tion of 7.7 g. (0.03 mole) of triphenylaluminum in a three-necked flask fitted with an inlet for nitrogen, a mechanical stirrer and a reflux condenser closed by a tube filled sufficiently with sulfuric acid to assure a positive nitrogen pressure, there was added 12 g. (0.1 mole) of acetophenone. No immediate reaction was perceptible. After thirty minutes a flocculent precipitate appeared. The mixture was now heated in an oil-bath at 100–115° for six hours after which it was allowed to stand for six hours at room temperature. The thick, pasty reaction mixture was poured into 100 cc. of water containing 2% nitric acid. The toluene layer was separated, washed with water and 10% sodium bicarbonate and dried over sodium sulfate. The solvent was removed by distillation and the residue was twice vacuum fractionated at 9 mm. Two fractions were obtained: (A) b. p. 108–120°, 3 g.; (B) b. p. 190–195°, 4 g.; residue, 3 g. that did not distill up to 270°. This residue set to a hard amber colored resin-like mass soluble in acetone but sparingly soluble in alcohol and ether.

Fraction B.—Dypnone by m. p. and mixed m. p. of oxime,[17] 133–134°.

Fraction A.—This material was shaken for fifteen hours with a saturated solution of sodium bisulfite to remove any ketone. The oil was then extracted with ether and dried over sodium sulfate. Distillation gave 2 g. of a product boiling at 272–277°; n^{14}_{D} 1.6070; 0.1 g. of this material in dry chloroform immediately discharged the color of bromine[18] to form an addition product that evolved hydrogen bromide when the solvent was removed.

Oxidation[18] of 0.8 g. of this oil at 80° for five hours gave a product which when extracted from alkaline solution by ether would not crystallize at room temperature, but gave 1 g. of an oxime, melting[18] (p. 150) at 140–141° and showing no depression of m. p. when mixed with a known sample of benzophenone oxime. It was concluded that the substance was α,α-diphenylethylene.

In a run in which acetophenone was refluxed with sodium-dried toluene for thirty-six hours, no dypnone was found.

The authors are grateful to Mr. Thomas Campbell who kindly prepared some of the starting materials.

Summary

1. The evolution of hydrogen halide in the Friedel–Crafts ketone synthesis is not a satisfactory criterion for judging the optimum period of reaction.
2. Drastic and prolonged reaction conditions and especially the use of an insufficient proportion of aluminum chloride tend to encourage condensation of ketones primarily formed by acylation.
3. Aluminum chloride is capable of condensing acetophenone to form dypnone and a mixture of acetophenone and benzaldehyde to form chalcone.
4. Triphenylaluminum similarly will produce dypnone from acetophenone.

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[17] Henrich and Wirth, *Ber.*, **37**, 731 (1904).

[18] Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., N. Y., Vol. I, First Edition, 1904, p. 194.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Oxidation of Ethyl Mercaptan and Ethyl Disulfide by Bromine in the Presence of Water

BY H. A. YOUNG

Dilute carbon tetrachloride solutions of ethyl mercaptan and ethyl disulfide are oxidized in a normal manner[1] to ethyl sulfonic acid by bromine water, as represented by the equations

$$\mathrm{RSH} + 3\mathrm{Br_2} + 3\mathrm{H_2O} = \mathrm{C_2H_5SO_3H} + 6\mathrm{HBr} \quad (1)$$

$$\mathrm{C_2H_5SSC_2H_5} + 5\mathrm{Br_2} + 6\mathrm{H_2O} = 2\mathrm{C_2H_5SO_3H} + 10\mathrm{HBr} \quad (2)$$

Ethyl mercaptan is converted instantaneously and quantitatively to the disulfide in the absence of water, in accord with the results of Otto and Rossing.[2]

Experimental Part

Equivalents of Bromine Used per Mole of Sulfur Compound

Ethyl Mercaptan.—Carbon tetrachloride solutions of the mercaptan were prepared and analyzed just before use by the iodimetric method of Reid.[3] A measured volume of mercaptan solution (approximately 0.005 *M*) was introduced into a 250-cc. glass-stoppered flask containing 100 cc. of water and a measured volume of a known solution of bromine (excess) in carbon tetrachloride was added immediately. The flasks were then put in a shaker in a 25° thermostat, and after various times were withdrawn, 2 g. of solid potassium iodide added, and the liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution. The results of a series of such experiments showed that 6.00 ± 0.03 equivalents of bromine were used per equivalent of

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[1] It is well known that strong oxidizing agents convert mercaptans and disulfides to the corresponding sulfonic acids. Friedman [*Beitr. Chem. Physiol. Path.*, **3**, 25, 38 (1903)] has shown that bromine oxidizes cystine and cysteine to cysteic acid.

[2] Otto and Rossing, *Ber.*, **19**, 3136 (1886).

[3] Sampey and Reid, THIS JOURNAL, **54**, 3405 (1932).

mercaptan and that the reaction was complete in about twenty-four hours.

Ethyl Disulfide.—Since no method of analysis is known for disulfides, it was necessary to weigh a sample of ethyl disulfide for each experiment. This was done by introducing the disulfide from a dropping pipet with a long capillary into a weighed, thin-walled glass weighing ampoule. The ampoule was iced, sealed, dried and reweighed, after which it was dropped into a 250-cc. glass-stoppered flask containing a known excess amount of bromine in carbon tetrachloride and 100 cc. of water. The subsequent treatment was the same as with the mercaptan.

In these experiments it was found that the bromine used was almost always about 1% high. Blank experiments showed that this error was due to loss of bromine during the manipulations, probably chiefly during the introduction of the ampoule containing the ethyl disulfide. Table I gives two typical experiments.

TABLE I

Expt.	R_2S_2, g.	Eq. Br_2 per mole R_2S_2	Correction	Eq. Br_2 per mole R_2S_2 corr.
1	0.0776	10.11	0.15	9.96
2	.1324	10.14	.14	10.00

In view of the above data it seems safe to conclude that these measurements are good to about 1.5% in spite of the relatively high volatility of every substance involved, and that the main reactions are probably those suggested in equations 1 and 2.

Oxidation of Ethyl Mercaptan by Dry Bromine.—The amount of bromine used by ethyl mercaptan in the absence of water was measured by mixing dilute carbon tetrachloride solutions of a known amount of ethyl mercaptan with a known excessive amount of bromine. After various times, the solutions were shaken with aqueous solutions of potassium iodide and the resulting iodine titrated with sodium thiosulfate solution.

The amount of hydrogen ion produced in the reaction was measured in a similar fashion by using excess ethyl mercaptan. The carbon tetrachloride solutions were extracted and washed with water and the extract titrated with standard sodium hydroxide solution.

The results of a series of experiments in which the mercaptan concentration varied from 0.003 to 0.03 *M* showed that 1.00 ± 0.01 equivalents of bromine were used per mole of mercaptan; those of a second series in which the bromine concentration varied from 0.003 to 0.025 *M* indicated that 1.00 ± 0.03 moles of hydrogen ion were liberated per equivalent of bromine used.

These experiments also showed that the reaction was complete within forty-five seconds after mixing, and that no further reaction took place.

Identification of Ethyl Sulfonic Acid.—The oxidation reactions were allowed to go to completion in reaction mixtures containing 12 g. of the sulfur compound and 100 g. of bromine. The water layer was separated, concentrated by evaporation, neutralized with sodium hydroxide and evaporated to dryness. After drying at 120° for three hours, the sodium ethyl sulfonate was extracted by use of hot 95% ethyl alcohol. The sodium salt was then converted to the corresponding acid chloride by the method of Marvel, Helfrick and Belsley.[4] The acid chlorides obtained boiled at 177° which compares with a boiling point of 177.5° given by Carius.[5]

Summary

1. Ethyl mercaptan and ethyl disulfide are oxidized to ethylsulfonic acid by bromine water, the oxidation requiring 3 and 5 moles of bromine per mole of the sulfur compound, respectively.

2. Ethyl mercaptan is very rapidly oxidized to ethyl disulfide by dry bromine.

(4) Marvel, Helfrick, and Belsley, THIS JOURNAL, **51**, 1272 (1929).

(5) Carius, *J. prakt. Chem.*, [2] **2**, 264 (1870).

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[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Rate of Oxidation of Ethyl Disulfide by Bromine

BY H. A. YOUNG AND M. B. YOUNG

In the preceding paper,[1] it has been shown that bromine oxidizes ethyl disulfide to ethylsulfonic acid in the presence of water, and that under proper conditions five moles of bromine are used for each mole of disulfide oxidized. While performing the experiments described in the above paper, it was noted that immediately upon the addition of ethyl disulfide to a carbon tetrachloride solution of bromine, the color of the latter changed perceptibly, becoming lighter and a more pronounced yellow. Also when excess disulfide was added to bromine, distributed between water and carbon tetrachloride, the bromine was almost completely removed from the water layer.[2] These observations suggest the rapid formation of an addition compound between bromine and ethyl disulfide. That the formation of the addition compound is reversible is shown by the fact that a known amount of bromine which has been treated for several hours

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(1) H. A. Young, THIS JOURNAL, **59**, 811 (1937).

(2) A similar effect is noticed with iodine. Excess ethyl disulfide in carbon tetrachloride will remove enough iodine from a water layer to prevent the formation of a blue color in the presence of starch, as first noted by Sampey and Reid, *ibid.*, **54**, 3405 (1932).