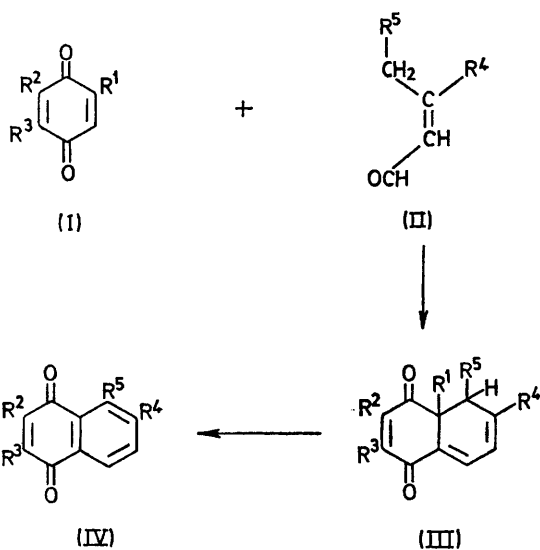


Addition of $\alpha\beta$ -Unsaturated Aldehydes to Quinone Systems: a New Annellation Reaction

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Summary $\alpha\beta$ -Unsaturated aldehydes react with quinones in the presence of ethoxymagnesium bromide to give polycyclic products.

We have found that quinones of the type (I) react with $\alpha\beta$ -unsaturated aldehydes (II) in boiling benzene in the presence of ethoxymagnesium bromide (1 mol) to give the corresponding annellation products (III) or, when R = H, the related dehydro-compounds (IV).

The products and yields are summarised in the Table.

The reaction is extremely sensitive to the nature of the base and does not occur when sodium alkoxides or aryl-oxides are used. Successful syntheses of anthraquinone (IVb) from benzoquinone and crotonaldehyde, and of tectoquinone¹ (IVd) from β -methylcrotonaldehyde and 1,4-naphthoquinone, suggest that this novel annellation method may be applicable to the preparation of many polycyclic quinones.

(IV)	R ²	R ³	R ⁴	R ⁵	(III)	R ¹	R ²	R ³	R ⁴	R ⁵
a;	H	H	H	H	a;	Me	Me	Me	H	H
b;	-C ₄ H ₄ -	-	H	H	b;	Me	Me	Me	Me	C ₁₅ H ₃₁
c;	Me	H	H	H	c;	Me	Me	H	H	Me
d;	-C ₄ H ₄ -	Me	-	H	d;	Me	-C ₄ H ₄ -	H	H	-

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Aldehyde	Quinone	Products ^a and yields (%) ^b
Crotonaldehyde	1,4-Benzoquinone	(IVa) 6.0, (IVb) (12.0)
Crotonaldehyde	Methylbenzoquinone	(IVc) 15.0
Crotonaldehyde	Trimethylbenzoquinone	(IIIa) 20.0
Crotonaldehyde	2-Methylnaphthoquinone	(IIIb) 5.4
Pent-2-enal	2,6-Dimethylbenzoquinone	(IIIc) 18.0
Phytal	Trimethylbenzoquinone	(IIIb) 24.0
β -Methylcrotonaldehyde	Naphthoquinone	(IVd) 27.0

^a Structures follow from spectroscopic data or from comparison with authentic specimens. ^b Determined by g.l.c.

¹ R. H. Thomson, 'Naturally Occurring Quinones,' Academic Press, London, 1971, p. 368.