Intermediates in the 1:2-Addition of 1,1-Diethoxyethene to Quinones: Synthesis of Deoxyerythrolaccin

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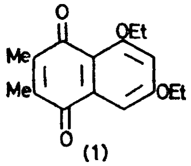
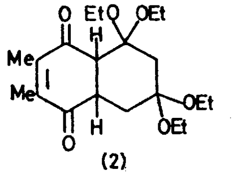
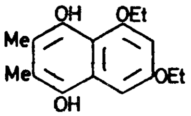
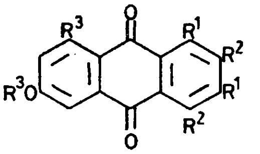
Summary Intermediate 1:2-adducts have been isolated from the reaction of 1,1-diethoxyethene with quinones, a process which has been extended to the synthesis of the insect pigment deoxyerythrolaccin.

ADDITION of 1,1-diethoxyethene to 1,4-quinones involves competing 1:1- and 1:2-processes.[1] The former leads to dihydrobenzofuran or cyclobutane adducts and to other derived products.[1,2] The latter is characterised by the formation of a benzenoid ring, as in the conversion of 2,3-dimethyl-1,4-benzoquinone into the naphthoquinone (**1**).[1] The course of this synthetically useful process is obscure, no reaction intermediates having hitherto been detected.


(**1**)


(**2**)


(**3**)



	R1	R2	R3
(**4**);	H	OEt	Me
(**5**);	OEt	H	Me

Careful treatment of 2,3-dimethyl-1,4-benzoquinone with 1,1-diethoxyethene in Me_2SO at room temperature gave a tan coloured product formulated as the 1:2-adduct (**2**), *m/e* 368 (M^+). It was unstable in air and light, particularly in the presence of acid or on silica; this led to (**1**) (λ_{max} 410 nm). It absorbed as an enedione (λ_{max} 255 nm).[3] Its ^1H n.m.r. spectrum ($CDCl_3$) was complex, with resonances entirely at fields above δ 4·0. On addition of HCl in the absence of air this changed strikingly to the spectrum of the quinol (**3**) [δ 2·21, 2·26 (2- and 3-Me), 6·32, and 6·91 (ArH)] plus 2 mol. equiv. of ethanol. The quinol (**3**), *m/e* 276 (M^+), λ_{max} 350 nm, with naphthalenic fine structure, was stable in the solid phase but in solution in air gave (**1**) quantitatively.

These data provide evidence for the conventional 1:2-addition proceeding through at least two intermediate stages [(**2**) and (**3**)] leading to the end product (**1**). Discrete adducts, spectroscopically similar to (**2**) but of lower stability, have also been isolated from the reactions of 1,4-benzoquinone and of 5-hydroxy-1,4-naphthoquinone. Analogous products have not so far been obtained from bromoquinones,[4] presumably because of the ease of elimination of HBr.

Development of the 1:2-addition process to synthesising polyketides based on 1,3,6-trihydroxyanthraquinone requires controlled addition to derivatives of 6-hydroxy-1,4-naphthoquinone. However application of standard procedures[1,4] gave the non-polyketide 1,3,7-orientation. Thus 7-methoxy-5-methyl-1,4-naphthoquinone and its 2-bromo-derivative, obtained by direct bromination,[5] both reacted with 1,1-diethoxyethene to give (**4**) (45%). The substrates were derived[6] from 7-methoxy-5-methyltetralone[7] and the direction of addition was compatible with electron release from the 7-substituent,[5] the orientational effect of bromo-groups,[4] and model conversions of 6-hydroxy- and 6-ethoxy-1,4-naphthoquinones into 1,3,7-trihydroxyanthraquinone.[8] However, the isomeric 3-bromo-derivative was usefully obtained by unconventional oxidative hydrobromination. It reacted with 1,1-diethoxyethene to give (**5**) (80%). On hydrolysis, this gave the insect pigment deoxyerythrolaccin.[9]

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