no difference since two different samples from different sources showed the same behavior. The first sample was obtained from the Eastman Kodak Co., and was carefully purified before using by boiling for six hours with an equal weight of zinc dust in glacial acetic acid, and then recrystallizing from acetic acid. The second sample was prepared by the method of Reyhler<sup>7</sup> from phenylmagnesium bromide and chloroform, and recrystallized from alcohol. Neither sample gave a yellow color with concentrated sulfuric acid (test for triphenylcarbinol) and both melted 93-94°. We have no explanation of the anomalous course of this reaction to propose.

<sup>7</sup> Reyhler, *Bull. soc. chim.*, [3] 35, 738 (1906).

All the results we have obtained are consistent with the idea that the different compounds listed in the first vertical column of Table I are acids of increasing strength, dimethylphenylmethane being the weakest and acetophenone the strongest; phenylacetylene, indene and phenylfluorene are of nearly the same strength. This list can undoubtedly be increased and by so doing it may be possible to find other compounds of sufficiently different acidity to place them between certain members of the present series. The more closely such a series of compounds overlaps the more service it will be in determining the relative strength of each new compound added to it. We are planning to continue this work in this direction. As an indication of the method to be employed we may cite the case of aniline. The acid strength of this compound may be roughly estimated by the following facts: aniline decolorizes an ethereal solution of potassium xanthyI but does not affect a solution of potassium fluoryl. Aniline therefore is of approximately the same acid strength as fluorene (certainly no stronger) and probably lies between this compound (No. 8) and xanthane (No. 7).

It is interesting to attempt to estimate the order of magnitude of the dissociation constants of these extremely weak acids, though, of course, no numerical values can be assigned with any certainty. If we define the acid strength ( $pK$ ) by the usual equation, the difference in  $pK$  values for two acids would be given by the following equation, in which the concentrations are those in the equilibrium mixture:

$$(pK)_1 - (pK)_2 = \log \frac{[R_1^-]}{[R_1H]} - \log \frac{[R_2^-]}{[R_2H]}$$

If we now assume that all the metallic salts with which we are concerned are approximately equally dissociated in ether solution we may substitute the concentration of the salts,  $[R_1Me]$  and  $[R_2Me]$  for the concentration of the ions in the above equation. (The salts are certainly very much more dissociated than the corresponding hydrogen compounds.) If no excess of the hydrogen compound was used in an experiment, we estimate that the metathesis  $R_1H + R_2Me \rightarrow R_1Me + R_2H$  will proceed to 90% completion if the acids differ by 2  $pK$  units. All the reactions indicated in Table I by a +, certainly were at least as complete as this but in the case of the colorimetric measurements about five-fold excess was employed, in which case a difference of 0.4  $pK$  units corresponds to 90% reaction. Therefore, we may conclude that the acid strengths of successive members in the series 1-8 differ by *at least* 0.4 or 2  $pK$  units depending on the nature of the experiment. As a starting point for our  $pK$  scale we may take rather arbitrarily the value for acetophenone as 20 (since it is a weaker acid than ethyl alcohol<sup>8</sup> for which  $K = 7 \times 10^{-20}$  (errors introduced by changes of solvent being neglected). The next three compounds higher on our list

<sup>8</sup> Danner, THIS JOURNAL, 44, 2841 (1922).

(Nos. 11, 10, 9), are phenylacetylene, indene and phenylfluorene; these appear to be of nearly the same strength and since an experiment with equimolecular quantities shows that acetophenone is stronger than indene we may give a  $pK$  value of 22 to the group. Similarly we may argue that there is a difference of 2 units between the  $pK$  values of each of the next three compounds on our list (Nos. 8, 7, 6). The minimum value of diphenylbiphenylmethane (No. 6) is thus 28. Above this a minimum difference of 0.4 must exist between the successive members of the series since colorimetric experiments with a five-fold excess are the basis of the scale. The weakest acid on our list, dimethylphenylmethane (No. 1), thus has an estimated minimum  $pK$  of 30.5–31. If one tries to interpret this large number with a kinetic picture of the degree of dissociation of the hydrocarbon into protons and negative ions, the result is probably meaningless. If one regards the value as the measure of an escaping tendency of protons, however, it has just as much meaning as very small values of vapor pressures obtained by extrapolation of data obtained at higher temperatures.

Weaker acids than the ones at the top of our list certainly are known, but their sodium and potassium salts are decomposed by ether. The work of Schorigin, Schlenk<sup>2</sup> and others indicates that toluene is weaker than diphenylmethane (whose value we estimate at 29.5), while ethane is still weaker than toluene. This would indicate a  $pK$  value for ethane of perhaps 34, though it seems likely that this number is much too small.

When this work was first started it was a matter of great interest to us to see whether all the metathetical reactions were practically instantaneous, as they are with stronger acids in water and alcohol. It was soon found that this was not the case. The stars in the squares of Table I indicate the slow reactions; some of these require months at room temperature (indicated by \* \* \* in Table I). No case of a slow reaction has been found with compounds more acidic than xanthane. However, there is no real parallelism between the rates and acidic strength since the potassium derivative of the weakest acid reacts rapidly with the next four acids in the series (Nos. 2, 3, 4, 5). One fact might indicate that the potassium derivatives react more rapidly than the sodium (6 + 4, Table I). This would be of considerable practical importance since if it takes months or even days for equilibrium to be established in a reaction between an acid and a salt, the usual methods of handling such reactions are materially altered.

Before this difference between the potassium and sodium salts was discovered some time was devoted to a quantitative study of the rates of two reactions which could be followed roughly by colorimetric comparison. These reactions were (1) between diphenylbiphenylmethane and sodium triphenylmethyl and (2) between xanthane and sodium diphenylbiphenylmethyl, both in dry ether. A considerable excess of the hydrogen com-

pound was taken in each case. Colorimetric standards were made from mixtures of the two sodium salts which would be present in the reaction mixture and the rate estimated by matching the reaction mixture against the standard. This crude method yielded surprisingly good results, bimolecular constants calculated from 12 to 50% conversion for reaction 1 and 50 to 90% for reaction 2 agreed within  $\pm 10\%$ . The average values are given in Table II together with the heats of activation calculated from the temperature coefficient of the reaction. Because of the errors in the method, the values are uncertain by  $\pm 540$  calories for reaction 1, and  $\pm 800$  cal. for reaction 2.

TABLE II

REACTION 1			REACTION 2		
Concn. hydrogen cpd. 0.167 <i>M</i>			Concn. hydrogen cpd. 0.167 <i>M</i>		
Concn. sodium cpd. 0.017 <i>M</i>			Concn. sodium cpd. 0.015 <i>M</i>		
Temp., °C.	Approx. <i>k</i>	<i>E</i>	Temp., °C.	Approx. <i>k</i>	<i>E</i>
25	0.0029	13,300 cal.	0	0.29	13,800 cal.
78	.080	(calcd. from	25	2.2	(calcd. from
100	.21	25° to 110°)	42	8.6	0 to 42°)
110	.41				

$k = \frac{1}{t} \cdot \frac{2.3}{b-a} \log \frac{a(b-x)}{b(a-x)}$  where *t* is time in hours, *a* and *b* initial concentrations of reactants, and *x* concentration of product.

### Experimental

Considerable difficulty was encountered in designing a storage flask for keeping the solutions of the metallic derivatives and a number of unsuccessful types were used and discarded before a really satisfactory one was developed. The difficulty lay in the fact that it was apparently impossible to find a grease for the stopcock through which the solution was to be drawn off which would hold against ether and at the same time not react with the metallic derivatives. If a vaseline-rubber grease were used the stopcock would leak so badly after having been opened once that air would enter the flask and decompose the metallic derivative in a few hours, while on the other hand if one of the ether-insoluble greases were used, the solution would be decolorized on passing through the stopcock. The problem was finally solved by using a vaseline-rubber grease which was inert toward the metallic derivatives, and by protecting the stopcock with a mercury seal. The apparatus consisted of a 200-cc. flask in which the metallic derivative was prepared and a roughly graduated buret attached as a side arm, much as described by Ziegler.<sup>9</sup> The stopcock in this buret was three-way, one opening leading to the vessel to be filled, the other connected with a small reservoir of mercury. When the buret was closed the mercury was admitted into the bottom, making a layer of a few millimeters which sealed the opening effectively. The tubes which were filled from this buret were arranged so that they could be evacuated and filled with oxygen-free dry nitrogen.

The method of preparing the metallic compounds depended somewhat on the nature of the compound. The potassium and sodium derivatives of diphenyl- $\alpha$ -naphthylmethane, triphenylmethane and diphenylbiphenylmethane (Nos. 4, 5, 6)

<sup>9</sup> Ziegler, Crössmann, Kleiner and Schäfer, *Ann.* **473**, 20-21 (1929).

were prepared by the action of sodium or potassium amalgam (sufficiently dilute amalgams to be liquid) on the corresponding chlorides in dry ether in nitrogen. The reaction here is really the formation of the free radical followed by the addition of alkali metal to the radical. The potassium derivatives of phenyldimethylmethane and xanthane (1 and 7) were prepared by the action of sodium-potassium alloy on the corresponding ether<sup>10</sup> in the one case and the cleavage of dixanthyl with the same reagent in the other. In some cases an indirect procedure was employed in which the metallic derivative of a less acidic substance was allowed to react with the compound. Such a method was used in preparing the potassium derivative of 1,1-diphenyl-2-methylethylene (No. 2), the potassium derivative of phenyldimethylmethane being allowed to react with a slight excess of the compound. The potassium derivative is a reddish brown substance only slightly soluble in ether. In the preparation of sodium fluoryl (No. 8) sodium phenylfluoryl (No. 9), sodium indyl (No. 10) and sodium phenylacetylde (No. 11), the method was slightly modified by breaking a capsule of the hydrocarbon in a reaction mixture containing sodium triphenylmethyl prepared from the chloride and sodium amalgam (all in dry ether and nitrogen, of course).

**Standardization of Solutions.**—Three different methods were used for standardizing the solutions of the various metallic derivatives. (a) Three cc. of the solution was run into water and the resulting alkali was then titrated with standard acid. (b) One drop of acetophenone from a calibrated dropping-tip was titrated with the solution until the formation of a permanent color. (c) A measured volume of a standard solution of benzoic acid in dry benzene was titrated with the solution until the formation of a permanent color. These methods were not particularly accurate, but, in consideration of the roughness of the work, they were quite satisfactory. The three different methods agreed with each other as well as any one method agreed with itself, *i. e.*, to within possibly 10–15%.

**Identification of Metallic Compounds.**—The identity of each of the metallic derivatives (except the one from acetophenone) was confirmed by treating the ethereal solution with dry carbon dioxide and isolating the carboxylic acid in the usual way. The yields of pure crystalline acid were 40–70%. The acids were for the most part known substances and their melting points (in some cases supplemented by their titration equivalents) served to identify them.<sup>11</sup> The following acids were new compounds and were analyzed as free acids and esters.

**$\alpha$ -Naphthyldiphenylacetic Acid.**—The yield of acid was 40% of the theoretical when dry carbon dioxide was allowed to act on the sodium derivative prepared from  $\alpha$ -naphthyldiphenylmethyl chloride and sodium amalgam in dry ether. The compound melted at 240°.

*Anal.* Calcd. for  $C_{24}H_{18}O_2$ : C, 85.2; H, 5.33; equiv. wt., 338. Found: C, 85.3, 84.9; H, 4.98, 4.73; equiv. wt. (by titration with sodium hydroxide, phenolphthalein indicator), 395.

**Methyl Ester of  $\alpha$ -Naphthyldiphenylacetic Acid.**—The acid was esterified by dissolving in a small amount of 10% sodium hydroxide and boiling with an excess of dimethyl sulfate. The product was recrystallized from methyl alcohol; it melted at 189–191°.

*Anal.* Calcd. for  $C_{26}H_{20}O_2$ : C, 85.2; H, 5.73; mol. wt., 352. Found: C, 84.8; H, 5.82; mol. wt. (freezing benzene), 348, 332.

<sup>10</sup> Ziegler and Schnell, *Ann.*, 437, 255 (1924).

<sup>11</sup> The acid obtained from sodium fluoryl melted at 223–224° and had an equivalent weight by titration of 218 (theoretical 210). These results confirm those of Kliegl [*Ber.*, 62, 1328–9 (1929)].



**Biphenyldiphenylacetic Acid.**—A 70% yield of this acid was obtained from the corresponding sodium derivative and carbon dioxide. The compound melted at 220–222°.

*Anal.* Calcd. for  $C_{26}H_{20}O_2$ : C, 85.7; H, 5.53; equiv. wt. 364. Found: C, 85.5; H, 5.69; equiv. wt. (by titration with sodium hydroxide) 368.

**Methyl Ester of Biphenyldiphenylacetic Acid.**—The ester was prepared by the action of dimethyl sulfate on an aqueous solution of the sodium salt of the acid; it melted at 170°. *Anal.* Calcd. for  $C_{27}H_{22}O_2$ : C, 85.7; H, 5.86; mol. wt., 378. Found: C, 85.4; H, 5.90; mol. wt. (benzene), 375, 390.

**Procedure for Following Reactions.**—All of the colorimetric reactions, with the exceptions noted below, were carried out in the following manner. A weighed quantity of the hydrocarbon (usually a several-fold excess) was placed in a carefully cleaned and dried  $14 \times 120$  mm. test-tube which was then drawn down to a thick-walled capillary and attached to the buret side arm of the storage flask; 3 cc. of the solution was then run out into the tube after the latter had been evacuated and filled with nitrogen and the tube was sealed off at the constriction. The hydrocarbon was brought into solution by shaking for a few minutes, and the tube was observed from time to time to see if any color change took place. In the case of those reactions which took place instantaneously, the drawing down and subsequent sealing off of the tube were of course unnecessary.

A special procedure was employed in those cases where the metallic derivatives were so insoluble that they precipitated. A  $14 \times 120$  mm. test-tube with bent sealed-off side-arm was cleaned and dried as before. The more acidic hydrocarbon was placed in the small side-arm, the less acidic one in the larger tube, which was then drawn down to a capillary. After 3 cc. of potassium phenylisopropyl solution had been introduced into this tube in the usual manner, the tube was sealed off at the constriction. Inside of an hour or so, the solution had turned to the color of the potassium salt of the hydrocarbon placed originally in the wider tube and a heavy precipitate of the metallic derivative had formed. The tube was then tipped so as to wash out the side arm and thus bring the second hydrocarbon into solution. In the course of several days the color of the solution and of the precipitate changed slowly to that of the potassium salt of the second (more acidic) hydrocarbon.

Since solubility effects enter into these reactions, the acid strengths of the hydrocarbons are not the only factors involved. Thus, the order of the acid strengths and the estimated minimum  $pK_a$ 's are not so definitely established here as in the other cases, but it is doubtful whether this very seriously affects the validity of the results. These complications occurred only with diphenylmethane and diphenylmethylethylene, whose potassium or sodium derivatives were very little soluble in ether.

If the metallic derivatives had to be prepared indirectly and if the reaction took place instantly, a third procedure had to be employed. This procedure was used with sodium fluoryl, sodium phenylfluoryl, sodium indyl, sodium phenylacetylde and the sodium derivative of acetophenone. The two hydrogen compounds to be compared were sealed off under nitrogen in thin-walled capsules, which were then broken in a solution of sodium triphenylmethyl. The hydrocarbons thus competed for the sodium furnished by the metallic derivative, and since the reactions took place instantly there can be no doubt that equilibrium was reached almost at once, with the stronger acid in possession of the sodium. The reaction mixture was then treated with carbon dioxide and the resulting acid was isolated and identified in the usual way. Since some of the reactions yielded a mixture of acids, a summary of the experimental results in these cases is given below.

Fluorene and indene were treated together with sodium triphenylmethyl solution, and then carbon dioxide yielded indene-3-carboxylic acid in a 50% yield. Phenyl-

fluorene and fluorene under the same conditions gave a 60% yield of 9-phenylfluorene-9-carboxylic acid. In both of these cases the crude acids appeared to be quite pure. They were identified by mixed melting point determinations and by determining the equivalent weight by titration with alkali. When phenylfluorene and phenylacetylene were used, however, the isolated acid was clearly a mixture. The equivalent weight (by titration) was found to be 181 (calcd. for phenylacetylene acid 146, for the fluorene derivative 286). The mixture was separated by fractional crystallization into the pure fluorene acid (identified by mixed melting points and equivalent weight determinations), and an impure phenylpropionic acid. Similarly phenylfluorene and indene yielded a crude acid (first separating as an oil) melting at 90–100° with an equivalent weight of 217 (calcd. for the phenylfluorenyl acid 286, for the indene acid, 160). Phenylacetylene and indene also yielded a mixture of acids as judged by the melting point 95–105°. The equivalent weight determination is here of little value; the calculated equivalent weights are 160 and 146; the value found was 161.

### Summary

1. The interaction of twelve extremely weak acids and the corresponding sodium or potassium compounds has been studied in anhydrous ether. From the results of these metatheses, it is possible to arrange the acids in a scale of increasing strength. The use of this scale in estimating the strength of other very weak acids is illustrated by a consideration of aniline.

2. The rates of interaction of certain phenylated hydrocarbons and the corresponding sodium derivatives have been estimated at several different temperatures.

CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

## ALIPHATIC AMMONO ALDEHYDES<sup>1</sup>

BY HAROLD H. STRAIN

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The aromatic imines, hydramides and Schiff's bases undergo many reactions which support the view that these substances are aldehydes of an ammonia system of compounds.<sup>2</sup> It is to be expected, therefore, that similar aliphatic nitrogen compounds should exhibit reactions characteristic of aliphatic aldehydes.

A search of the literature revealed to our surprise that but few aliphatic imines and hydramides are known. Subsequent experiments demonstrated that conditions conducive to the formation of aromatic ammono aldehydes did not necessarily promote the formation of the corresponding aliphatic compounds. Our present knowledge of the occurrence of the common aliphatic ammono aldehydes is summarized in Table I.

<sup>1</sup> Original manuscript received May 19, 1930.

<sup>2</sup> (a) Franklin, *THIS JOURNAL*, **46**, 2137 (1924); (b) Strain, *ibid.*, **49**, 1558 (1927); (c) **50**, 2218 (1928); (d) **52**, 1216 (1930); (e) **51**, 269 (1929).