Addition of 1,1-Diethoxyethene to Quinones: Synthesis of Acetylemodin

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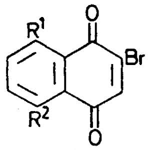
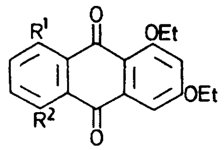
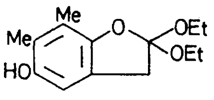
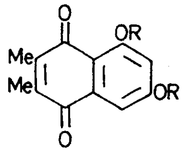
Summary Addition of 1,1-diethoxyethene to quinones involves concurrent 1:1- and 1:2-pathways, application of which has led to synthesis of the insect pigment acetylemodin (**11**).

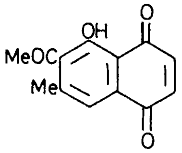
ADDITION of 1,1-diethoxyethene to 1,4-quinones involves two pathways. A 1:1-process, typified by reaction of simple benzoquinones, bromobenzoquinones, and naphthoquinone, led to ethoxyfurans or substances derivable from them.[1] A 1:2-process typified by reaction of 2(3)-bromonaphthoquinones, led to 1,3-diethoxyanthraquinones;[2] this was regiospecific, *e.g.* (**1**) and (**2**) gave (**3**) and (**4**) respectively.

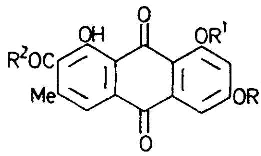

(1) R^1 = OH, R^2 = H
(2) R^1 = H, R^2 = OH


(3) R^1 = OH, R^2 = H
(4) R^1 = H, R^2 = OH
(8) R^1 = H, R^2 = OMe


(5)


(6) R = Et
(7) R = H


(9)


(10) R^1 = Et, R^2 = Me
(11) R^1 = H, R^2 = Me
(12) R^1 = H, R^2 = OH

In seeking clarification of these two seemingly exclusive processes we have observed that they co-occur, albeit in proportions that vary widely with reaction conditions. This applies to benzo- and naphtho-quinones whether brominated or not. For example, addition of neat 1,1-diethoxyethene to 2,3-dimethyl-1,4-benzoquinone gave a mixture of the orthoester (**5**) (63%) and the naphthoquinone (**6**) (9%). Addition in Me$_2$SO at room temperature gave only the latter (56%), hydrolysis of which led to the dihydroxy analogue (**7**).[3]

Compound (**5**), a stoicheiometric 1 : 1 adduct was isolated by work up with avoidance of heating and protic solvents. Such compounds were readily convertible into the corresponding ethoxyfuran, lactone, or quinonylacetic acid derivatives such as have been observed as 1 : 1 adducts in previous work.[1] These are evidently artefacts, orthoesters of type (**5**) being the primary products of addition. Compound (**5**), m.p. 53—55 °C, was fully characterised; its n.m.r. spectrum (CDCl$_3$) showed methylene and benzenoid singlet resonances at δ 3·10 and 6·33 along with signals characteristic of two ethoxy and two methyl groups.

Polyketide type anthraquinones have been synthesised *via* 1 : 2-addition to naphthoquinones, prior bromination being unnecessary. Such additions are markedly accelerated in polar solvents and there is orientational specificity in favourable cases. Addition to 5-hydroxy-1,4-naphthoquinone in Me$_2$SO gave compound (**3**) (39%) whereas the 5-methoxy derivative gave exclusively the alternative orientation (**8**) (44%). Products (**3**) and (**8**) underwent hydrolysis to give 1,3,8- and 1,3,5-trihydroxyanthraquinones[4] respectively.

The various 1 : 1- and 1 : 2-additions are all interpretable in terms of initial nucleophilic attack of 1,1-diethoxyethene at a quinonoid carbon.

Extrapolation to the naphthoquinone stypandrone (**9**)[5] yielded (**10**) (60%), hydrolysis of which gave the insect pigment acetylemodin (**11**) quantitatively. This could not be synthesised by conventional procedures such as acylation of emodin but it was identical with authentic material.[6] Since it has previously been converted into endocrocin (**12**)[6] the procedure affords a new synthesis of the latter also.

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