which was characterized. It was separated by dissolving 10 g. of the fraction in 75 cc. of 5% sodium hydroxide solution at 100°, and cooling to 0°. This procedure precipitated out the sodium salt of (V) which upon acidification yielded 2.0 g. of the acid (V). The filtrate was saturated with carbon dioxide which precipitated a small amount of diphenylbarbituric acid (II). After filtering off (II) the solution was diluted to 400 cc., heated to boiling, acidified with hydrochloric acid and filtered hot. The material which was filtered off, when dried, weighed 3.0 g. It was a dark brown material, melting between 100–200° to a very tacky liquid. The filtrate upon cooling yielded a crystalline precipitate, which, when filtered and dried, weighed 2.1 g. This product was boiled with 100 cc. of glacial acetic acid. The insoluble portion, when filtered and dried, weighed about 1.3 g. Recrystallization of this material from water gave 1.0 g. of a crystalline substance which still contained sodium and did not melt below 380°. This compound is believed to be the sulfonated diphenylbarbituric acid. Titration showed the neutral equivalent of the substance to be about 370 (calcd., 382).

When 0.496 g. of this material was subjected to a quantitative hydrolysis as described above, the ammonia evolved amounted to 0.043 g. (calcd. 0.044) and the carbon dioxide amounted to 0.118 g. (calcd. 0.114). The acid precipitated upon acidification weighed 0.290 g. (calcd. for the sodium salt of the monosulfonate of diphenylacetic acid, 0.4082). Evaporation of the solution to dryness, and extraction of the finely ground salt with absolute alcohol yielded an additional 0.0843 g. of the acid. The material showed a neutral equivalent of 318 (calcd., 314).

Anal. Calcd. for $C_{14}H_{11}O_6SNa$: C, 53.50; H, 3.53. Found: C, 53.78; H, 4.09.

Attempts were made to remove the sulfonic acid group by boiling for six hours with 20% hydrochloric acid and by heating for five hours in a sealed tube at 190–200° with 20% hydrochloric acid. Neither of these procedures produced any diphenylacetic acid.

Summary

Further study of the condensation of alloxan with benzene has showed that diphenylbarbituric acid is the main reaction product. Diphenylacetylurea, 4-hydroxybenzofuro-[2,3-*d*]-pyrimid-2(4*a*)-one, and a sulfonated diphenylbarbituric acid have been found to be associated products.

MADISON, WISCONSIN RECEIVED AUGUST 9, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

The Dehydrogenation of Hydroaromatic Hydrocarbons with an Alkyl Disulfide

BY JOHN J. RITTER AND EVA DOUGLASS SHARPE

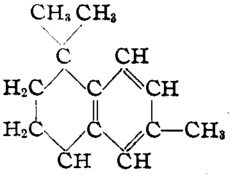
Previous chemical methods for the dehydrogenation of hydroaromatic substances have been limited principally to the well-known sulfur and selenium treatments of Vesterberg[1] and Diels.[2] Dehydrogenation with an alkyl(isoamyl) disulfide has now been accomplished in this Laboratory in the conversion of tetralin to naphthalene and of ionene (1,1,6-trimethyltetralin) to 1,6-dimethylnaphthalene. The general characteristics of the new method, as far as can be concluded from the data at hand, indicate that it is about as efficient as sulfur dehydrogenation in the case of tetralin and distinctly superior in the arylization of ionene. The yield of naphthalene from tetralin (70%) is equal to that resulting from sulfur dehydrogenation[3] while ionene yielded 32% of 1,6-dimethylnaphthalene as compared with the 10–12% reported in the literature.[3,4]

The action of the disulfide on tetralin proceeds as follows

$$C_{10}H_{12} + 2R—S—S—R \longrightarrow C_{10}H_8 + 4RSH$$

Tetralin which contains products of auto-oxidation reacts promptly and comparatively rapidly; after removal of these by distillation over sodium there is no evidence of reaction until three hours have elapsed. This suggests an accelerating effect of oxygen compounds which remains to be confirmed by the study of their dehydrogenation.

The case of ionene presents some interesting aspects. It dehydrogenates in a comparatively short time with formation of somewhat more isoamyl mercaptan than expected from the equation



$$+ 2R—S—S—R \longrightarrow 3RSH + R—S—CH_3 + C_{12}H_{12}$$

No methyl isoamyl thioether could be detected among the reaction products. It was found, however, that about one-half mole of neutral gases is evolved from one mole of ionene during the dehydrogenation. The gases consist in small

---

[1] A. Vesterberg, *Ber.*, **36**, 4200 (1903).

[2] O. Diels, W. Gadke and P. Kording, *Ann.*, **459**, 1 (1927).

[3] L. Ruzicka and E. A. Rudolph, *Helv. Chim. Acta*, **10**, 915 (1927).

[4] M. T. Bogert and Victor G. Fourman, THIS JOURNAL, **55**, 4670 (1933).

part of unsaturates which have not been identified; the greater portion (85%) has been identified as methane, arising in all probability from the methyl group removed from ionene.

This quite unexpected finding suggested incidentally a reëxamination of the sulfur dehydrogenation of ionene according to the usual procedure[3] to discover whether evolution of a hydrocarbon gas occurs as well in this reaction. It was found again that one mole of ionene yields about one-half mole of methane when dehydrogenated with sulfur. This seems noteworthy in view of the common assumption that interfering methyl groups are eliminated in dehydrogenation with sulfur as methyl mercaptan.[3,5]

The foregoing disulfide method (which appears to be the first recorded case of dehydrogenation with combined sulfur) is under further investigation with reference to its suitability in the dehydrogenation of other typical and significant compounds as well as the comparative usefulness of several types of disulfides as dehydrogenating agents.

Experimental Part

Materials.—Isoamyl disulfide (Eastman Kodak Co.) was used without further purification. Disulfide obtained by oxidation of isoamyl mercaptan according to the procedure described later in this article was also used. Tetralin was prepared by refluxing and distilling the commercial product three times over sodium, b. p. 200–201° (uncorr.). Ionene was obtained according to Bogert and Fourman[4] from α-ionone donated by the van Amerigen-Haebler Company at Elizabeth, N. J.

Dehydrogenation of Tetralin.—Tetralin (26.4 g.) and isoamyl disulfide (82.4 g.) are mixed in a flask fitted with an 8″ (20-cm.) Hempel column and air condenser arranged for distillation. The flask is heated at 250–260° in a metal bath for ten hours, or as long as isoamyl mercaptan (b. p. 115°) distils over. The temperature of the bath is varied between the stated limits as necessary to maintain slow and continuous distillation of the mercaptan at the proper temperature; 75 g. of mercaptan is obtained, corresponding to 88% dehydrogenation. A dark colored residue which solidifies on cooling remains in the flask. This is steam-distilled to isolate the naphthalene, which is purified in the ordinary way, yield, 18 g. (70%).

Dehydrogenation of Ionene.—Ionene (34.8 g., 0.2 mole) and isoamyl disulfide (82.4 g., 0.2 mole) are mixed and treated as in the preceding paragraph. The evolved gases are collected in an aspirator after washing with strong caustic potash solution, and proved by combustion to be mostly methane (85.3 mole per cent.) containing some unsaturates. The ionene–disulfide solution is heated for four hours at 250° or until 70 g. of isoamyl mercaptan has distilled and 1400–1500 cc. of gas (over water at room temperature and atmospheric pressure) collected in the aspirator. The crude dehydrogenate, which is a dark colored mobile liquid even at room temperature, is distilled at 13 mm. to remove the volatile compounds from a tarry residue; wt., 25 g. boiling at 120–135°. This is refluxed over sodium and redistilled at 13 mm. to yield 24 g. boiling at 125–130°. This is added to a solution of 20 g. of picric acid in 75 cc. of hot alcohol. The first crop of 1,6-dimethylnaphthalene picrate is increased by further concentration of the mother liquor: wt. of the combined picrates, 25 g. (32%); m. p. 112°. The mixed m. p. with picrate obtained from the sulfur dehydrogenation of ionene showed no depression.

Sulfur Dehydrogenation of Ionene.—Ionene (32 g.) is dehydrogenated with sulfur (11.8 g.) at 250–260° as in the disulfide dehydrogenation. After eleven hours, 1050 cc. of gas (over water, at 31° and atmospheric pressure) collects in the aspirator. This proved to consist entirely of methane mixed with some air present in the system initially. 1,6-Dimethylnaphthalene picrate is isolated as outlined by Ruzicka and Rudolph;[3] yield, 8 g. (*ca.* 10%); m. p. 112°.

Oxidation of Isoamyl Mercaptan to Disulfide.—Mercaptan recovered from dehydrogenation experiments (324 g.) is dissolved in an equal volume of glacial acetic acid in a 2-liter three-necked flask fitted with a mechanical stirrer, thermometer and dropping funnel. The flask is immersed in an ice-water bath and stirred until the temperature of the mixture falls to 5°; 225 g. of superoxol (about 25%) dissolved in an equal volume of glacial acetic acid is added slowly from the dropping funnel with constant stirring. The peroxide addition requires one hour, and the temperature is not permitted to rise above 20°. The progress of the oxidation is noted from time to time by testing with starch–iodide paper, addition of the peroxide being interrupted for a short interval when the blue color appears rapidly on the test paper. The reaction mixture is stirred for four hours after all of the peroxide has been added and is allowed at the same time to warm to room temperature. A further quantity of superoxol in acetic acid may be added during this period if necessary to give a positive starch–iodide test. The mixture separates into two layers, the upper one consisting mainly of the disulfide. The layers are separated and the lower (acetic acid) layer added to three volumes of saturated salt solution to separate a further quantity of the product. This is combined with the main portion and the combined material washed successively with salt solution, water, 20% potassium hydroxide solution and finally twice with water. It is dried over anhydrous potassium carbonate and distilled at 10 mm. The entire product boils at 122–124°, yield 276 g. (86% of calcd.).

Summary

The dehydrogenation of tetralin and of ionene with isoamyl disulfide has been accomplished.

Elimination of the methyl group from ionene in both sulfur and disulfide dehydrogenation has been shown to occur with detachment of that group as methane.

NEW YORK, N. Y.

RECEIVED SEPTEMBER 9, 1937

---

[5] L. Ruzicka, J. Meyer, and M. Mingazzini, *Helv. Chim. Acta*, **5**, 345 (1922).