# A Facile Transacylation Reaction in the Anthracene Series

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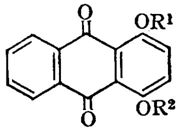
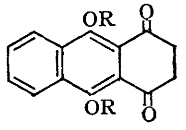
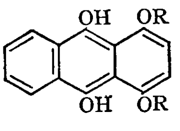
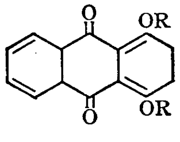
IT is well known[1] that the reduction of quinizarin (I; $R^1 = R^2 = H$) gives the stable dihydro-derivative leucoquinizarin (II; R=H)[2]. Zahn and Ochwat claimed[3] that treatment of leucoquinizarin with acetyl chloride and pyridine yielded a colourless diacetate $C_{18}H_{14}O_6$, m.p. 214–215° (decomp.), which was also formed by the action of heat on solutions of 1,4-diacetoxy-9,10-dihydroxyanthracene (III; R = Ac) in glacial acetic acid. Because of these alternate modes of formation this compound was assigned the unusual structure (IV; R = Ac).


(I)


(II)


(III)


(IV)

Repetition of these reactions under modified conditions afforded high yields of the compound described by Zahn and Ochwat. It gave leucoquinizarin on acid hydrolysis, and 1,4,9,10-tetraacetoxyanthracene on acetylation with pyridine–acetic anhydride in an inert atmosphere. Although stable to oxygen as the solid or in boiling dioxan, benzene, or pentanol, it suffered smooth aerial oxidation in glacial acetic acid at 100° to give an almost quantitative yield of quinizarin diacetate (I; $R^1 = R^2 =$ Ac). In pyridine solution at 100° it similarly gave a mixture of quinizarin monoacetate (I; $R^1 =$ H, $R^2 =$ Ac) and diacetate. A comparison of the infrared and ultraviolet absorption spectra of the compound [$\lambda_{\max.}$ 264 m$\mu$ (log $e_{\max.}$ 4·68), 305 (3·57), 348 (3·53), and 362 (3·61); $\lambda_{C=O}$ 5·70$\mu$ (ester) and 5·91 (aromatic ketone)] with that of 1,2,3,4-tetrahydro-1,4-dioxoanthracene[4] [$\lambda_{\max.}$ 265 m$\mu$ (log $e_{\max.}$ 4·77), 293 (3·72), 347 (3·39), and 362 (3·55); $\lambda_{C=O}$ 5·92 $\mu$] shows clearly that it is in fact 9,10-diacetoxy-1,2,3,4-tetrahydro-1,4-dioxoanthracene (II; R=Ac); hence both its formation from (III; R=Ac) and its oxidation to quinizarin diacetate must involve the migration of both acetyl groups. Leucoquinizarin dibenzoate (II; R=Bz) behaves similarly.

Zahn and Ochwat also claimed to have prepared the stable dimethyl ether (IV; R=Me) by the reduction of 1,4-dimethoxyanthraquinone (I; $R^1 = R^2 =$ Me). The infrared absorption spectrum of this compound shows, however, the presence of strong O–H bands at 2·9 and 3·0 $\mu$ and the complete absence of C=O bands; it must therefore be (III; R=Me), as indeed its chemical properties[3] suggest.

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[1] K. H. Meyer and A. Sander, *Annalen*, 1920, **420**, 116, 122.
[2] M. St. C. Flett, *J.*, 1948, 1441.
[3] K. Zahn and P. Ochwat, *Annalen*, 1928, **462**, 72.
[4] D. B. Bruce and R. H. Thomson, *J.*, 1952, 2759.