CXCI.—2-*Phenyl*-5-*styryloxazole.*

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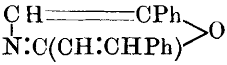
MINOVICI (*Ber.*, 1896, **29**, 2102) obtained a product melting at 62°, regarded as 5-phenyl-2-styryloxazole (I), by the condensation of benzaldehydecyanohydrin and cinnamaldehyde effected by hydrogen chloride, and in a similar manner Lister and Robinson (T., 1912, **101**, 1303) found that cinnamaldehydecyanohydrin with benzaldehyde yielded a substance melting at about 88°, which might be 2-phenyl-5-styryloxazole (II). Since, however, the latter authors (*loc. cit.*) proved that 5-phenyl-2-styryloxazole, prepared by the dehydration of ω-cinnamoylaminoacetophenone (III), melts in reality at 106°, and that the product melting at 62° is a mixture, it became desirable to synthesise 2-phenyl-5-styryloxazole also, in order to fix its melting point. Actually, we find that this substance melts at 105°, and can readily be produced by submitting styryl benzoylaminomethyl ketone (IV) to the action of concentrated sulphuric acid:



$$\left.\begin{array}{l}\mathrm{CH{=\!=\!=\!=}CPh}\\ \mathrm{N{:}C(CH{:}CHPh)}\end{array}\right\rangle \mathrm{O}$$

(I.)

$$\left.\begin{array}{l}\mathrm{CH{:}C(CH{:}CHPh)}\\ \mathrm{N{=\!=\!=\!=}CPh}\end{array}\right\rangle \mathrm{O}$$

(II.)

$\mathrm{COPh{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH{:}CHPh}$

(III.)

$\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}COPh}$

(IV.)

$\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}NH_2}$

(V.)

$\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH{:}NOH}$

(VI.)

This amide is obtained by the action of benzoyl chloride and sodium acetate on an acetic acid suspension of the stannichloride of styryl aminomethyl ketone (V), which, in its turn, is prepared by the reduction of styryl oximinomethyl ketone (VI) by means of a solution of stannous chloride in concentrated hydrochloric acid. The yields at all stages are excellent.

EXPERIMENTAL.

Salts of Styryl Aminomethyl Ketone (V).

In order to obtain satisfactory yields of styryl oximinomethyl ketone it was found necessary to modify Claisen and Manasse's process (*Ber.*, 1889, **22**, 529), and the following procedure was ultimately adopted: Styryl methyl ketone (5 grams) was dissolved in light petroleum (b. p. 50—60°, 100 c.c.), and gradually treated with freshly distilled *iso*amyl nitrite (12 grams) and concentrated hydrochloric acid (2 c.c.). The temperature was not allowed to rise above 20°, and after allowing to remain for three hours the oximino-derivative which had crystallised from the solution was collected.

Styryl Aminomethyl Ketone Stannichloride.—Finely powdered styryl oximinomethyl ketone (10 grams) was stirred with a solution of stannous chloride (30 grams) in concentrated hydrochloric acid (70 c.c.). After remaining overnight the crystalline precipitate was collected on a platinum cone, washed with concentrated hydrochloric acid, and dried in the air on porous porcelain. This stannichloride is soluble in hot water or methyl alcohol, but separates in prismatic crystals when hydrochloric acid is added to its solution in these solvents. This crystallisation is, however, always accompanied by a certain amount of decomposition, so that satisfactory analytical results were never obtained.

Platinichloride.—Hydrogen sulphide was passed into a solution of the above stannichloride in hot dilute hydrochloric acid for such a length of time that the tin was almost, but not quite, completely precipitated as sulphide. The platinichloride separated on the addition of platinic chloride to the filtered solution, and was obtained in orange-yellow needles by crystallisation from dilute hydrochloric acid:

0·1420 gave 0·0395 Pt. Pt=27·8.

$(C_{10}H_{11}ON)_2H_2PtCl_6$ requires Pt=26·6 per cent.

This derivative is sparingly soluble, and, when heated, begins to decompose at 190°.

Picrate.—Aqueous picric acid was added to the solution of the hydrochloride obtained as above by eliminating tin from the solution of the stannichloride. The copious, yellow precipitate was collected, and crystallised from methyl alcohol, in which it is rather sparingly soluble. The long, yellow needles so obtained melt and decompose at 167°:

0·1665 gave 0·3018 CO_2 and 0·0541 H_2O. C=49·4; H=3·6.

$C_{10}H_{11}ON,C_6H_3O_7N_3$ requires C=49·2; H=3·6 per cent.

Styryl Benzoylaminomethyl Ketone (IV).

Styryl aminomethyl ketone stannichloride (10 grams) was suspended in glacial acetic acid (50 c.c.), and, together with benzoyl chloride (10 grams) and fused sodium acetate (20 grams), heated on the steam-bath during a quarter of an hour. Dilute hydrochloric acid was then added, and the liquid extracted with a large volume of ether. The ethereal solution was washed with dilute aqueous sodium hydroxide and much water, dried, and at the same time treated with animal charcoal, filtered, and evaporated to small bulk. The benzoyl compound crystallised from the solution, and was purified by recrystallisation from methyl alcohol. It occurs in long, glistening needles, melting at 121°, and is sparingly soluble in ether, cold benzene, or alcohol:

0·1316 gave 0·3707 CO_2 and 0·0686 H_2O. C=76·8; H=5·8.
$C_{17}H_{15}O_2N$ requires C=77·0; H=5·7 per cent.

2-*Phenyl*-5-*styryloxazole* (II).

The above amide (2 grams) dissolved readily in concentrated sulphuric acid (10 c.c.), and the reaction was complete after allowing the solution to remain during three minutes.

Water and ammonia were added to the liquid, and the precipitated oxazole after collection was crystallised from light petroleum (b. p. 70°). The colourless, prismatic needles melted at 105°:

0·1358 gave 0·4116 CO_2 and 0·0665 H_2O. C=82·7; H=5·4.
$C_{17}H_{13}ON$ requires C=82·6; H=5·3 per cent.

The substance is, for a compound of this type, unusually sparingly soluble in boiling light petroleum, but very readily so in ether, alcohol, or benzene. Its solution in light petroleum exhibits intense blue fluorescence, and this property is also apparent in the solid, which has the appearance of triphenylmethane. A mixture of the two phenylstyryloxazoles could not be separated by crystallisation from light petroleum. The apparently homogeneous substance melted at about 90°, and it is accordingly probable that when cinnamaldehydecyanohydrin and benzaldehyde are condensed by means of hydrogen chloride the formation of 2-phenyl-5-styryloxazole is accompanied by that of 5-phenyl-2-styryloxazole, due, possibly, to a reaction between the cyanohydrin and the aldehyde resulting in the production of a certain amount of benzaldehydecyanohydrin and cinnamaldehyde.

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