# Substituted Naphthalenes from Benzynes and Dienolate Anions

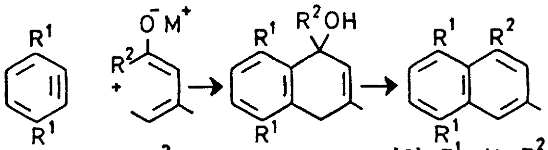
By Peter G. Sammes* and Timothy W. Wallace
(*Chemistry Department, Imperial College, London* SW7 2AY)

*Summary* A new, direct route to substituted naphthalenes and naphthols from benzynes 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 $\gamma$-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 added[6] 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°.[7]

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



(**1**) $R^2$ = OMe
(**4**) $R^2$ = Me
(**2**) $R^1$ = H, $R^2$ = OH
(**3**) $R^1$ = OMe, $R^2$ = OH
(**5**) $R^1$ = OMe, $R^2$ = Me

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°.‡

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).

[1] R. W. Hoffman, 'Dehydrobenzenes and Cycloalkynes,' Academic Press, New York, 1967, ch. 3.
[2] T. Matsuda and T. Mitsuyasu, *Bull. Chem. Soc. Japan*, 1966, **39**, 1342.
[3] R. A. Watt, unpublished results.
[4] H. Heaney and J. M. Jablonski, *Chem. Comm.*, 1968, 1139.
[5] R. A. Lee, C. McAndrews, K. M. Patel, and W. Reusch, *Tetrahedron Letters*, 1973, 965.
[6] P. Caubère and B. Loubinoux, *Bull. Soc. chim. France*, 1968, 3857.
[7] M. Tischler, L. F. Fieser, and N. L. Wendler, *J. Amer. Chem. Soc.*, 1940, **62**, 2866.
[8] R. G. Cooke and H. Dowd, *Austral. J. Sci. Res.*, 1952, **5**A, 760.
[9] P. Caubère, M. S. Mourad, and D. Canet, *Tetrahedron Letters*, 1973, 2221.