

AROMATIC ALLYL- AND PROPENYL-COMPOUNDS ¹⁾III. *iso*-Safrole Dibromide.

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isoSafrole dibromide was obtained by O. Wallach and F. J. Pond ²⁾ as a colourless oil, P. Hoering and F. Baum ³⁾ obtained a substance melting at 51° C., and Mannich ⁴⁾ also obtained a solid product melting at 52—53° C.

Crystallisation of the oily dibromide does not occur spontaneously on cooling, but it may be started by the addition of a crystal of the solid substance.

Mannich prepared his dibromide from *isosafrole* (100 g) in petroleumether (100 g), which he carefully treated with a solution of bromine (100 g) in light petroleum (100 g); the lower layer solidified when inoculated with a crystal.

Bromine estimation. Found Br. = 49.41 %. Theor. 49.66 %.

R. P. Foulds and R. Robinson ⁵⁾ brominated in carbon disulphide solution and obtained the crude product as a viscous oil containing 46.4 % of bromine. It appears that they were ignorant of the results obtained earlier by other investigators. S. Nagai ⁶⁾ worked according to this method and obtained dark brown viscous oils after bromination of his "*cis*"- and "*trans*"-*isosafroles*. Although his *isosafroles* were undoubtedly mixtures of *safrole* and *isosafrole* ⁷⁾, his results will be considered, because they are mentioned in the literature ⁸⁾. His dibromides were optically active.

The properties as given by Nagai were:

trans isosafrole dibromide:

$$d_4^{15} 1.7545 - 1.7561 \quad d_4^{20} 1.745 - 1.746 \text{ calculated to } 20^\circ \text{ with the factor}$$

$$n_D^{15} 1.6028 - 1.6042 \quad n_D^{20} 1.6006 - 1.6020 \quad \frac{\Delta \text{ S.W.}}{\Delta t} = -0.00195 \text{ (} \frac{1}{1000} \text{ of the Spec. grav. } ^9)$$

$$\text{M.R. found } 62.70 - 63.36, \text{ calc. } 61.40. \quad \frac{\Delta n}{\Delta t} = -0.00045$$

$$[\alpha]_D^{20} + 4.45 - + 4.53. ^9)$$

¹⁾ Former papers, this Journal 47, 849 and 1027 (1928).

²⁾ Ber. 28, 2719 (1895).

³⁾ Ber. 42, 3076 (1909).

⁴⁾ Arch. Pharm. 248, 166 (1910).

⁵⁾ J. Chem. Soc. 105, 1921 T (1914).

⁶⁾ J. Coll. Eng. Tokyo Imp. Univ. 11, 83 (1921).

⁷⁾ H. I. Waterman and R. Priester, l.c.

⁸⁾ G. Cohn, Die Riechstoffe, 2e Aufl., 1924, 123.

⁹⁾ See W. A. Roth and F. Eisenlohr, Refraktometr. Hilfsbuch 1911, p. 75, 76.

cis isosafrole dibromide:

d_4^{15} 1.7525 — 1.7550 d_4^{20} 1.743 — 1.745 calculation see above.

n_D^{15} 1.6015 — 1.6061 n_D^{20} 1.5993 — 1.6039

M.R. found 63.26 — 63.32, calc. 61.40 $[\alpha]_D^{20}$ + 13.35 — + 13.71.

Although the bromination is generally carried out in carbon tetrachloride, we followed Fould's and Robinson's method. We started from a commercial isosafrole (product B) [this Journal 47, 851 (1928)] and obtained an olive green, very viscous oil after bromination, which had *no optical rotation*. d_4^{20} 1.7661, n_D^{20} 1.6061.

The dibromide undergoes a change at room temperature to a slight extent into bromoisosafrole and hydrogen bromide; by distilling under diminished pressure much hydrogen bromide is evolved and bromoisosafrole is obtained. Foulds and Robinson have prepared the monobromide in this way. In this connection we would draw attention to the fact, that it is inadvisable to distill a large quantity of dibromide at once and to raise the temperature above 170° (measured in the oil bath), because spontaneous decomposition may occur with the production of sufficient heat and gas to burst the flask. The contents of the flask are then completely changed into a porous, carbonaceous mass. An attempt to distill the dibromide in a cathode light vacuum failed because decomposition was observed at about 70° C. (measured in the oil bath). A part of the dibromide must have distilled without decomposition because the distilled oil evolved considerable quantities of hydrogen bromide on the application of gentle heat.

A viscous oil devoid of optical activity was obtained from an isosafrole purified by means of the addition compound with picric acid. We succeeded in distilling this oil without decomposition in a special cathode light vacuum apparatus, constructed by Waterman and Elsbach¹⁰⁾.

With a bath temperature of about 60° C. and a vapour temperature of 48—48.5°, 1—2 drops of a colourless oil distilled per minute; on cooling, the oil solidified and the melting point was 52—53°.

Bromine determination by the method of Stepanow¹¹⁾ 49.4 % bromine, calc. 49.66 %.

d_4^{20} 1.7682, n_c^{20} 1.6033, n_D^{20} 1.6095, n_F^{20} 1.6261.

The order of the different coloured bands in Pulfrich's refractometer was reversed (anomalous dispersion).

M.R. found 63.08, calc. 61.40.

The product had no optical activity.

Summary.

Pure isosafrole dibromide has a melting point of 52—53° as found

by Mannich. Foulds' and Robinson's product as well as that of S. Nagai were impure. We can neither explain nor confirm the optical rotation found by Nagai. isosafrole dibromide can be distilled in the cathode light vacuum without decomposition on condition the temperature of the liquid does not rise above 60° C.

The refractivity and the specific gravity of the distilled product were determined.

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¹⁰⁾ A subsequent paper will appear on this subject.

¹¹⁾ Ber. 39, 4056 (1906), see also van 'Duin, this Journal 45, 363 (1926).