[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ARYLSULFURCHLORIDES AND ARYLSULFURANILIDES

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There are two types of arylsulfurchlorides described in the literature: first, substances containing a nitro group in position ortho to the sulfurchloride radical[2] and, second, compounds which have no nitro group in the molecule, the ortho and para positions being free or substituted.[3]

Both types of substances are colored intensely orange-red. But while the arylsulfurchlorides of the first class give highly-colored derivatives, we find the derivatives of the second class (with no substitution of a nitro group) to be colorless. Zincke, who first prepared and studied these substances, has already stated these facts.[3] He concluded that the color of the mother substances is due to the sulfur-chlorine linkage, while the color of the derivatives is caused by the nitro group.

Lecher, who prepared the phenylsulfurchloride,[4] attributes the color of this compound to the loose sulfur-chlorine bond, calling it a new chromophore. He also shows the analogy to SCl_2.[5] Neither explanation is entirely satisfactory, as they do not explain the different appearance of the derivatives of the two types of arylsulfurchlorides from a unifying point of view. That the sulfur-chlorine linkage is undoubtedly a loose one is readily apparent from the high reactivity of the compounds and from the investigations of Lecher. Another interesting behavior may be noted. If they are treated in indifferent solvents with hydriodic acid, iodine is immediately liberated; but if they are shaken with silver nitrate or silver carbonate, silver chloride is precipitated even with careful exclusion of moisture. Thus, the arylsulfurchlorides seem to exhibit the properties of chlorine in hydrochloric acid as well as chlorine in sodium hypochlorite. From an electronic conception this dual behavior indicates that these sulfurchlorides, when submitted to the action of different classes of reagents, react as if electromers were present. Experiments on this matter have been carried out with the 4-chloro-2-nitrophenylsulfurchloride.

That this peculiar behavior of the chlorine atom as such in these compounds is not responsible for the color of the arylsulfurchlorides, can be shown by comparison with the analogous aliphatic chloro-amines. Here, too, we find that addition of hydriodic acid is followed by liberation of

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[1] International Research Fellow.

[2] Zincke, *Ann.*, **416**, 86 (1918).

[3] Zincke and Eismayer, *Ber.*, **51**, 755 (1918).

[4] Lecher and Holschneider, *Ber.*, **57**, 755 (1924).

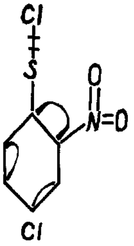
[5] In this case the suggestion that the behavior of the sulfur-chlorine bonds is the direct cause for the development of color is very probable as no further alteration of the molecule can occur.

iodine but, on the other hand, reactions occur with potassium cyanide.[6] The chloro-amines are not appreciably colored. Furthermore, this loose sulfur-chlorine linkage itself does not seem to be the essential chromophore, as Lecher has suggested. It seems, rather, to cause an alteration[7] of the benzoid structure of the molecule and, as a consequence of a shifting of the valences, a quinoid state in the benzene ring is approached. This assumption does not imply that a fixed quinoid structure in the customary sense of the word results from these valence changes.[8]

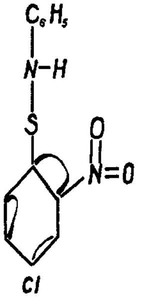
In order to make this assumption clear, it will be explained and discussed on the example of a definite nitro-substituted arylsulfurchloride and an anilide.

The 4-chloro-2-nitrophenylsulfurchloride (II) is unsaturated. We accordingly find, as already mentioned, a tendency for a quinoid structure initiated by the loose sulfur-chlorine bond. This unsaturated state of the molecule remains the same when the anilide (derivative) is formed, because of the unsaturation of the nitro group itself. Therefore, the approached "quinoid" structure of the derivative of type (III) is possible. An aci form (IV), too, is conceivable. In the formulas the attempt has been made to indicate this unsaturation of the molecule by means of curved lines, which represent primary valences not yet shifted to the quinoid end-stage. It is difficult to express this conception with the usual symbols for quinones since we associate with them only an end-stage of unsaturation in the molecule.

I



II



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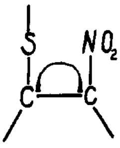

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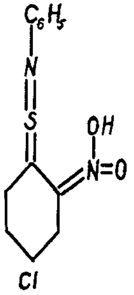

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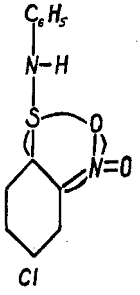

V

To decide whether the actual structure of the 4-chloro-2-nitrophenylsulfuranilide is that expressed in formula (III) or the aci form (IV), the corresponding methylanilide was prepared. In case that the latter (or any ring formation, where the anilido-nitrogen atom participates) should

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[6] Berg, *Ann. chim. phys.*, [7] **3**, 338, 350 (1897).

[7] For a similar conception, to a certain extent, see Georgievics, "Die Beziehungen zwischen Farbe und Konstitution," Schulthess and Co., Zurich, **1921**, pp. 14–15.

[8] Difficulties encountered in avoiding the formation of higher chlorinated products by some arylsulfurchlorides, Ref. 3, for other references see Ref. 4, seem to indicate the expected higher reactivity of such "quinoid" substances.

prove correct, a distinctly less colored derivative would have been expected but, as a matter of fact, a highly-colored orange solution was obtained, indicating that equilibration of the valence forces occurs in the grouping as expressed in formulas (III) and (IIIa). However, from the point of view of the theory of H. Kaufmann[9] a ring formation through residual valences as indicated in formula (V), too, could explain the color phenomena encountered; but the assumption of the approached quinoid state seems to simplify the matter, involving no conception of a "Valenzzersplitterung" and besides representing better the impression of valence force fields.

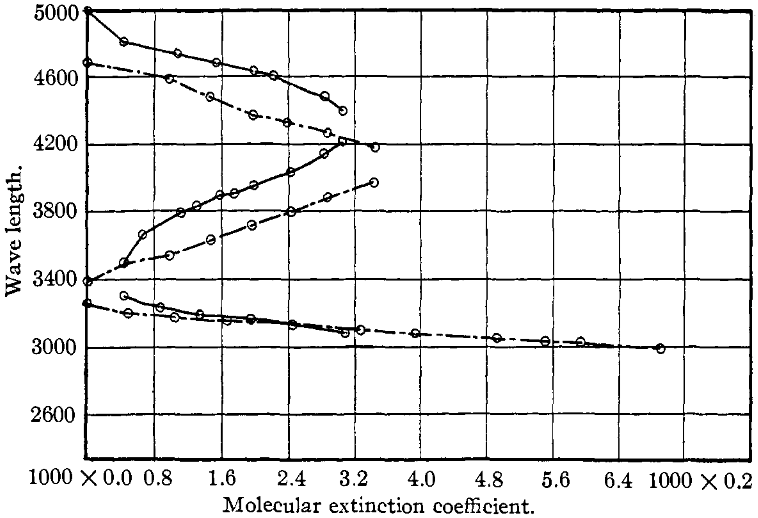

Fig. 1.— —— = 4-chloro-2-nitrophenylsulfurchloride, 0.000449 *M*; — - - — = 4-chloro-2-nitrophenylsulfuranilide, 0.0002018 *M*, in CHCl$_3$.

In the molecule of the arylsulfurchlorides not substituted with a nitro group we find the same loose sulfur-chlorine bond, causing a similar shifting of the valence forces in the whole molecule. But by replacing it by the stronger sulfur-nitrogen linkage, shifting back to the benzoid structure occurs, as there is no possibility of maintaining the initial state, as a consequence of the lack of another unsaturated group. From this point of view, the explanation of the fact of the color in the case of the nitro-substituted arylsulfurchlorides and their derivatives has been shown to be as easy as the explanation of the fact that the derivatives of the also highly-colored sulfurchlorides, not substituted with a nitro group, are colorless.

To verify this assumption, Mr. Palmateer of Chicago University was kind enough to take pictures of the absorption spectra of 1, (a) 4-chloro-2-nitrophenylsulfurchloride and (b) 4-chloro-2-nitrophenylsulfuranilide; 2, (c) 4-chlorobenzenesulfurchloride, (d) 2,5-dichlorobenzenesulfurchloride,

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[9] Kaufmann, "Die Auxochrome," Ahrens Vortrage, **1908**, 12, 1.

(e) 2,5-dichlorobenzenesulfuranilide. The pictures show that the colored substances (a)-(d) appear to have the same structure, and (a) and (b) check almost exactly. No change in the degree of unsaturation occurred through the formation of the anilide. From that it follows that the cause for the color from (a) and (b) is the same, not as Zincke suggested a different one. That the S-Cl bond as such is not the chromophore can be deduced from the same fact. If this were the case we should expect an altered curve for (b), as the supposed chromophore has been changed chemically.

Furthermore, the similarity of (a) and (c) shows that the nitro group as such has no essential part in the development of the color, but only augments the rise of the curves.

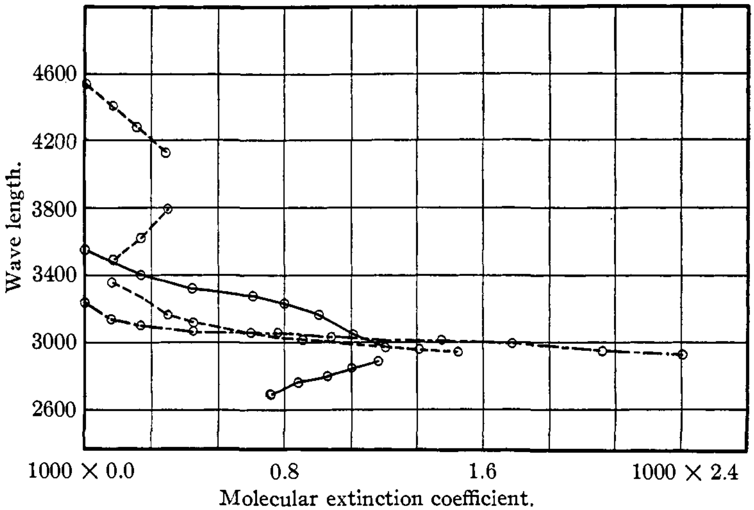

Fig. 2.—$M/1000$ - - - - = 4-chlorobenzenesulfurchloride; $M/1000$ —— = 2,5-dichlorobenzenesulfurchioride; $M/1000$ — - — = 2,5-dichlorobenzenesulfuranilide in $CHCl_3$.

Finally, we see in (e) a new form of the absorption spectrum, indicating an entire change in the structure.

The substances (c) and (d) which were prepared show in their chemical and physical properties a distinct analogy to the phenylsulfurchloride of Lecher, and they have been prepared in the same way. In addition, an anilide of the 4-chloro-2-nitrophenylsulfurchloride was prepared with amino-azobenzene, which is highly red in color. The 4-chloro-2-nitrophenylsulfur radical produced in this case, as expected, a positive color change. It might be possible to utilize this observation in dyestuff chemistry. I hope to present in the future other cases in which an approached quinoid state of organic substances will explain color phenomena.

Experimental Part

The 2,5-dichlorobenzenesulfurchloride was prepared by dropping a solution of 5 g. of well-dried 2,5-dichlorothiophenol into 150 cc. of dry, ice-cold carbon tetrachloride through which was passed a slow current of chlorine. During the reaction the solution, which became yellow, was well stirred. After evaporating the carbon tetrachloride in vacuo the product was obtained by fractionation in a high vacuum. The substance which boiled constantly under 3 mm. at 92° analyzed well for a 2,5-dichlorobenzenesulfurchloride.

Anal. Subs., 0.0971, 0.1511: AgCl, 0.1970, 0.3060; $BaSO_4$, 0.1080, 0.1667. Calcd. for $C_6H_3Cl_3S$: Cl, 49.86, S, 15.03. Found: 50.19, 50.10, 15.28, 15.15.

The corresponding anilide was obtained by treating one molecule of the 2,5-dichlorobenzenesulfurchloride with two molecules of redistilled aniline in well-dried chloroform or carbon tetrachloride. After filtration from aniline hydrochloride and evaporation of the filtrate in a vacuum, the residue was crystallized from ligroin. White needles melting at 85° were obtained.

Anal. Subs., 0.1002: N, 4.6 cc. (763 mm., 22°); 0.1294 g., 5.9 cc. (765 mm., 20°). Calcd. for $C_{12}H_9Cl_2SN$: 5.19. Found: 5.33, 5.35.

The 4-chlorobenzenesulfurchloride was obtained in an analogous way to the 2,5-dichlorobenzenesulfurchloride. Its boiling point under 6 mm. pressure was 94°.

Anal. Subs., 0.1643, 0.1081: AgCl, 0.2650, 0.1740; $BaSO_4$, 0.2177, 0.1417. Calcd. for $C_6H_4Cl_2S$: Cl, 39.62; S, 17.92. Found: 39.90, 39.81, 18.20, 18.00.

If one molecule of 4-chloro-2-nitrobenzenesulfurchloride in ether solution is treated with an ethereal solution of amino-azobenzene, reaction occurs. After filtering off the amino-azobenzene hydrochloride which forms, red crystals are obtained by evaporation of the solution. On recrystallization from ether they melt at 188°. The values from the N combustion agree well with the calculated figures for an **anilide of 4-chloro-2-nitrophenylsulfurchloride with amino-azobenzene.**

Anal. Subs., 0.1424, 0.1167: N, 18.3 cc. (758 mm., 22°), 14.9 cc. (760 mm., 22°). Calcd. for $C_{18}H_{13}N_4O_2ClS$: N, 14.56. Found: 14.83, 14.77.

2,4-Diamino-azobenzene and **4-chloro-2-nitrobenzenesulfurchloride** react apparently in the same way, yielding small brownish-red crystals.

To prepare the **4-chloro-2-nitrophenylsulfurmethylanilide,** 2 moles of methylaniline were treated with 1 mole of 4-chloro-2-nitrophenylsulfurchloride in absolute ether solution. After filtration, the deeply-colored solution was evaporated. The resulting orange-red, sirupy mass could not be obtained in a crystalline form, but solidified after several days. No better results have been observed by the use of other solvents such as chloroform and redistilled methylaniline. Further attempts to obtain this product in a crystalline form will be made. The analysis of the solidified material showed the presence of the expected product.

Anal. Subs., 0.1329, 0.1537: N, 11.1 cc. (765 mm., 21°); 12.9 cc. (750 mm., 21°). Calcd. for $C_{13}H_{11}N_2SClO_2$: N, 9.51. Found: 9.76, 9.58.

The author wishes to express his appreciation to Professor Lauder W. Jones for his assistance in this investigation.

Summary

1. A modified conception of the quinoid theory of colored substances has been offered.

2. Color phenomena in the series of the arylsulfurchlorides and their derivatives have been discussed and explained from this point of view.

3. Absorption spectra of some arylsulfurchlorides and their anilides have been presented and discussed.
4. New arylsulfurchlorides and anilides have been prepared.

PRINCETON, NEW JERSEY

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ACTION OF THE GRIGNARD REAGENT ON ALKYLBARBITURIC ACIDS

BY ARTHUR W. DOX

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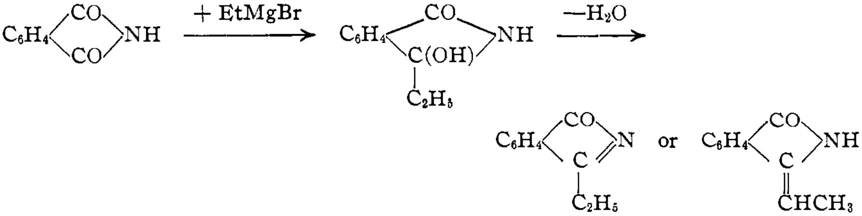
The 5,5-dialkylbarbituric acids, a number of which have come into extensive use as sleep-producing drugs, all contain three carbonyl groups, one or more of which should be expected to react with the Grignard reagent. Although commonly termed "acids," because the unsubstituted parent substance has certain very pronounced acid properties, these derivatives possess more the character of imides. For example, their solubility in alkali is due to a replacement of imide hydrogen by metal. Although two such imide groups are present only one is thus replaceable.

According to Béis[1] the more familiar types of imides, such as phthalimide, react with the Grignard reagent, but here only one of the two carbonyls is affected. With Grignard reagent prepared from normal alkyl halides, Béis noted a dehydration of the initial reaction product. This is attributed to a splitting out of water between the hydroxyl on the nucleus and a hydrogen of the side chain. The product obtained from phthalimide and ethyl magnesium bromide would be, therefore, not an ethyl-*iso*-indolone (Formula I) but rather an ethylidene phthalimidine (Formula II). The phenyl group, on the other hand, cannot give up a hydrogen in this manner and dehydration does not occur, the product with phenyl magnesium bromide being a phenylhydroxy-*iso*-indolinone. However, Sachs and Ludwig[2] obtained from N-ethylphthalimide and ethyl magnesium bromide a product analogous to Béis' phenyl Grignard product. In other words, with imide hydrogen already replaced by alkyl the dehydration



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[1] Béis, *Compt. rend.*, **138**, 987; **139**, 61 (1904).

[2] Sachs and Ludwig, *Ber.*, **37**, 388 (1904).