

Dehydrogenations by means of Sulfur: Adaptation as an Experiment for General Organic Chemistry Course

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The literature contains numerous references to reactions between sulfur and pure individual organic compounds. While the action of sulfur on organic compounds is frequently thought of merely as a means for preparing hydrogen sulfide, the reaction may serve for dehydrogenation, ring closure, addition of sulfur and other purposes.

Although the element sulfur has for many decades been used for removing hydrogen from compounds, this property has not received much attention in the general organic chemistry course. Most introductory text books ignore sulfur dehydrogenation, or, at most, make only brief reference to the subject; probably none of the laboratory manuals include any experiments on this procedure. Over the years a fairly large variety of dehydrogenations has been reported. By heating a mixture of sulfur and diphenyl methane, Ziegler obtained the olefin tetraphenyl ethylene. Using a sealed tube, Aronstein obtained stilbene (or 1, 2-diphenylethylene) from sulfur and toluene. Hydroaromatic compounds such as tetrahydronaphthalene can be made to liberate their surplus hydrogen by heating with sulfur at 180°-250°. Various alkylated tetrahydronaphthalenes yield similar results. In the study of terpenes, sulfur dehydrogenations have played an important part. Other types of compounds which have been dehydrogenated by this process include certain acids, as abietic acid; aromatic ethers, and even certain sulfur compounds, such as diphenyl sulfide and cyclohexanthiol.

Some of these dehydrogenations could be adapted to form interesting experiments in a general organic chemistry course. A single example will be considered.—A rather intriguing reaction is one investigated by von Mantz and Graebe about 50 years ago. By heating a mixture of sulfur and fluorene at 350° these astonished researchers obtained hydrogen sulfide and a red solid. Repeated attempts to purify their product failed to remove the color from the reddish needle-like crystals, whose formula indicated the unsaturated compound, bis diphenylene-ethylene.

This procedure can readily be carried out by a student by heating a mixture of 5 g. fluorene and 1½ g. sulfur to gentle boiling for ¾ hour, during which time hydrogen sulfide is evolved. The red compound may then be isolated by extracting the black residue with several portions of hot benzene. After treating the solution with charcoal the product can be separated as a reddish orange powder. When this powder is recrystallized from chloroform, microscopic crystals are obtained.

Although this dehydrogenation involves only simple procedures the experiment is of interest since a colorless hydrocarbon is transformed into a colored compound merely by removing hydrogen. Other dehydrogenations could be selected to provide any desired degree of difficulty.