[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. X. The Identification of Methyl Groups as Dimethyl Ditelluride

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All the numerous methods that have been used[2] for the identification of the fragments produced in the thermal decomposition of organic compounds suffer from the drawback that the primary product formed by combination with the free radical cannot be separated readily from the excess of organic compound and identified but must first be converted into some other compound having more suitable properties. Obviously it would be advantageous to find a substance which would combine with free radicals to give a compound which could be separated readily from the excess of the original substrate and could also be identified easily. We have found that metallic tellurium is almost ideal in this respect. When the fragments obtained in the thermal decomposition of butane, acetone or diethyl ether are brought into contact with metallic tellurium, a deep red liquid, dimethyl ditelluride $CH_3TeTeCH_3$ is the only product. This compound has a low vapor pressure at room temperature (probably less than 0.1 mm.) so that it can be separated easily from the excess of the organic compound used to produce the free radicals; further, it is stable in the air and melts sharply at −19.5°.

Experimental

Butane was passed through a quartz tube heated by means of an electric furnace to about 900°; approximately 2 cm. beyond the end of the furnace a small piece of tellurium (0.1 to 0.2 g.) had been distilled onto the walls of the quartz tube, so that it formed a very heavy mirror. We used a sliding furnace on the quartz tube; during a run the end of the furnace was kept about 1.0 cm. from the edge of the mirror. In spite of the fact that the quartz tube at this point was kept cool by an air jet the tellurium mirror was probably at some temperature in the range 100–200°, owing to radiation from the furnace. We may note that Paneth[3] has shown that the products of interaction of arsenic, antimony and bismuth mirrors with methyl or ethyl radicals depend somewhat on the temperature of the mirror. The gases leaving the furnace passed over the tellurium and then passed through a U-tube at −80°; they were then passed through a liquid air trap and finally through the pumping system. A bright red solid condensed in the U-tube at −80°, while the butane and its decomposition products passed through to the liquid air trap. The condensate in the U-tube melted to a deep red liquid resembling bromine and an analysis for carbon and hydrogen gave 8.64% carbon and 2.14% hydrogen; the corresponding values for dimethyl ditelluride are 8.42 and 2.10%, respectively. The material remains unchanged on exposure to air for several hours but very prolonged exposure apparently causes polymerization. Bright sunlight also causes some sort of polymerization, producing a deep red solid even in the absence of air. The original liquid is soluble in the usual organic solvents such as alcohol, benzene and ether. It is insoluble in water and does not react with it. It melts sharply at −19.5° and boils with decomposition at 196°. This substance does not appear to have been described in the literature although Drew[4] mentions an orange oil, which he states is probably dimethyl ditelluride, formed by the reduction of dimethyl telluronium dihalides.

In order to confirm the identity of the compound we placed 0.156 g. of tellurium in the tube just beyond the furnace and passed butane through the furnace until all the tellurium was removed. We recovered 0.163 g. of product, which corresponds to a 94% yield of dimethyl ditelluride. Analysis of this sample[5] gave C, 8.78 (theoretical, 8.42), H_2, 2.06 (theoretical, 2.10). It is clear, therefore, that nothing is formed in significant amounts by the action of the fragments from butane on metallic tellurium except dimethyl ditelluride. Similar results were obtained when we used diethyl ether or acetone instead of butane.

Summary

Metallic tellurium has been shown to be an excellent agent for the identification of methyl groups. The product of their interaction is dimethylditelluride $CH_3TeTeCH_3$. This compound is a deep red liquid, f. p. −19.5°, b. p. (with decomposition) 196°; it is comparatively stable in air, insoluble in water but soluble in the common organic solvents.

It was found that methyl groups are the only fragments that escape from the furnace when butane, acetone or diethyl ether is decomposed at low pressures in the range 800–900°.

BALTIMORE, MARYLAND RECEIVED AUGUST 11, 1934

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[1] General Motors Research Corporation Fellow, 1930–1934.

[2] (a) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929); (b) Paneth and Lautsch, *ibid.*, **64**, 2702 (1931); (c) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932); (d) Simons and Dull, *ibid.*, **55**, 2696 (1933); (e) Rice and Evering, *ibid.*, **56**, 2105 (1934).

[3] Paneth, *Trans. Faraday Soc.*, **30**, 179 (1934).

[4] Drew, *J. Chem. Soc.*, 560 (1929).

[5] We also attempted to find the molecular weight of this sample by measuring the rise in boiling point in benzene solution [Smith and Milner, *J. Mikrochem.*, **9**, 117 (1931)]. We obtained the value 314 as compared with the theoretical value of 285. However, our experimental error was probably ±10% so that we may conclude that the compound has the normal molecular weight in benzene within these limits.