

## The Displacement of Alkyl Side-chains from *ortho*-Quinones

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**Summary** Treatment of 4-alkyl-1,2-benzoquinones with *p*-anisidine in methanol solution results in displacement of the 4-alkyl group by a *p*-anisidyl group.

WHILE re-investigating the reaction of aromatic amines with *o*-quinone we have found the course of the reaction depends on the nature of the reaction medium, the nucleophile attacking the carbonyl group in non-hydroxylic solvents, but undergoing conjugate addition [*i.e.* attack at the 4(5)-position] in methanol.<sup>1</sup> We have now extended these studies to alkyl substituted *o*-quinones and have discovered what we believe to be a quite unprecedented displacement of alkyl groups from the quinone ring. The

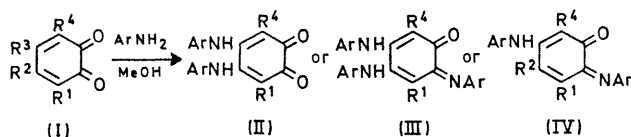
attack only takes place *via* conjugate addition, alkyl displacement is always accompanied (preceded) by direct addition to the carbonyl. It is also significant that with 3,5-dimethyl- and 4,5-dimethyl-quinones only one methyl group [in the 4(5)-position] is displaced. When the reaction was investigated with 3,5-di-*t*-butyl-1,2-benzoquinone (I; R<sup>1</sup> = R<sup>3</sup> = But<sup>t</sup>; R<sup>2</sup> = R<sup>4</sup> = H) no displacement of the *t*-butyl group was observed. This may be due to steric hindrance, but it is also consistent with the idea

TABLE

The reaction of *ortho*-quinones with *p*-anisidine in methanol (Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>)

(II, III, and IV can exist in a number of tautomeric forms)

(Ia) → (IIa)  
 (Ib) → (IIb)  
 (Ic) → (IIIa) (Me displaced)  
 (Id) → (IIIb) or (IIIb') (Me displaced)  
 (Ie) → (IVc) or (IVc') ( " " )  
 (If) → (IIIa) (Et displaced)



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>		R <sup>1</sup>	R <sup>4</sup>		R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
a;	H	H	H	H	a;	H	H	c;	H	Me	—	H
b;	Me	H	H	H	b;	Me	H	c';	H	—	Me	H
c;	H	Me	H	H	b';	H	Me	<i>i.e.</i> R <sup>2</sup> displaced, R <sup>3</sup> retained.				
d;	Me	H	Me	H								
e;	H	Me	Me	H								
f;	H	Et	H	H								

*principal* product from the different quinones are listed in the Table (in most cases traces amounts of other adducts were present). The arylamino-*p*-quinone monoanil (IIIa) formed in the reactions with 4-methyl-1,2-benzoquinone and 4-ethyl-1,2-benzoquinone is also formed in low yield together with much of the diarylamino-*o*-quinone (IIa) in the reaction with *o*-quinone itself (in ether solution it is the predominant product<sup>1</sup>). A feature to notice about these results is that although with compounds (Ia) and (Ib)

that alkyl displacement involves quinone methides as intermediaries. Just as addition to unsubstituted *o*-quinone is affected by changing the solvent, so the reaction with alkyl substituted quinones is altered, although some displacement of alkyl groups still appears to take place in the nonhydroxylic solvent ether. Experiments are at present in progress in order to elucidate further the mechanism of the reaction.

All the products listed in the Table have been fully characterised (analysis; mass spec., n.m.r., and i.r.) and their structures confirmed. The authors acknowledge support from the A.R.C.

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<sup>1</sup> W. M. Horspool, P. Smith, and J. M. Tedder, *J. Chem. Soc. (C)*, in the press.