

of the flask in cold water if it became too hot. After the reaction had subsided somewhat, the remainder of the ester-alcohol mixture was added, and the contents refluxed until all traces of magnesium had disappeared.

The flask contents were chilled and the excess alcohol drained off by placing the flask on its side. Anhydrous ether (50 cc.) and 27.8 g. of triphenylchloromethane were then added to the solid magnesio-malonic ester and the flask gently warmed under reflux upon the water-bath. The reaction then proceeded spontaneously and a solid, partly magnesium chloride and partly the desired ester, separated out. After the spontaneous reaction ceased, the flask was warmed on the water-bath for another hour, and the contents were then removed to a separatory funnel where the magnesium chloride was removed by shaking several times with water. The ether solution was dried over anhydrous sodium sulfate, filtered, ether removed and the residue allowed to stay in contact with 200 cc. of absolute methyl alcohol for twenty-four hours. The solid, recrystallized from alcohol and dried in an 80° oven, amounted to 32 g. (80% yield), and melted at 131–132°. Lund^{7a} and Henderson^{9b} report a melting point of 133°.

Anal. (Schoeller). Calcd. for $C_{26}H_{26}O_4$: C, 77.57; H, 6.51. Found: C, 77.50; H, 6.40.

Preparation of 5-Triphenylmethylbarbituric Acid.—Four grams of urea (an excess) and 13 g. of triphenylmethylmalonic ester were added to sodium ethylate made from 2.7 g. of sodium and 60 cc. of absolute alcohol. The mixture was refluxed for four hours, chilled and 125 cc. of water added. After briefly stirring, the solid was washed on a Büchner funnel with 25 cc. of cold water. The filtrate was made strongly acid with concentrated hydrochloric acid while chilling. The white solid was washed on a Büchner funnel until free of acid and then dried.

The solid was treated with 25 cc. of hot benzene (to remove any triphenylpropionic acid or its ethyl ester) and washed on a Büchner funnel once with hot benzene. The residue, freed from benzene by suction, was washed repeatedly with hot water to free it of any unsubstituted barbituric acid and finally dried in the oven at 80°; yield 2 g.

The barbituric acid is insoluble in cold water, somewhat difficultly soluble in hot benzene, and readily soluble in alcohol and acetone. Insolubility in benzene is a characteristic of monosubstituted barbituric acids.^{5a} The acid is readily soluble in cold dilute alkaline solutions. The m. p. is 197.6° (U. S. P. Corrected), the solid gradually turning purple before melting.

Anal. (micro-Dumas). Calcd. for $C_{23}H_{18}O_3N_2$: N, 7.56. Found: N, 7.67, 7.70.

The barbituric acid gave the characteristic triphenylmethyl group yellow color with concentrated sulfuric acid.

Alkaline Saponification.—One gram of the barbituric acid was refluxed for seventy-five hours with dilute sodium hydroxide. During this refluxing, an increasing amount of crystalline material separated out, having a total weight of 0.172 g. Triphenylcarbinol (m. p. 159°) was isolated by sublimation from this mixture and another crystalline product which, on the basis of the nitrogen assay and without further identification, was considered as triphenylmethylacetylurea. This compound, m. p. 141°, also gave a yellow color with concentrated sulfuric acid.

Anal. (micro-Dumas). Calcd. for $C_{22}H_{20}O_2N_2$: N, 8.14. Found: N, 8.31, 8.15.

The alkaline filtrate was not examined. Acidification resulted in the throwing out of a white solid amounting to 0.715 g. The alkaline solution gave no biuret reaction and produced no color with ferrous sulfate solution.

The author wishes to record his appreciation of the helpful advice of Drs. George D. Beal and Leonard H. Cretcher, Assistant Directors of Mellon Institute.

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RECEIVED SEPTEMBER 1, 1937

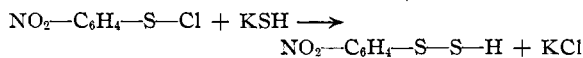
The Reaction of *o*-Nitrophenylsulfur Chloride with Potassium Hydrosulfide

By GREGG DOUGHERTY AND OTTO HAAS

The compound phenyl hydrogen disulfide, $C_6H_5-S-S-H$, has been postulated as the primary intermediate in the reaction of sulfur with benzene in the presence of aluminum chloride.¹ It has been suggested also by White² that compounds of this type are formed as intermediate products in a number of chemical processes such as, for example, the formation of sulfur dyes. White² described very briefly the preparation of a naphthyl hydrogen disulfide.

Lately we have attempted the synthesis of a substituted phenyl hydrogen disulfide with the object in view of determining whether it could be isolated or, if not, the nature of the decomposition products. When *o*-nitrophenylsulfur chloride and potassium hydrosulfide were brought together in equimolar amounts in absolute alcohol, a reaction took place at room temperature. The products were potassium chloride, hydrogen sulfide, sulfur and 2,2'-dinitrodiphenyl disulfide. The disulfide and sulfur were separated by fractional crystallization from alcohol. The dinitrodiphenyl disulfide had the correct melting point of 194° and the same melting point was obtained when it was mixed with some of the disulfide obtained from another source: found S, 20.5%; calcd. S, 20.78%. No compound corresponding to the nitrophenyl hydrogen disulfide was found.

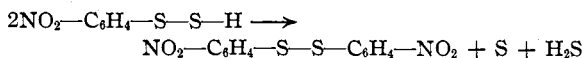
Presumably, as evidenced by the formation of potassium chloride, the following reaction took place



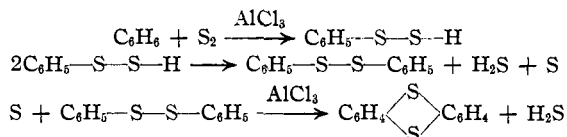
(1) Gregg Dougherty and Philip D. Hammond, *THIS JOURNAL*, **57**, 117 (1935).

(2) G. N. White, *J. Chem. Soc.*, **113**, 608 (1918).

The hydrogen disulfide decomposed, however, as rapidly as it was formed



In view of this result it seems likely that the correct explanation of the formation of thianthrene from sulfur, benzene and aluminum chloride is



That is, it is not necessary to assume, as was done by Dougherty and Hammond,¹ that the diphenyl disulfide was formed from diphenyl sulfide and sulfur. The reaction would undoubtedly take the easier course as outlined in the above equations.

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RECEIVED AUGUST 26, 1937

The Electron Diffraction Investigation of Some Higher Aliphatic Halides

By J. A. A. KETELAAR AND K. J. PALMER

The van der Waals cohesion forces acting between different molecules is without doubt also active between different parts of the same molecule when, as in the higher aliphatic hydrocarbons, due to the rotation around the C-C bond, these parts can come close together without an appreciable increase of energy.¹ Consequently these molecules will tend to have a bent or even a more or less spherical form rather than that of a stretched chain.

In order to test this by a direct method, we have taken electron diffraction photographs of 1,10-dibromodecane, 1,5-dibromopentane, and 1,4-diiodobutane. These photographs show only a very few diffuse rings and much background; this appearance can be accounted for by the interactions between halogen and the two nearest carbon atoms and gives no indication of the halogen-halogen interaction, which would have a large effect in case the halogen-halogen distances were constant. The interpretation of these more or less negative results seems to be that the chains

(1) Even if free rotation is not possible as indicated by the results of J. D. Kemp and K. S. Pitzer, *J. Chem. Phys.*, **4**, 749 (1936), [*THIS JOURNAL*, **59**, 276 (1937)], and of J. B. Howard, *Phys. Rev.*, **51**, 53 (1937), this consideration will remain true, as equilibrium positions differing by a rotation over 120° can be reached, thus leading to a large number of possible configurations.

are indeed not in the stretched form nor in any one contracted form, but that they occupy at the temperature of the experiment a large number of configurations so that no constant large interatomic distances are present. This temperature effect will no doubt also be shown by other large molecules.

We are indebted to the Experimental Station of du Pont de Nemours, Wilmington, Delaware, to Dr. J. van Alphen, Leyden, and to Dr. H. de Vries Robles, Amsterdam, for providing us with samples of the substances used in this investigation.

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RECEIVED SEPTEMBER 28, 1937

The Isolation of Sucrose from Soybeans

By H. R. KRAYBILL, R. L. SMITH AND E. D. WALTER

Street and Bailey¹ have reported the presence of sucrose in soybeans based on an increased reducing value of an extract of the beans following hydrolysis with invertase. Since invertase hydrolyzes other sugars in addition to sucrose, this does not give conclusive evidence of the presence of sucrose. Other workers^{2,3} have reported the difficulty in crystallizing the sugars from soybean extract. Tanret⁴ reported the isolation of sucrose from soybeans but he did not give supporting data characterizing the substance isolated. We have isolated a crystalline substance from soybeans and identified it as sucrose.

In experiments^{5,6} on the extraction of soybeans with different solvents it was noted that a crystalline substance was deposited on the sides of the flask when acetone was used as the solvent. The impure substance collected from the sides of the flask gave negative tests for nitrogen and a positive Molisch test. The substance failed to reduce Fehling's solution.

A larger quantity of the substance was obtained by extracting the beans with petroleum ether to

(1) J. P. Street and E. M. Bailey, *J. Ind. Eng. Chem.*, **7**, 853-858 (1915).

(2) Block, *Bull. sci. pharmacol.*, **14**, 536-551 (1907).

(3) Sadakichi and Sato, *Technology Reports*, **2**, No. 2 (1921), Imperial University, Sendai, Japan.

(4) Georges Tanret, *Bull. soc. chim.*, **13**, 176-182 (1913).

(5) R. L. Smith, Master of Science Thesis, Purdue University, May, 1931.

(6) Annual Report Purdue Univ. Agr. Expt. Station, 1931, p. 54.