CCCXC.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part III. Some Reactions of Thionylalizarin.*

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SINCE thionylalizarin appears to be the most reactive of the thionyl compounds previously examined (J., 1924, **125**, 1450; 1926, 2198; this vol., pp. 500, 554, 2341), a further study of its reactions has been carried out.

It is now shown that although the interaction between the thionyl compound and *weak* organic acids provides a general method of preparing the corresponding 2-acyl derivatives of alizarin, yet with the stronger organic acids the thionyl derivative reverts to alizarin. The following acids yield 2-monoacyl derivatives : acetic (*loc. cit.*), phenylacetic, phenoxyacetic, cinnamic, benzoic, *o*-toluic, *m*-bromobenzoic, and *p*-bromobenzoic. Monochloroacetic acid gives a mixture of alizarin and a substance having the appearance of its monochloroacetate, whilst with dichloroacetic, trichloroacetic, and dibromoacetic acids thionylalizarin gives alizarin only.

It is thus clear that the reaction which a thionyl compound undergoes with an organic acid depends on the nature of that acid. The nature of the thionyl compound is also a factor, for while the thionyl derivatives of alizarin and of pyrocatechol are quantitatively converted into their monoacetates (*loc. cit.*) by acetic acid, yet under the same conditions thionylhystazarin (*loc. cit.*) gives hystazarin only.

Diacyl derivatives are obtained by the action of benzoic anhydride, benzoyl chloride and acetyl chloride, but succinic and phthalic anhydrides react neither with thionylalizarin nor with alizarin itself. This may be accounted for by the fact that the production of alizarin succinate (or phthalate) would necessitate the formation of a cyclic structure of eight atoms. Dibenzoylalizarin has been obtained in two crystalline modifications, melting at 160° (labile) and at 187° respectively.

The thionyl compound is rapidly decomposed, with evolution of sulphur dioxide, by boiling absolute ethyl alcohol and by hot phenol and in both cases the products are pure alizarin.

In attempts to prepare ethers by the condensation of thionylalizarin with alkyl halides and with alkyl sulphates no reaction was observed.

Thionylalizarin reacts readily with hot primary aromatic amines, with evolution of sulphur dioxide, to give alizarin, which then undergoes further slow reaction with the bases to yield secondary amines. For example, in one experiment, the product obtained after boiling thionylalizarin in dry aniline for 1 hour contained less than 1% of nitrogen, gave the reactions of alizarin and melted at 265—268°. This melting point was raised to 275—277° by admixture with pure alizarin. Similar results were obtained with other aromatic amines, and the reaction was not investigated further.

EXPERIMENTAL.

Interaction of Thionylalizarin with Acids, Acid Anhydrides, and Acid Chlorides.—Methods. A. In the case of the lower-melting acids, a slight excess was heated with thionylalizarin at 150—170°. When the evolution of sulphur dioxide was no longer vigorous (usually 10 to 15 minutes), the melt was allowed to cool, boiled with ether to remove any unchanged acid, and the residue was recrystallised from benzene or absolute alcohol. Yields of 90 to 95% of the pure products were obtained.

B. The acid or anhydride and thionylalizarin were heated in dry nitrobenzene at 170° for 40 to 60 minutes. On cooling, a portion of the product usually crystallised. A further quantity was obtained by adding ether to the solution and allowing it to stand. The yields averaged 60%.

C. Benzoyl chloride reacted vigorously at its boiling point with thionylalizarin, and dibenzoylalizarin, m. p. 187°, crystallised on cooling. With acetyl chloride no reaction was observed after 4 hours' boiling, but when the substances were heated in a sealed tube at 150—170° for 2 hours, diacetylalizarin was obtained in 80% yield.

Alizarin benzoates. 2-Monobenzoylalizarin (methods *A* and *B*) was obtained from absolute alcohol in small, chrome-coloured needles, m. p. 208—210° (D.R.-P. 297,261 gives 214—216°). When mixed with a specimen prepared from alizarin and the theoretical amount of benzoyl chloride in pyridine solution, it showed the same m. p. (Found: C, 73·3; H, 3·6. Calc. for $C_{21}H_{12}O_5$: C, 73·3; H, 3·5%).

Dibenzoylalizarin (*B* and *C*). When prepared from the thionyl compound and benzoic anhydride in nitrobenzene solution, *dibenzoylalizarin* separated in clusters of small, pale chrome crystals, m. p. 160°, which was unchanged by further immediate crystallisation from benzene (Found: C, 74·8; H, 3·7. $C_{28}H_{16}O_6$ requires C, 75·0; H, 3·6%). This labile form, on being kept for a week in contact with a little of the original nitrobenzene solution, was transformed to the stable modification, which consisted of stout, primrose prisms, m. p. 187° (Found: C, 74·9; H, 3·7%) (compare Barnett and Cook, J., 1922, **121**, 1389). Other preparations of this derivative from alizarin and benzoyl chloride in pyridine gave the higher-melting form.

The following 2-*monoacyl* derivatives of alizarin were also prepared. The methods of preparation are indicated, and the calculated values for C, H, and Br are given in brackets after the found values.

2-Acyl derivatives of alizarin.	Appearance and m. p.	Recrystallisation solvent and analyses.
Phenylacetyl (*A*) ...	Greenish-yellow needles, m. p. 165°.	Benzene. 73·7; 4·0 (73·7; 3·9).
Phenoxyacetyl (*A*) ...	Small, yellow needles, m. p. 179°.	Benzene. 70·7; 3·7 (70·6; 3·7).
Cinnamoyl (*A* and *B*)	Golden-yellow prisms, m. p. 209°.	Benzene. 74·5; 3·7 (74·6; 3·8).
o-*Toluoyl* (*A*)	Fine, ochre needles, m. p. 192°.	Benzene or absolute alcohol. 73·7; 3·9 (73·7; 3·9).
m-*Bromobenzoyl* (*A*)	Small, greenish-yellow needles, m. p. 214°.	Toluene. Br, 18·7 (18·9).
p-*Bromobenzoyl* (*B*)	Greenish-yellow needles, m. p. 195°.	Benzene. Br, 18·9 (18·9).

Condensations with Halogen-substituted Acetic Acids.—(1) *Monochloroacetic acid.* Thionylalizarin (2 g.) was treated with the carefully purified acid, according to method *A*. The product, crystallised from benzene, consisted of 1·6 g. of an intimate mixture of fine, yellow needles, which closely resembled the monoacyl compounds previously examined, and of fine, reddish-brown flakes. The mixture contained 5·8% of chlorine (the monochloroacetate requires 11·2%). Similar results were obtained by varying the experimental conditions. After repeated extraction of the mixtures with light petroleum, a residue of pure alizarin was obtained; m. p. 288°, either alone or mixed with an authentic specimen.

(2) Thoroughly dried and purified dichloro-, trichloro-, and dibromo-acetic acids in all experiments gave theoretical yields of halogen-free alizarin, which was identified by mixed melting-point determinations with the pure substance, and by conversion into the diacetate.

The products from alcoholic and phenolic solutions of thionylalizarin were shown to be alizarin in the same manner.

The author wishes to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed part of the cost of this research.

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