

Substituted Naphthalenes from Benzyne and Dienolate Anions

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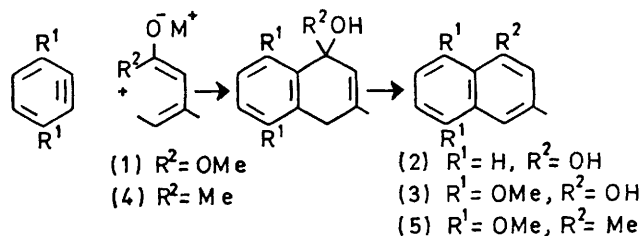
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Summary A new, direct route to substituted naphthalenes and naphthols from benzyne and dienolate anions has been devised.

REACTIONS of arynes with conjugated dienes to give (2 + 4) cycloaddition products are well established.¹ In contrast, conjugated carbonyl compounds tend to give (2 + 2) addition products.^{2†} With electrophilic arynes addition across the carbonyl group of unsaturated aldehydes has also been reported.⁴ In principle, however, the dienolate anions derived from $\alpha\beta$ -unsaturated carbonyl compounds bearing γ -hydrogen atoms should behave as diene components leading to (2 + 4) cycloaddition products. Since conditions whereby stable dienolate ions can be formed have recently been defined,⁵ we have been able to verify this prediction.

For example, methyl 3-methylbut-2-enoate (8 mm) was treated with lithium di-isopropylamide [8.4 mm, from the amine and butyl-lithium in hexane (4 ml)] in dry tetrahydrofuran (10 ml) at -5 to -10° for 1 h to give the dienolate anion (1). Sodamide (8 mm) and sodium *t*-butoxide (3 mm) were added⁶ and the suspension cooled to -60° prior to the addition of bromobenzene (1.4 mm). The mixture was left at -60° for 30 min before allowing it to warm to room temperature over a period of 5 h. The mixture was then stirred at room temperature overnight before work-up to give the major product, 3-methyl-1-naphthol (2) (37%), m.p. $88-91^\circ$.⁷

Similarly, 2,5-dimethoxybromobenzene with the anion (1) afforded 5,8-dimethoxy-3-methyl-1-naphthol (3) (27%), m.p. $117-118^\circ$,⁸ which was previously prepared by a seven-stage synthesis from 1,4-dimethoxybenzene.⁸



The reaction could also be applied to the preparation of substituted naphthalenes. Formation of the dienolate anion (4) from mesityl oxide, followed by reaction with the benzyne derived from 2,5-dimethoxybromobenzene, gave 1,4-dimethoxy-5,7-dimethylnaphthalene (5) (35%), m.p. $56-58^\circ$.[‡]

The above reactions probably proceed by a non-concerted cycloaddition reaction between the dienolate anion and benzyne components.[§] Loss of methanol or water from the initial adducts during work-up accounts for the formation of the naphthalene chromophore.

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† Methyl vinyl ketone reacts with benzyne to give 1-acetylbenzocyclobutene ($> 30\%$).³

‡ Satisfactory analysis; all compounds exhibited the expected spectroscopic properties.

§ A similar reaction, leading to anthranols, has recently been reported (see ref. 9).

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