[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Properties of Unsaturated Sulfur Compounds. II. Alpha, Beta-Unsaturated Ketosulfones

BY E. P. KOHLER AND R. G. LARSEN

In the first paper of this series[1] we compared the properties of an α,β-unsaturated sulfone with those of the corresponding unsaturated ketone. We now present the results of a study of an unsaturated ketosulfone which is analogous to a well known 1,4-diketone.

$$\underset{\text{I}}{C_6H_5COCH{=}CHSO_2C_6H_5} \qquad \underset{\text{II}}{C_6H_5COCH{=}CHCOC_6H_5}$$

The ketosulfone, like the diketone, occurs in two forms—the one yellow in color and melting at 114°, the other colorless and melting at 149°. The behavior of this pair of geometrical isomers under the influence of light, heat and isomerizing chemical agents is almost identical with that of the corresponding pair of 1,4-diketones. On exposure to sunlight the lower melting yellow form passes completely into its colorless isomer. At temperatures slightly above the melting point of the higher melting form both isomers are converted into an equilibrium mixture. And when a few bubbles of hydrogen chloride are passed into a solution of the colorless form in glacial acetic acid, or when a trace of sodium methylate is added to its solution in methyl alcohol, it passes completely into the yellow isomer. Both in the diketones and in the ketosulfones, therefore, the higher melting colorless form appears to be the less stable and less symmetrical *cis* isomer. In the case of the diketone this configuration has been established by relating the two forms to a cyclic compound;[2] in the ketosulfones it is the only reasonable inference from the facts.

Perhaps the most conspicuous property of unsaturated 1,4-diketones is the ease with which they are reduced.[3] The two ketosulfones are also reduced with great ease and like the diketones they do not as readily as monoketones form dimolecular reduction products. The resulting saturated compound resembles α,β-disulfonic acids and α,β-disulfones in the manner in which it is cleaved by bases.

$$\underset{\text{III}}{C_6H_5COCH_2CH_2SO_2C_6H_5} \longrightarrow C_6H_5SO_2M + CH_2{=}CHCOC_6H_5$$

The unsaturated ketosulfones are also easily oxidized and they combine with bromine to form dibromides from which the *trans* form is regenerated both by zinc and alcohol and by methyl alcoholic potassium iodide. This dibromide serves as a means of securing another pair of geometrical isomers, namely, the two bromine derivatives represented by the formula

$$C_6H_5COCBr{=}CHSO_2C_6H_5 \quad \text{IV}$$

The relation of these isomers is precisely the same as that of the parent compounds; only the lower melting yellow form is obtained by elimination of hydrogen bromide from the dibromide and on exposure to sunlight this form passes completely into a higher melting and less soluble colorless isomer.

The most interesting addition reactions of the unsaturated compounds are those with unsymmetrical addenda. With hydrogen bromide the ketosulfones combine to form a single monobromo derivative of the saturated sulfone. Another monobromo derivative of this sulfone is obtained by direct bromination, which likewise gives a single product. These two reactions therefore lead to the two isomeric bromine compounds which are represented by the formulas

$$\underset{\text{V}}{C_6H_5COCHBrCH_2SO_2C_6H_5} \qquad \underset{\text{VI}}{C_6H_5COCH_2CHBrSO_2C_6H_5}$$

As ketones are brominated far more easily than sulfones it was probable *a priori* that the bromination product would be represented by V and the addition product by VI. This relation between the formulas and the substances was definitely established by synthesizing the bromination product from dibromo propiophenone

$$C_6H_5COCHBrCH_2Br + NaSO_2C_6H_5 \longrightarrow C_6H_5COCHBrCH_2SO_2C_6H_5$$

Other unsymmetrical reagents are added in the same manner as hydrogen bromide. Thus when the unsaturated ketosulfones are dissolved in cold methyl alcoholic potassium hydroxide they form a salt of an hydroxyl compound which is sufficiently sensitive to acids to give all the reactions of benzoylacetaldehyde.

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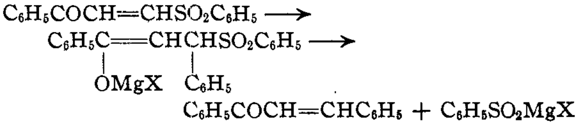
[1] Kohler and Potter, THIS JOURNAL, **57**, 1316 (1935).

[2] Paal and Schulze, *Ber.*, **35**, 168 (1902).

[3] Conant and Lutz, THIS JOURNAL, **49**, 1083 (1927).

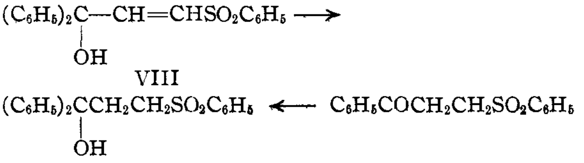
$$\begin{array}{l} C_6H_5COCH{=}CHSO_2C_6H_5 \longrightarrow \\ \quad C_6H_5COCH_2CHOHSO_2C_6H_5 \longrightarrow \\ \qquad\qquad\qquad \text{VII} \\ \qquad\qquad\qquad\qquad C_6H_5COCH_2CHO + C_6H_5SO_2H \end{array}$$

With phenylmagnesium bromide the principal reaction likewise consists in 1,4-addition to the conjugated system C=C—C=O, but in this case cleavage of addition product occurs during the reaction and the cleavage products immediately react further.



$$\begin{array}{l} C_6H_5COCH{=}CHSO_2C_6H_5 \longrightarrow \\ \quad C_6H_5\underset{\displaystyle OMgX}{C}{=}CH\underset{\displaystyle C_6H_5}{C}HSO_2C_6H_5 \longrightarrow \\ \qquad\qquad\qquad C_6H_5COCH{=}CHC_6H_5 + C_6H_5SO_2MgX \end{array}$$

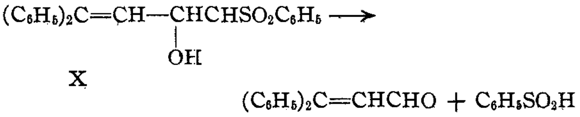
Owing to this rapid cleavage the final products resulting from this mode of addition are β,β-diphenylpropiophenone and diphenyl sulfoxide. Besides these products two other compounds are formed in smaller quantities. The structure of one of these substances was established by reducing it catalytically and identifying the reduction product with the substance obtained by the action of phenylmagnesium bromide on the saturated ketosulfone.



$$\begin{array}{l} (C_6H_5)_2\underset{\displaystyle OH}{C}{-}CH{=}CHSO_2C_6H_5 \longrightarrow \\ \qquad\qquad \text{VIII} \\ (C_6H_5)_2\underset{\displaystyle OH}{C}CH_2CH_2SO_2C_6H_5 \longleftarrow C_6H_5COCH_2CH_2SO_2C_6H_5 \end{array}$$

IX

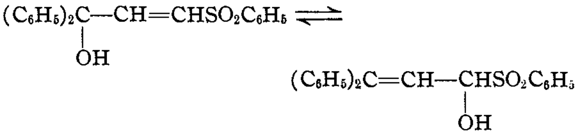
The structure of the second substance was established by cleavage and identification of the cleavage products as β-phenyl cinnamic aldehyde and phenyl sulfinic acid



$$\begin{array}{l} (C_6H_5)_2C{=}CH{-}\underset{\displaystyle OH}{C}HCHSO_2C_6H_5 \longrightarrow \\ \qquad \text{X} \\ \qquad\qquad\qquad (C_6H_5)_2C{=}CHCHO + C_6H_5SO_2H \end{array}$$

XI

These two hydroxyl compounds are manifestly due to 1,2-addition of phenylmagnesium bromide to carbonyl. They are interesting by reason of the very remarkable ease with which they undergo the allylic rearrangement. Both substances are stable below their melting points but when either of them is dissolved in any ordinary solvent it more or less rapidly undergoes partial rearrangement into its isomer. Most solutions, on chilling, deposit a mixture of both isomers but by slow crystallization from properly selected solvents it is possible to secure both isomers in a pure condition—the tertiary alcohol VIII from benzene and the secondary alcohol X from methyl or ethyl alcohol. Solutions of these substances in all common solvents, therefore, appear to contain equilibrium mixtures in which the equilibrium is adjusted with considerable rapidity.



$$\begin{array}{l} (C_6H_5)_2\underset{\displaystyle OH}{C}{-}CH{=}CHSO_2C_6H_5 \rightleftharpoons \\ \qquad\qquad\qquad (C_6H_5)_2C{=}CH{-}\underset{\displaystyle OH}{C}HSO_2C_6H_5 \end{array}$$

As will be seen from the foregoing account α,β-unsaturated ketosulfones and the corresponding unsaturated 1,4-diketones have many properties in common. The resemblance is most conspicuous in the geometrical isomerism where both classes exhibit the same peculiarities. If, as is probable, the increase in stability which makes it possible to isolate both isomers in the case of the diketones is associated with their more perfect conjugation, then the sulfonyl group must likewise make a contribution of considerable moment toward a more complete conjugation.

Experimental Part

The unsaturated ketosulfone can be obtained in a single operation by heating alcoholic solutions of β,β-dibromopropiophenone with one equivalent of pure sodium benzene sulfinate and slightly more than one equivalent of potassium acetate. The yields are fair but the dibromo compound is not easily accessible. We therefore obtained most of our unsaturated compound by preparing the saturated ketosulfone, converting it into its bromo derivative and eliminating hydrogen bromide.

The saturated sulfone was made both by adding benzene sulfinic acid to vinyl phenyl ketone and by treating β-chloropropiophenone with sodium benzene sulfinate. We preferred the second method. Our procedure was as follows.

A solution of 17.6 g. of β-chloropropiophenone and 20 g. of pure sodium benzene sulfinate in the necessary quantity of boiling 95% alcohol was boiled for three hours and filtered while hot. On cooling, the solution deposited 22.7 g. of fluffy white needles—a yield of 68%. After recrystallization from methyl alcohol, from which it separated in large prisms, the ketosulfone melted at 98°.

Anal. Calcd. for $C_{15}H_{14}O_3S$: C, 65.7; H, 5.1. Found: C, 65.9; H, 5.3.

Cleavage with Bases.—The ketosulfone is very sensitive to bases. A suspension in 5% aqueous potassium hydroxide when warmed formed a clear solution from which, by suitable manipulation, it was possible to isolate 72% of the calculated quantity of benzene sulfinic acid, and an oil which was, presumably, a polymer of methyl phenyl ketone. When sodium ethylate was substituted for the hydroxide, the products were benzene sulfinic acid and a sparingly soluble solid which was obtained in crystalline form by crystallization from acetone and methyl alcohol. The solid melted with decomposition at about 96° and the analysis indicated that this substance likewise is a polymer of vinyl phenyl ketone.

Anal. Calcd. for C_9H_8O: C, 81.8; H, 6.1. Found: C, 81.4; H, 6.3.

Bromination: β-Bromo-β-benzoyl Ethylphenyl Sulfone, V.—A solution of bromine in chloroform was added gradually to a similar solution of the saturated ketosulfone. Bromination started promptly and stopped when one mole of bromine had been added. The solution was allowed to evaporate and the residue was recrystallized from methyl alcohol. The bromo compound crystallized in thin plates and it melted at 71°. The yield was practically quantitative.

Anal. Calcd. for $C_{15}H_{13}O_3SBr$: C, 51.0; H, 3.7. Found: C, 50.9; H, 3.7.

Synthesis.—In order to establish the structure of the bromo compound an alcoholic solution containing 4.0 g. of α,β-dibromopropiophenone and 4.0 g. of sodium benzene sulfinate was boiled for thirty hours. The surprisingly slow reaction was incomplete even after this prolonged boiling. The residue, left after removing the solvent and the salts, gradually deposited nearly 0.5 g. of the unsaturated ketosulfone, then in succession 0.3 g. of benzene sulfinic acid and 0.2 g. of the bromo compound melting at 71°, and finally a small quantity of dibromopropiophenone. The yield of monobromo ketone was only about 5%.

Elimination of Hydrogen Bromide: the Unsaturated Ketosulfone, II.—The usual method of eliminating hydrogen bromide by heating an alcoholic solution of a bromine derivative with excess of methyl alcoholic potassium acetate resulted in the formation of a large quantity of red oils. An attempt to avoid the formation of oils by operating in glacial acetic acid was more successful but owing to the formation of an acetate resulted in a considerable loss of material. The following method of elimination proved to be satisfactory. Two methyl alcoholic solutions, the one saturated with 3.55 g. of the bromo compound at 40° and the other saturated with 1.06 g. of potassium acetate at the same temperature were poured together. Reaction occurred at once and was complete in five minutes. The mixture was immediately cooled in an ice-bath; it deposited the unsaturated compound in yellow plates which, after washing and recrystallization from methyl alcohol, melted at 114°. The yield was 2.46 g. or 92%.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.2; H, 4.4. Found: C, 66.0; H, 4.6.

Isomerization.—A suspension of 2 g. of the yellow compound in ether was exposed to sunlight in a Pyrex flask. The color of the supernatant liquid disappeared rapidly, the pale yellow plates gradually dissolved and colorless prisms took their place. In four hours the transformation into the colorless isomer was complete. The crude product melted at 149° and the melting point was not changed by recrystallization.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.2; H, 4.4. Found: C, 66.0; H, 4.6.

Effect of Heat.—Two-tenth-of-a-gram samples of the isomers were heated in sealed Pyrex tubes for four hours at 160°, then chilled for examination. Both samples melted at about 109°, and both samples when ground with successive small quantities of dry ether left about 0.05 g. of the colorless form. The ethereal solutions on evaporation left almost pure yellow form.

Reduction.—When a solution of the yellow form in aqueous acetic acid was warmed with zinc dust it became colorless within fifteen minutes and the product was the saturated ketonesulfone. When a solution of the same isomer in alcohol was warmed with zinc dust and a crystal of mercuric chloride, it gradually became deeper yellow in color. The mixture was boiled for half an hour, then filtered while hot and evaporated. The pale yellow residue was dissolved in ether and the ethereal solution was washed with dilute acid—whereupon it became colorless. It yielded 1.95 g. of the saturated ketosulfone from 2 g. of the unsaturated compound. No dimolecular reduction product was detected but the yellow color may be due to the formation of a metallic derivative of a more complex reduction product.

Addition of Bromine.—One gram of each of the isomers was suspended in a small quantity of glacial acetic acid and treated with the calculated quantity of bromine in the same solvent. Both solutions soon became colorless but it was impossible to isolate solid products. Bromination in chloroform and in carbon disulfide likewise gave only oily product. A dilute solution in aqueous acetic acid on slow evaporation deposited a small quantity of a colorless solid which crystallized in plates and melted at 95–100° but which could not be recrystallized. An analysis of a sample of oil obtained by evaporating a dried ethereal solution *in vacuo* showed that the oil is a dibromide or, more probably, a mixture of dibromides.

Anal. Calcd. for $C_{15}H_{12}O_3SBr_2$: C, 41.7; H, 2.8. Found: C, 41.9; H, 3.0.

β-Bromo-β-benzoylvinyl Phenyl Sulfone, IV.—A solution of 2 g. of the unsaturated sulfone in glacial acetic acid was treated first with an equivalent quantity of bromine and then, when it had become colorless again, with a slight excess of potassium acetate. The mixture was warmed for an hour and allowed to evaporate in a current of air. The residue, by suitable manipulation, yielded a yellow solid which crystallized from ether and petroleum ether in prisms and which melted at 105°.

Anal. Calcd. for $C_{15}H_{11}O_3SBr$: C, 51.3; H, 3.1. Found: C, 51.1; H, 3.3.

Isomerization.—A suspension of the yellow form in a small quantity of ether was exposed to sunlight for six hours in a Pyrex flask. The yellow prisms gradually disappeared, being replaced by colorless needles which melted at 128°.

Anal. Calcd. for $C_{15}H_{11}O_3SBr$: C, 51.3; H, 3.1. Found: C, 51.3; H, 3.3.

Addition of Hydrogen Bromide: α-Bromo-β-benzoylethyl Phenyl Sulfone, VI.—A saturated solution of hydrogen bromide in glacial acetic acid was added in excess to a suspension of the unsaturated ketosulfone in the same solvent. The solid dissolved and the solution immediately began to deposit a much less soluble product. The solution was diluted with ice water; the solid was collected and recrystallized from methyl alcohol. It separated in small prisms and melted at 135°.

Anal. Calcd. for $C_{15}H_{13}O_3SBr$: C, 51.0; H, 3.7. Found: C, 50.6; H, 3.9.

Addition of Water: α-Hydroxy-β-benzoylethyl Phenyl Sulfone, VII.—The unsaturated sulfone was dissolved at the ordinary temperature in a methyl alcoholic solution of an equal weight of potassium hydroxide. The resulting very pale yellow solution was diluted with ice, cautiously acidified with iced hydrochloric acid and evaporated in a current of air. It deposited a mixture which was in part very readily and in part very sparingly soluble in ether. The readily soluble component was identified as benzoyl acetaldehyde by converting it into its sodium salt and this in turn into the copper salt and the benzoate melting at 75°.

The sparingly soluble component was recrystallized from a large quantity of dry ether. It was thus obtained in colorless needles melting with decomposition at 95–100°.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.1; H, 4.8. Found: C, 62.1; H, 5.0.

The properties of the hydroxy sulfone are somewhat surprising. It readily dissolves in sodium bicarbonate, forming a colorless solution which on evaporation deposits a colorless sodium compound. It therefore is an acid capable of forming a stable sodium salt. When any acid is added to the solution in sodium bicarbonate, it immediately turns yellow and not more than 30–40% of the hydroxyl compound can be recovered, the remainder being converted into benzoyl acetaldehyde and benzene sulfinic acid. As a consequence of this instability in the presence of acids the substance gives the color reaction of the aldehyde with ferric chloride, forms the copper derivative of the aldehyde with copper acetate and the benzoate melting at 75° when the solution in sodium bicarbonate is shaken with benzoyl chloride.

Addition of Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide which contained 1.44 g. of magnesium and which was cooled with ice was added gradually a solution of 4.08 g. of the *trans* modification in benzene and ether. The mixture gradually assumed an orange color and a precipitate accumulated on the walls of the flask. As soon as all of the sulfone had been added, the mixture was decomposed with iced ammonium chloride and the benzene–ether layer was washed and dried. Upon removal of the ether the benzene solution began to deposit the tertiary alcohol VIII in thin needles. The precipitation was made as complete as possible by addition of petroleum ether, the solid was removed, and the solution was concentrated until a second product began to crystallize. This solid was identified as β,β-diphenylpropiophenone by an analysis and by comparison with a sample on hand.

The mother liquors were distilled with steam. They left an oily residue which by suitable treatment with ether and petroleum ether was separated into diphenylpropiophenone and a third product that crystallized in large cubes, melted at 69°. This last product was identified as diphenyl sulfoxide by comparison with an authentic sample.

β-Hydroxy-β,β-diphenylvinyl Phenyl Sulfone, VIII.—The tertiary alcohol crystallizes from benzene in small thin needles. In a capillary tube it melts at 193° to a clear colorless liquid which resolidifies if it is removed from the bath at once and which almost immediately begins to decompose if it is left in the bath.

Anal. Calcd. for $C_{21}H_{18}O_3S$: C, 72.0; H, 5.1; mol. wt., 350. Found: C, 71.9; H, 5.2; mol. wt., 342.

Reduction: β-Hydroxy-β,β-diphenylethyl Phenyl Sulfone, IX.—A solution of 1 g. of the unsaturated tertiary alcohol in ethyl acetate was shaken in the presence of Adams catalyst with hydrogen under an excess pressure of about one atmosphere. The absorption of hydrogen was very slow. In order to complete the reduction it was necessary to add additional catalyst at intervals but in the end the calculated quantity of hydrogen was absorbed. The result was 1 g. of a mixture from which it was possible by repeated crystallization in methyl alcohol to obtain a pure compound which crystallized in needles and melted at 206°. This same compound was obtained in a yield of 83% by treating the saturated ketosulfone with phenylmagnesium bromide.

Anal. Calcd. for $C_{21}H_{20}O_3S$: C, 71.6; H, 5.7. Found: C, 71.4; H, 6.0.

α-Hydroxy-β,β-diphenylpropenyl Phenyl Sulfone, X.—When the tertiary alcohol VIII is dissolved in any of the common solvents except benzene, the solutions on evaporation deposit more or less pure secondary alcohol. The substance is most easily obtained by employing methyl alcohol. Thus a solution of 0.19 g. of the substance in 15 cc. of hot methyl alcohol was set aside. It deposited 0.07 g. of pure secondary alcohol in five hours and on evaporation yielded an additional 0.09 g. of the same substance. In a capillary tube the secondary alcohol melts, with instant decomposition to a green oil, at about 164°. In bulk it slowly decomposes even at the temperature of a steam-bath. In hot benzene it reverts to the tertiary alcohol melting at 193°.

Anal. Calcd. for $C_{21}H_{18}O_3S$: C, 72.0; H, 5.1. Found: C, 71.8; H, 5.2.

Decomposition by Heat.—A 0.24-g. sample of the secondary alcohol was heated at 100° for forty-five minutes during which time it decomposed completely to a green oil. The oil was dissolved in alcohol, the solution was filtered to remove a small quantity of brown resin and treated with 0.25 g. of phenylhydrazine. It deposited 0.15 g. of a product which was identified later as the phenylhydrazone of β-phenylcinnamic aldehyde.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.6; H, 6.0. Found: C, 84.8; H, 6.2.

β-Phenylcinnamic Aldehyde.—A Grignard reagent was prepared in the usual manner from 17.5 g. of β,β-diphenylvinyl bromide and 1.6 g. of magnesium. To this ethereal solution was added in the course of ten minutes 7.0 g. of ethyl orthoformate. The solution was boiled for six hours, then distilled until the temperature reached 62° where the residue decomposed with vigorous frothing and solidified to a gelatinous mass. After decomposition with iced hydrochloric acid and ether, the ethereal solution was freed from solvent and the residue was boiled with 3% hydrochloric acid to hydrolyze the acetal. The resulting aldehyde was converted into the bisulfite addition product by shaking its ethereal solution with saturated 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 $C_{15}H_{12}O$: 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.

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[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

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[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.