-18.3 kcal. being obtained in the first work reported on this compound. In harmony with this value for ΔF we find that measurements on the extinction coefficient indicate the complete removal of NaR by R. This explanation for the observed facts leaves only one unexplained fact, namely, that in the previous experiments the second reaction always took place when determining the equilibrium constant, while in the present work the equilibrium constant was determined without this reaction interfering. An obvious way out of this difficulty is, of course, to say that some catalyst was present in the previous experiments which was absent in the later work. This is not very satisfying but may possibly be the case. In the later work many improvements in technique may have resulted in purer materials and the absence of some catalytic material.

Summary

1. The peculiarities of color observed in studying diphenylanisylmethyl have been studied by determining the extinction coefficient of various solutions and by determinations of ΔF for the reaction of addition of sodium.

2. The experimental facts may be explained by assuming the following reactions, "R" representing diphenylanisylmethyl

$$\mathrm{R} + \mathrm{Na} = \mathrm{NaR}$$
$$\mathrm{NaR} + \mathrm{R} = \mathrm{NaR_2}$$

The second reaction is somewhat erratic, taking place in only certain experiments. When the color of the solution indicated that the second reaction took place the equilibrium data were consistent in giving a more negative value for ΔF.

CAMBRIDGE, MASS.

RECEIVED MAY 20, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. IX. Pentaphenylethyl and Biphenylenetriphenylethyl

BY MAURICE DORFMAN

This work is a continuation of that carried out by Professor H. E. Bent[1] and co-workers on the electron affinity of various organic free radicals. The reaction studied is the addition of sodium to a free radical in ether solution to give sodium ions and free radical ions according to the reaction

$$\mathrm{Na\ (amalgam)} + \mathrm{R} \longrightarrow \mathrm{Na^+} + \mathrm{R^-}$$

The equilibrium point can be approached from either side by varying the concentration of the amalgam used (or using mercury). From the equilibrium constant the free energy of the reaction can be calculated. A comparison of the free energy values for various free radicals serves as a comparison of the values of the electron affinities in the gaseous state.

In the first five papers of this series, the work on carbon free radicals was confined to those with three aromatic groups on the central carbon atom. The values for ΔF for the addition of sodium were found to be approximately the same, varying from -16.7 kcal. for di-α-naphthylxanthyl to -20.6 kcal. for tribiphenylmethyl. It seemed desirable to ascertain whether the value would differ for another type of free radical if the aromatic groups were not directly attached to the central atom. To this end pentaphenylethyl and biphenylenetriphenylethyl were chosen.[2] These free radicals have been isolated by Schlenk and Mark[3] who by molecular weight determinations found them to be completely dissociated in solution.

Preparation of Materials

Pentaphenylethyl.—For the purpose of making equilibrium measurements the chlorides (prepared from the carbinols) of the free radicals are convenient starting materials. Schmidlin[4] failed to obtain the chloride from pentaphenylethylcarbinol although trying a number of reagents. This experience was confirmed by Schlenk and Mark, who finally obtained the free radical by two methods as indicated below.

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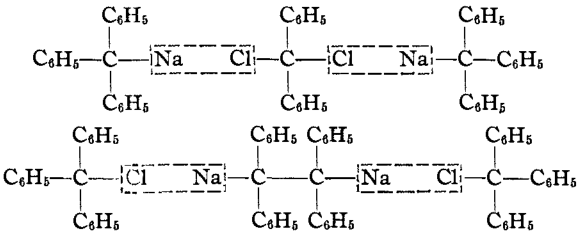
[1] (a) Bent, THIS JOURNAL, **52**, 1498 (1930); (b) *ibid.*, **53**, 1786 (1931); (c) Bent and Dorfman, *ibid.*, **54**, 1393 (1932); (d) Bent, Dorfman and Bruce, *ibid.*, **54**, 3250 (1932); (e) Bent and Gould, *ibid.*, **57**, 1217 (1935); (f) Bent and Ebers, *ibid.*, **57**, 1243 (1935); (g) Bent and Dorfman, *ibid.*, **57**, 1259 (1935); *ibid.*, **57**, 1452 (1935).

[2] Isopropylxanthyl described in 1f contains a similar aliphatic linkage. This investigation was carried out at the same time as the present one and will be considered in the discussion.

[3] Schlenk and Mark, (a) *Ber.*, **55**, 2285 (1922); (b) *ibid.*, **55**, 2299 (1922).

[4] Schmidlin, "Das Triphenylmethyl," Verlag F. Enke, Stüttgart, 1914.



$$\begin{array}{ccccc} C_6H_5 & & C_6H_5 & & C_6H_5 \\ | & & | & & | \\ C_6H_5-C- & \boxed{Na \quad Cl} & -C- & \boxed{Cl \quad Na} & -C-C_6H_5 \\ | & & | & & | \\ C_6H_5 & & C_6H_5 & & C_6H_5 \end{array}$$

$$\begin{array}{ccccccc} C_6H_5 & & C_6H_5 & & C_6H_5 & & C_6H_5 \\ | & & | & & | & & | \\ C_6H_5-C- & \boxed{Cl \quad Na} & -C- & - & C- & \boxed{Na \quad Cl} & -C-C_6H_5 \\ | & & | & & | & & | \\ C_6H_5 & & C_6H_5 & & C_6H_5 & & C_6H_5 \end{array}$$

They prepared the chloride by the direct addition of chlorine to the free radical. In the first method a solution of sodium triphenylmethyl in ether was added to benzophenone dichloride. The resulting octaphenylpropane was found to dissociate completely to give triphenylmethyl and pentaphenylethyl, the latter being separated by crystallization. In the second method, similarly, triphenylmethyl chloride was mixed with disodium tetraphenylethylene, resulting in pentaphenylethyl which does not associate to give decaphenylbutane. In both methods they found side reactions (especially leading to the formation of tetraphenylethylene) to take place. From the published account of the work it appeared that the first method was the better but six attempts to prepare the chloride via the free radical by this method failed to yield a product which added more than 63% of the equivalent amount of sodium.

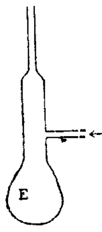


Fig. 1.

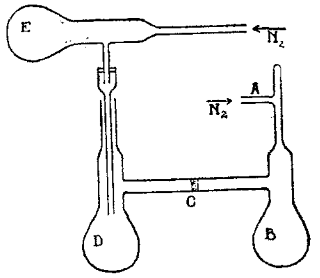


Fig. 2.

The second method was then tried at the suggestion of Professor H. Mark[5] and on the second trial a very satisfactory yield was obtained. Since specific directions have not been given previously the procedure used and the technique for preparing and handling this free radical, which has been developed over a period of several years in this Laboratory, will be described. A complete procedure for preparing, filtering, recrystallizing, weighing and transferring materials without coming into contact with air has been worked out which differs in certain details from procedures previously described.

Ten grams of finely ground tetraphenylethylene was placed in a 500-cc. vessel shown in Fig. 1, which was made from a Kjeldahl flask. Then 300 cc. of pure dry ether and an excess of sodium powder were added against a stream of purified nitrogen. The top and side arm were then sealed and the flask shaken for two days. A deep red color appeared in ten minutes and soon a dark precipitate of disodium tetraphenylethylene formed. This flask was then opened by scratching the tip and inserting over it a rubber tube through which nitrogen was streaming before breaking. The side arm was then opened and by means of an adapter the suspension was decanted into flask D in an atmosphere of nitrogen as shown in Fig. 2. A solution of triphenylchloromethane containing 10 g. in 100 cc. of anhydrous ether was added drop by drop to the ether suspension in D with constant shaking until no further change was noted. The deep red color of the disodium derivative was changed to the orange of pentaphenylethyl, which later precipitated together with the sodium chloride formed. The top of D was then sealed off, the nitrogen displaced by pumping, and A then sealed. C is a sintered Pyrex disk[6] for filtering the solution in case decantation were not possible. The clear mother liquor was poured from D to B. Then fresh ether was distilled back into D by cooling this flask with ice, thus bringing more pentaphenylethyl into solution, and this repeated several times. The orange pentaphenylethyl crystals formed in B were washed three times with 200-cc. portions of ether at 0°. Nitrogen was then let in through A, the flask B sealed off and B evacuated to remove solvent. The top was then opened in nitrogen and the solid loosened by a stiff nichrome wire and transferred to a special container A in nitrogen as shown in Fig. 3. The cap to A was then replaced and the container evacuated. A yield of 4 g. from a possible 20 g. was obtained. This material added 97% of one equivalent of sodium, which furnishes an excellent indication of its purity.

Weighed quantities of pentaphenylethyl were transferred to the apparatus for making equilibrium measurements as shown in Fig. 4. D is a four-liter inverted wide-mouth bottle with the bottom cut off, and F a cardboard cover. Through a wide rubber stopper with appropriate holes and slits, the weighed container A with cap and the equilibrium apparatus E with a rubber cap are placed as shown. D is then flushed out with a rapid stream of carbon dioxide.[7] The caps to A and E are removed and slow streams of nitrogen flow out. This prevents any carbon dioxide which might be contaminated with a little air from diffusing down. A small funnel is placed in the top of E and with the aid of a long silver spatula material was transferred from A to E. The compound thus came into contact with the carbon dioxide atmosphere which contained not more than 0.2% oxygen for about a second.

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[5] The author worked at Heidelberg University, Germany, during the summer of 1932 on the preparation of this compound and of biphenylenetriphenylethyl. He wishes to express his thanks to Professor H. Mark (who with Professor W. Schlenk first prepared these free radicals) at that time connected with the I. G. Farbenindustrie and to Professor Karl Ziegler of Heidelberg University for their kind assistance and suggestions.

[6] Bruce and Bent, THIS JOURNAL, **53**, 990 (1931).

[7] Instead of carbon dioxide, propane (or argon) could be used for cases where carbon dioxide would be reactive. A gas somewhat heavier than air must be employed.

Usually no solid stuck to the funnel which could not be jarred loose by tapping. In case it did, the material was brushed down with a camel's-hair brush. The cap was then placed back on A which was evacuated and reweighed.

It was found possible to prepare potassium pentaphenylethyl from pentaphenylethane and potassium phenylisopropyl by a simple metathesis. This was suggested by Professor Ziegler. Undoubtedly the free radical could be made from the potassium derivative by removing the metal with an appropriate reagent such as tetramethylethylene dibromide. This was not carried out since in the meantime the free radical had been prepared by one of the old methods.

Fig. 3.

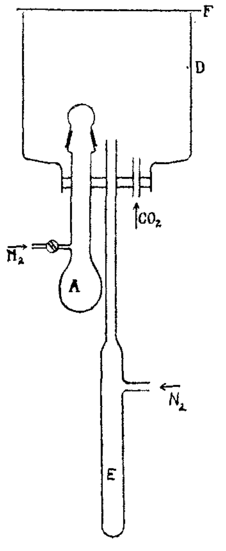


Fig. 4.

Biphenylenetriphenylethyl.—This was prepared with certain modifications according to the directions of Schlenk and Mark.[3b] Sodium triphenylmethyl and fluorenone dichloride (in ether) were mixed in an atmosphere of nitrogen. Violet crystals of the free radical separated. The mother liquor was decanted; the solid washed with ether, then alcohol and then water, to remove sodium chloride, then alcohol followed by ether and dried in vacuum. One gram, from a possible yield of 4 g., was obtained. This material added 98–99% of the equivalent quantity of sodium in ether to yield a red-brown solution.

Procedure.—The apparatus for making the equilibrium measurements has been somewhat simplified and stopcocks eliminated. That used in approaching equilibrium from the free radical side is shown in Fig. 5. About 50 mg. of free radical was introduced into A, the top of A fused to the high vacuum system,[1c] in a nitrogen stream through the apparatus and then the top of B sealed off. After evacuation about 150 g. of amalgam in which the concentration of sodium was about 0.01 mol per cent. was added and then ether admitted. After cooling and sealing off, tube A was covered to exclude light, placed in a thermostat and shaken. Tube B was constructed in such a way that any ether condensing in it, as a result of the fact that it was not thermostated, would flow back into A. After shaking for two days the solution in A was decanted into B, the tubes broken apart, the amount of ether weighed and the concentrations of sodium in the ether and amalgam determined by hydrolysis and titration. The concentration of the amalgam decreased from about 0.01 to 0.0001 mol per cent. An appreciable quantity of free radical remained, the number of equivalents equaling the original number minus the number of equivalents of sodium addition compound formed.

The apparatus used when approaching the equilibrium from the sodium addition compound side contained an extra tube connected to the other two with a constriction in the connecting arm. Free radical was introduced into the first tube as before and mercury was introduced into the second tube. The entrapped air between the mercury and glass was removed by boiling. The system was then sealed to the vacuum line in nitrogen and 5 mol per cent. sodium amalgam and ether introduced into the first tube. The sodium addition compound is completely (about 98%) formed in ether solution. This solution is transferred to the second tube and shaken in contact with the mercury, the first tube having been sealed off.

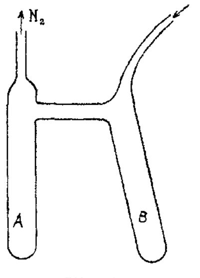


Fig. 5.

Results

The results are shown in Table I, in which the concentrations of the various constituents at equilibrium are given. For both compounds in runs 1 and 2 the equilibrium was approached by shaking an ether solution of the sodium addition compound with mercury, and in runs 3, 4 and 5 by shaking a solution of the free radical with very dilute amalgam. K_2 and ΔF are for the reaction

$$Na + R = Na^+ + R^-$$

where R represents the free radical. 10^{-4} is the value for K_3 taken as the ionization constant[1e] for

TABLE I

EQUILIBRIUM DATA FOR THE ADDITION OF SODIUM TO FREE RADICALS

Run	G. atoms of free radical $\times 10^4$	G. atoms of NaR $\times 10^4$	N of amalgam $\times 10^4$	Moles of ether	Log K_2 $K_3 = 10^{-4}$	ΔF kcal.
			Pentaphenylethyl			
1	0.207	2.30	0.0963	0.341	14.78	
2	.598	3.10	.111	.332	14.42	
3	.170	1.26	.0719	.177	14.74	
4	.214	1.44	.0766	.192	14.63	
5	.262	1.30	.0765	.184	14.54	
				Average	14.62	−19.9
			Biphenylenetriphenylethyl			
1	0.235	1.370	0.0864	0.340	14.50	
2	.393	1.875	.128	.293	14.29	
3	.162	0.938	.0781	.166	14.58	
4	.243	1.277	.0911	.198	14.48	
5	.208	1.292	.0810	.206	14.60	
				Average	14.49	−19.8

the sodium addition compound in ether for the sake of comparison with earlier papers of this series.

Discussion of Results

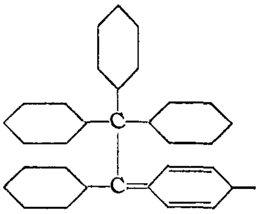
The values of ΔF for the addition of sodium to pentaphenylethyl and biphenylenetriphenylethyl are practically the same, -19.8 and -19.9 kcal., respectively, the difference being less than the experimental error. This confirms the generalization of the previous papers that the electron affinity of an organic carbon free radical is as a first approximation a constant. The values obtained to date are summarized in Table II.

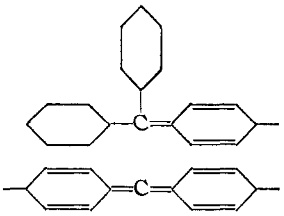
TABLE II

FREE ENERGIES OF THE ADDITION OF SODIUM TO VARIOUS CARBON FREE RADICALS

	Compound	ΔF in kcal.
1	Isopropylxanthyl	-13.9
2	Diphenylanisylmethyl	-15.7
3	α-Naphthylxanthyl	-16.7
4	Phenylxanthyl	-16.9
5	Triphenylmethyl	-17.9
6	Diphenyl-β-naphthylmethyl	-18.6
7	Diphenyl-α-naphthylmethyl	-18.6
8	Diphenylbiphenylmethyl	-19.1
9	Phenyl-α-naphthylbiphenylmethyl	-19.5
10	Phenyldiphenylmethyl	-19.8
11	Biphenylenetriphenylethyl	-19.8
12	Pentaphenylethyl	-19.9
13	α-Naphthyldibiphenylmethyl	-20.2
14	Tribiphenylmethyl	-20.6

A very striking feature of Table II is that the order in which the hydrocarbons are arranged is the same as the order in which the ethanes dissociate to give free radicals. This includes all but the three compounds in the table which contain oxygen. It is perhaps not surprising that oxygen should have a specific effect on the reaction of addition of sodium. Since the order is the same as for the dissociation of the free radicals, the natural assumption to make is that at least some of the same factors are involved in both phenomena and hence, since steric hindrance should be relatively unimportant in the addition of sodium, that the difference between the resonance energy of the free radical and the negative ion is proportional to the total resonance energy. The only point requiring special consideration is then the fact that compounds 11 and 12 have the same value as 10 which contains the same number of benzene rings. In these compounds three of the benzene rings are not attached to the central carbon atom and therefore would not be expected to contribute much to the resonance energy of the free radical. This point has been discussed by Pauling and Wheland.[8] The evidence from Table II is that for some reason these structures have a great deal of resonance. This would suggest that structures of the following type[9] may be important.





The second structure does not mean that pentaphenylethyl actually dissociates but simply that the additional resonance energy available when the bond is broken between the two central carbon atoms is sufficiently large to contribute an important amount to the stability of pentaphenylethyl as a whole. The fact that isopropylxanthyl is at the top of the table is quite in harmony with these ideas, as the resonance of the isopropyl group is probably much less than of a phenyl group.

These ideas are apparently quite capable of accounting for the behavior of the chlorine derivatives. The addition of chlorine undoubtedly forms a non-polar bond essentially analogous to that in the ethane. Hence one would predict that chlorine should be given off most readily by those compounds whose ethanes dissociate most readily to give free radicals, the resonance energy of the free radical promoting dissociation in both cases. In harmony with this concept we find that pentaphenylchloroethane gives off chlorine at the boiling point of ether. Triphenylchloromethane gives off its chlorine with less ease, reacting readily, however, in solution at room temperature with silver, mercury and other metals, while chloromethane will not give up its chlorine at all under these conditions.

The author wishes to thank Professor H. E. Bent for suggesting this problem and for his many valuable suggestions and criticisms.

Summary

1. ΔF for the addition of sodium to pentaphenylethyl and biphenylenetriphenylethyl in ether solution has been determined.

2. The values obtained are compared with

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[8] Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[9] Wheland, *ibid.*, **2**, 474 (1934), postulated in the case of ethyl, structures which are similar to these in that no bond is present between certain atoms in the molecule.

those found for other free radicals and interpreted in terms of resonance energy.

3. A complete description of the method used for preparing pentaphenylethyl, together with the technique developed in this Laboratory for preparing and handling materials out of contact with air, is given.

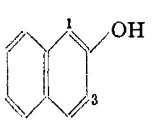
CAMBRIDGE, MASS. RECEIVED JUNE 1, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Structure of Naphthalene

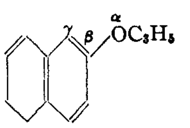
BY LOUIS F. FIESER AND WARREN C. LOTHROP

In 1893 Marckwald[1] called attention to the remarkable difference between the two positions ortho to the functional group of β-naphthol or β-naphthylamine, and he interpreted the difference in terms of Erlenmeyer's symmetrical formula for naphthalene. According to this formula (I) the ortho carbon atom at C_1 is joined to the atom carrying the functional group by a double linkage while the connection to C_3 is by means of a single bond. If these positions represent a fixed condition of the bonds, Marckwald argued, the differences between C_1 and C_3 are easily understandable. As applied to the bond structure of the substituted ring of β-naphthol, this argument has never been contested, and indeed many facts have accumulated in support of the view that there is a double bond at C_1-C_2 and a single bond at C_2-C_3.



I

One line of evidence is from the coupling reaction, or rather from its failure in certain specific cases. β-Naphthol couples at C_1, but if this position is blocked by a stable group (alkyl) no coupling with diazotized amines occurs, while a less stable group (carboxyl, halogen) is displaced by the reagent. In no case is the other ortho position attacked. The failure to react cannot be ascribed to the lower degree of reactivity of the β-position of naphthalene as compared with the α-position, for a 1-naphthol substituted at C_4 couples easily in the β-position, C_2. It is not merely a difference in the degree of reactivity which is involved, but a difference in kind. The exact interpretation depends upon the mechanism assumed for the coupling reaction, but the same conclusion is reached in any case. Whether a diazotized amine adds to the enol double bond of β-naphthol or to the conjugated system of which the unsaturated oxygen atom forms a part, or whether a diazo ether or an oxonium salt forms and rearranges, a double bond is involved in one way or another and the course of the reaction in one case and its failure in the other serves to locate the position of unsaturation at C_1-C_2. The conversion of β-naphthol allyl ether (II) into 1-allyl-2-naphthol by heating clearly is a true molecular rearrangement, and it conforms to the same rules, a substituent at C_1 effectively preventing the rearrangement.[2] Considering the reaction as a simple α,γ-shift, it may be said that the failure of the 1-substituted ether to rearrange shows that the carbon atom at C_3 does not and cannot form the end of an α,γ-system and hence that there is no double bond between C_2 and C_3. The Skraup reaction may involve still another kind of substitution, but it shows the same peculiarity. While β-naphthylamine forms a hetero ring extending to the 1-position, substances of the type of III are reluctant to form naphthoquinolines.[1,2a]



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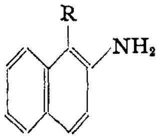
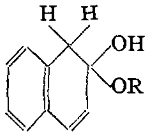


III

Further evidence of a fixed bond structure in at least a part of the naphthalene molecule is furnished by reactions involving the replacement or modification of a functional group rather than a nuclear substitution. According to the theory suggested by Henry[3] and extended by Wegscheider,[4] the etherification of β-naphthol with alcohol and a mineral acid probably involves an addition product  which loses water. The

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(1) Marckwald, *Ann.*, **274**, 331 (1893); **279**, 1 (1894).

(2) Claisen, *Ber.*, **45**, 3157 (1912).

(2a) Fries, *Ann.* **516**, 285, footnote (1935).

(3) Henry, *Ber.*, **10**, 2041 (1877).

(4) Wegscheider, *Monatsh.*, **16**, 140 (1895).