sodium bisulfite for six hours. The bisulfite compound was freed from adhering oil by thorough washing with ether, then shaken with 3% sodium carbonate which liberated the aldehyde as a pale yellow crystalline solid. The solid was recrystallized from low-boiling petroleum ether. It separated in pale yellow prisms and it melted at 44°. The yield was 53%.

Anal. Calcd. for $C_{16}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.5; H, 5.7.

The **phenylhydrazone**, prepared in the usual manner, crystallized in yellow needles and melted at 173°. A comparison with the phenylhydrazone obtained from the decomposition product of the secondary alcohol proved the two products to be identical.

Action of Phenylmagnesium Bromide on Benzene Sulfinic Acid.—In order to account for the diphenyl sulfoxide that was formed in the reaction between the unsaturated ketosulfone and phenylmagnesium bromide, 12 g. of benzene sulfinic acid was added to a solution of phenylmagnesium bromide containing 7.2 g. of magnesium. The mixture was boiled for an hour and then decomposed with acid in the usual manner. From the ethereal layer sodium bicarbonate extracted 0.53 g. of unchanged sulfinic acid. By suitable treatment the washed and dried ethereal solution yielded 10.1 g. of diphenyl sulfoxide and 0.85 g. of diphenyl sulfide—identified by oxidation to the sulfone.

Summary

This paper contains a description of the stereoisomerism and the addition reactions of the ketosulfone $C_6H_5COCH{=}CHSO_2C_6H_5$. The stereoisomerism is similar to that of dibenzoylethylene. The addition reactions with unsymmetrical reagents are very much like those of β-benzoylacrylic esters, the mode of addition being controlled by the conjugated system $C{=}C{-}C{=}O$. Phenylmagnesium bromide combines to some extent with the carbonyl group to form a tertiary alcohol with unusual properties.

CAMBRIDGE, MASSACHUSETTS RECEIVED JUNE 10, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Electron Affinity of Free Radicals. VIII. Diphenylanisylmethyl and the Color of its Sodium Addition Compound

BY HENRY E. BENT AND MAURICE DORFMAN

The addition of sodium to an organic free radical or to triarylboron compounds results in a decided change in the color of the solution. Organic free radicals are, in general, not as intensely colored as the sodium addition compounds. These color changes are useful in following the course of reactions and in the case of certain experiments[1] have been the bases for calculations of the equilibrium constant of a reaction involving the sodium addition compound. For these reasons it is important to establish the relation between the amount of sodium addition compound present in a solution and the color of the solution.

Recent work[2] on triphenylboron and tri-α-naphthylboron established the fact that a considerable amount of a sodium addition compound may be present in solution without a corresponding color. An explanation was given in terms of a reaction between the sodium addition compound and the triarylboron compound. Some time ago similar observations were made on diphenylanisylmethyl.[3] This was the only one of the carbon free radicals reported in this series of papers which behaved peculiarly. Conant and Wheland[4] report anomalous colors when studying α-naphthyldiphenylmethyl and triphenylmethane. When sodium diphenylanisylmethyl was shaken with mercury the sodium was partially removed. The color of the solution, however, always indicated that a larger amount of sodium was removed than was given by the analyses. In the case of triphenylboron it is easy to see how a molecule of sodium triphenylboron could be attached to triphenylboron, two electrons from the sodium completing the octet for the boron. Diphenylanisylmethyl, however, has seven electrons around the central carbon and therefore is not able to combine with a molecule of the sodium addition compound in this way.[5] A further study of diphenylanisylmethyl seemed necessary in order to obtain quantitative data regarding the color of the solution.

We first attempted to repeat the experiment

---

[1] Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

[2] Bent and Dorfman, *ibid.*, **57**, 1259 (1935).

[3] Bent, Dorfman, and Bruce, *ibid.*, **54**, 3252 (1932).

[4] Conant and Wheland, *loc. cit.*, p. 1215.

[5] The assumption of a three-electron bond [Pauling, THIS JOURNAL, **53**, 3229 (1931)] would possibly offer an explanation. However, it is not evident that such a bond would be sufficiently strong to be of any importance, even considering the resonance energy resulting from the bond shifting between the two carbon atoms attached to the sodium.

reported in 1932 of preparing sodium diphenylanisylmethyl and removing the red color completely with mercury. To our surprise the compound behaved perfectly normally, the intensity of the color being just what one would expect from the amount of sodium compound determined by analysis. Several experiments all failed to duplicate the former experiment in which we repeatedly removed the color by pouring onto mercury and then restored the color by shaking with amalgam. There seems no possibility of the earlier observations being in error due to experimental technique, as any leak in the apparatus would have permanently destroyed the color and prevented the experiments being repeated many times with the same sample. The only conclusion which we have been able to draw is that in our earlier experiments a subsequent reaction took place on removing part of the sodium which resulted in a loss of color of the remaining sodium addition compound without destroying it and that in the more recent experiments this reaction did not take place. The same sample of Eastman diphenylanisylcarbinol was used in both investigations. However, extensive purification is necessary in preparing the chloride and it seems at least possible that in the more recent work some impurity was absent which catalyzed a reaction in the earlier experiments.

These results suggested that the equilibrium constant should be again determined as any reaction of the type R + NaR = NaR_2 would tend to give too negative a value for the free energy of addition of sodium. This follows from the fact that at equilibrium the concentration of NaR was much less than that of R as will be seen in Table I. Consequently the reaction Na + R = $Na^+ + R^-$ will be shifted to the right by a reaction removing R and NaR on account of the much greater percentage change in the concentration of NaR. We therefore determined the equilibrium constant again for the reaction Na + R = $Na^+ + R^-$, approaching the equilibrium from both sides. The value for the ionization constant for the sodium addition compound is the same as that used in the previous investigation, for the sake of comparison. As will be observed from Table I, the results are quite consistent and the value −15.7 is considerably more positive than the value −18.3 kcal. calculated from the data previously obtained. The difference between these two values, 2.6 kcal., would be ample to account for the disappearance of the color of the sodium addition compound by reaction with the free radical. We may also compare this value with that obtained for phenylxanthyl and triphenylmethyl.[6] ΔF in the case of phenylxanthyl is −16.9 and for triphenylmethyl is −17.9 kcal. Thus the introduction of an oxygen atom in triphenylmethyl to give phenylxanthyl results in an increase in ΔF of one kcal., while the introduction of a methoxy group in triphenylmethyl to give diphenylanisylmethyl results in an increase of 2.2 kcal. The effect is not large in either case but is probably significant in indicating the sign and the magnitude of the effect of an oxygen atom.

TABLE I

EQUILIBRIUM DATA FOR THE REACTION OF ADDITION OF SODIUM TO DIPHENYLANISYLMETHYL

Several preliminary runs in which the sodium addition compound was prepared from a saturated amalgam and analyzed by titration with acid indicated a purity of the chloride of 98–99%. In Runs 4, 6 and 9 the equilibrium was approached by removing sodium from NaR by means of mercury. In Runs 5 and 10 the equilibrium was approached by treating the chloride with a dilute amalgam.

Run	Moles $R \times 10^4$	Moles $NaR \times 10^4$	Mole fraction amalgam $\times 10^4$	Moles ether	Log k_2 $K_1 = 10^{-2}$ $K_3 = 10^{-4}$	ΔF kcal.
4	1.97	0.216	2.033	0.31	11.18	
5	1.218	.405	7.46	.269	11.23	
6	1.57	.098	1.89	.277	11.79	
9	1.28	.101	1.58	.344	11.90	
10	0.84	.50	6.89	.347	11.51	
				Average	11.52	−15.7

In only one type of experiment did we observe in our recent work an apparent disagreement between the amount of sodium in the solution, as estimated from the color, and the amount of sodium determined by analysis. These experiments involved adding the free radical, prepared by shaking the chloride with mercury, to the sodium addition compound. The resulting solution was invariably much less intense in color than would be expected. In order to be sure that the effect was not due to an incomplete reaction of mercury with the chloride, we determined the amount of sodium necessary to convert the free radical completely to the sodium addition compound. Somewhat more than one equivalent was required in every case, indicating that the reaction of the chloride with mercury was not complete, taking place to only about 75%. However, this amount of chloride would be insufficient to account for the quantitative data given in

---

[6] Bent and Gould, THIS JOURNAL, **57**, 1217 (1935).

Table II. These data were obtained by preparing in a closed apparatus two solutions, one of the sodium addition compound and one of the free radical. A tube was provided in which known amounts of the two solutions could be mixed and the resulting solution poured into a small cell with plane glass windows for measurements of the extinction coefficient. As the free radical is yellow and the sodium addition compound red it is quite easy to choose a wave length at which the extinction coefficients differ greatly for the two compounds. The apparatus used was a Keuffel and Esser colorimeter. In the equation $\log I_0/I = kc$, I_0 is the intensity of the transmitted light when the cell is filled with ether, I the intensity when the cell contains a solution and c the concentration of the solution expressed as a fraction of the initial concentration. The absolute values are of no particular significance for this experiment. The cell was about 3.0 mm. in thickness and the mole fraction of the free radical solution and of the solution of the sodium addition compound was 4.5×10^{-4}. Values of "k" were determined at intervals of 50 mμ from 450 to 650 mμ. The most useful wave length was found to be 550 mμ. The absorption of both the free radical and sodium addition compound was appreciable at this wave length but not so great as to prevent a determination of "k." Also the values of "k" differed greatly for the two compounds, the value for the sodium addition compound being 1.45 and for the free radical 0.07. We may then use equation (1)

$$\log I_0/I = 1.45\ C_{\text{NaR}} + 0.07\ C_{\text{R}} \qquad (1)$$

to calculate the intensity of the light transmitted for a mixture of the sodium addition compound and the free radical. Or we may transpose equation (1) to give equation (2) which permits one to calculate the concentration of NaR from the concentration of free radical and the light transmitted.

$$C_{\text{NaR}} = (1/1.45)\ (\log I_0/I - 0.07\ C_{\text{R}}) \qquad (2)$$

TABLE II

DETERMINATION OF THE CONCENTRATION OF NaR IN SOLUTIONS CONTAINING R BY MEANS OF THE EXTINCTION COEFFICIENT AT λ = 550 mμ

Accuracy in the initial number of moles is ±0.05.

Initial moles of R	Initial moles of NaR	Concentration of NaR in mixture Assuming R retains its color	Concentration of NaR in mixture Assuming all color to be due to NaR
0.57	0.43	0.027	0.054
.40	.61	.28	.30
.51	.49	.03	.04
.40	.60	.14	.16

In using this equation one may make several assumptions to account for the loss of color of the solution on mixing the free radical with the sodium addition compound. We first must make some assumption regarding the color of any product which may be formed by a reaction of these two materials. We have made the assumption that the product is colorless, as this assumption will give a maximum value to the concentration of NaR. The next assumption concerns the effect of the reaction on the free radical and the sodium addition compound. Inasmuch as the resulting solution appears to the eye to have the color of the free radical, one is inclined to assume that the reaction involves only the destruction of the color of the compound NaR. This assumption gives rise to the values in the next to the last column of Table II. If we assume that the total color of the solution is due to NaR, which gives a maximum value to the concentration of this material, we obtain the values in the last column of the table. These figures prove beyond question that a solution prepared by mixing the free radical and the sodium addition compound reacts with the destruction of the color of the latter compound.[7]

We may sum up the situation described by the above experiments as follows. Diphenylanisylmethyl combines with sodium according to the equation Na + R = NaR, as in the case of other free radicals which have been studied. The value of ΔF for this reaction (-15.7) is somewhat lower than that for triphenylmethyl. This is quite in harmony with the experiments on phenylxanthyl and α-naphthylxanthyl, which compounds also contain an oxygen atom and give somewhat lower results than for triphenylmethyl. In the case of diphenylanisylmethyl, however, a second reaction may take place of the type NaR + R = NaR_2. As a consequence of this reaction and the removal of the product of the first reaction ΔF is apparently decreased, the value of

---

(7) Undoubtedly part of the destruction of NaR is due to the reaction NaR + RCl = NaCl + 2R, the RCl arising from incomplete reaction of mercury with the chloride initially. However, as will be observed from the table it is not possible to account for all of the destruction of color on this basis. The data indicate that one mole of free radical destroys the color of approximately one mole of the sodium addition compound. One might also question the purity of the original chloride and assume a small amount of hydrogen chloride to be present. However, the chloride was kept in a bottle which was evacuated. This would remove any hydrogen chloride except that which might be held as an oxonium salt. The fact that the number of equivalents of sodium found by titration when the chloride was treated with a saturated amalgam checks with the number of moles of chloride introduced into the apparatus indicates that we could not be dealing with any appreciable amount of impurity.

−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

$$R + Na = NaR$$
$$NaR + R = NaR_2$$

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

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

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.

---

[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.