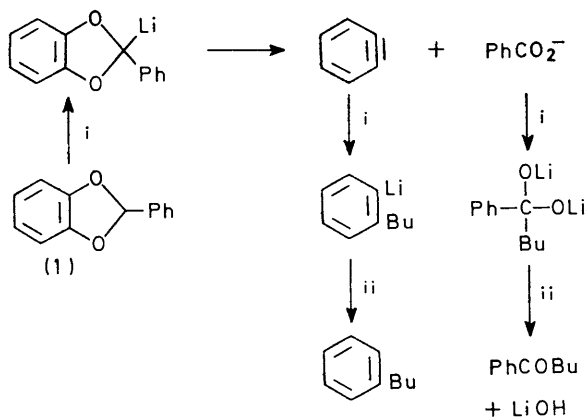


Reaction between 2-Phenyl-1,3-benzodioxole and n-Butyl-lithium; an Unsuccessful Attempt to Synthesize Benzyne

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2-Phenyl-1,3-benzodioxole (1) on treatment with n-butyl-lithium in hexane did not fragment to give benzyne. Instead *o*-(1-phenylpentoxy)phenol (3), catechol, and *cis*- and *trans*-1-phenylpent-1-ene (2) were obtained. A mechanism for the formation of these products is suggested.

THE fragmentation of 2-aryl-1,3-dioxolans in the presence of alkyl-lithium reagents has been developed into a stereospecific synthesis of disubstituted olefins.¹ The aim of the present work was to investigate the reaction



SCHEME 1 Reagents: i, BuⁿLi; ii, H₂O

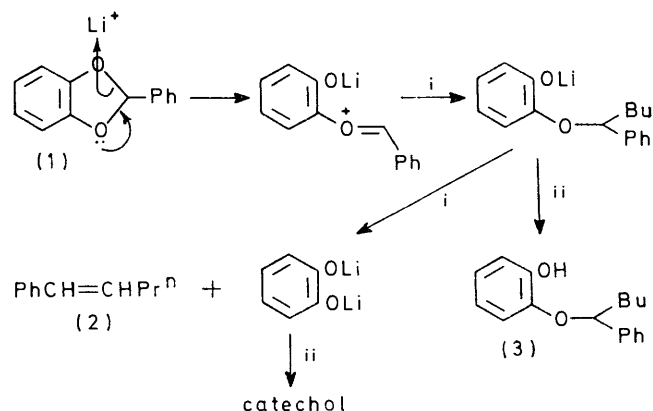
between n-butyl-lithium and 2-phenyl-1,3-benzodioxole (1).² Fragmentation, in the usual manner, of the anion formed by abstraction of the benzyldiene proton in compound (1), would give rise to benzyne. The benzyne was expected to react further with unchanged n-butyl-lithium to form n-butylbenzene,³ and so the expected products from this reaction were n-butylbenzene and valerophenone¹ (Scheme 1). It was also hoped that by modification of the procedure, and with benzyne trapping agents present, some of the characteristic benzyne transformation products would be formed.

2-Phenyl-1,3-benzodioxole² (1) was treated with an excess of n-butyl-lithium in light petroleum. None of the expected valerophenone (Scheme 1) was detected in the product mixture by t.l.c. or by i.r. spectroscopy.

¹ J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Comm.*, 1968, 1593.

In fact t.l.c. showed three products, which were separated and purified by chromatography and distillation. The least polar component was a mixture of *cis*- and *trans*-1-phenylpent-1-ene (2) [yield 55% based on (1)]. The second component (C₁₇H₂₀O₂) had a strong i.r. band at 3520 cm⁻¹, and a weak molecular ion at *m/e* 256 in its mass spectrum. Its n.m.r. spectrum showed signals at τ 2.5–2.9 (5H, m), 3.0–3.5 (4H, m), 4.48 (s, exchangeable), and 4.96 (1H, dd), and multiplets characteristic of an n-butyl group at 7.6–9.2. It was identified as the catechol monoether (3) [isolated yield 30% based on (1)]. The most polar component was identified as catechol by comparison with authentic material. It was isolated in 23% yield, although some may have been lost in the work-up by oxidation.

A possible mechanism for the formation of these products is outlined in Scheme 2. With the n-butyl-lithium acting as a Lewis acid, the dioxolan ring in (1)



SCHEME 2 Reagents: i, BuⁿLi; ii, H₂O

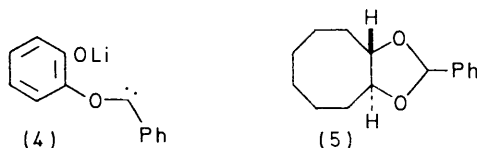
may have been opened to form a stabilized, benzylic carbonium ion. Capture of this carbonium ion by n-

² B. Capon and M. I. Page, *J.C.S. Perkin II*, 1972, 522.

³ T. L. Gilchrist and C. W. Rees, 'Carbenes, Nitrenes, and Arynes,' Nelson, London, 1969, ch. 8.

butyl-lithium would have given the catechol monoether (3) on addition of water. *cis*- and *trans*-1-Phenylpent-1-ene (2) may have been formed by elimination of catechol from (3).

The opening of the dioxolan ring in (1) and the reaction of the resulting carbonium ion with *n*-butyl-lithium have been shown here as separate steps; however these two processes may be concerted.⁴ 1,3-Dioxolans are known to react with Grignard reagents by ring opening and formation of products analogous to (3), but the mechanisms of these reactions do not seem to have been investigated.⁵ However reactions of orthoesters with Grignard reagents are believed to proceed by two steps: elimination of alkoxide followed by attack of Grignard reagent.⁶ Another possible mechanism for the formation of (3) would involve the carbene (4).⁷ This carbene, formed from the metallated dioxolan, might react with the *n*-butyl-lithium to give (3) after addition of water. This mechanism was discarded because quenching the reaction mixture with deuterium oxide gave product (3) shown by n.m.r. to have the benzylidene proton intact. It was also shown that (3) did indeed fragment slowly to give catechol and olefin (2) in the presence of *n*-butyl-lithium.



The isolated yields of compounds (2) and (3) accounted for over 80% of (1); thus little, if any, metallated (1) fragmented to give benzyne. Abstraction of the benzylidene proton in (1) by *n*-butyl-lithium would have been irreversible and therefore formation of (3), possibly *via* a benzylic carbonium ion, must have been the faster process. The reaction of (1) with *n*-butyl-lithium was a little slower than the reaction between *n*-butyl-lithium and 10-phenyl-9,11-dioxabicyclo[6.3.0]undecane (5) which gave *trans*-cyclo-octene by fragmentation of metallated (5).¹ However the difference in rates between the two reactions was not great and it was difficult to draw any firm mechanistic conclusions. The dioxolan (1) is strained and this strain can be relieved by opening the dioxolan ring. Perhaps this was one of the factors that favoured cleavage of the dioxolan ring and formation of the observed products rather than metallation and formation of benzyne.

EXPERIMENTAL

N.m.r. data were obtained with a Perkin-Elmer R14 instrument (100 MHz). A Pye series 104 chromatograph, fitted with a 15% Carbowax-on-Celite column (100–120

mesh), was used for g.l.c. 2-Phenyl-1,3-benzodioxole (1) was prepared as described in the literature.² Light petroleum refers to the fraction of b.p. 30–40°.

Reaction between *n*-Butyl-lithium and 2-Phenyl-1,3-benzodioxole (1).—A solution of *n*-butyl-lithium in hexane (2.15N; 14 ml) was added to a solution of the dioxolan (1) (1.98 g) in light petroleum (15 ml) at 20° under dry nitrogen. The mixture was stirred under nitrogen for 38 h, deuterium oxide was added, the aqueous layer was acidified, and the products were extracted into ether. The extracts were combined and dried, and the ether was removed. Three products were detected by t.l.c. (A, B, and C, in order of increasing polarity). The crude product mixture was taken up in light petroleum; a crystalline solid then separated. This solid (250 mg) (product C) was identified as catechol by comparison (t.l.c., colour with ferric chloride, reaction with bromine water, i.r. data, and m.p.) with authentic material. Products A and B remained in solution in the light petroleum and were separated by chromatography on a column of silica gel (elution with 10% ether–light petroleum). Product A (800 mg) was distilled (b.p. 88–90° at 12 mmHg) and identified as a mixture of *cis*- and *trans*-1-phenylpent-1-ene (2) (lit.,⁸ b.p. 84° at 7 mmHg), showing two peaks on g.l.c. (relative retention times 4 : 6, relative peak areas 1 : 2.7) (Found: C, 90.1; H, 9.5. Calc. for C₁₁H₁₄: C, 90.35; H, 9.65%), ν_{\max} 692, 698, 735, 770, 910, 960, and 1660 cm⁻¹,^{8,9} τ 2.6–3.0 (5H, m, aromatic), 3.2–4.6 (2H, m, olefinic), 7.6–8.0 (2H, m, allylic), 8.2–8.8 (2H, m, CH₂), and 8.8–9.2 (3H, m, CH₃), *m/e* 146 (*M*⁺) and 117 (*M*⁺ – 29, base peak). Product B could not be distilled nor crystallized. It gave one spot on t.l.c. and was identified as *o*-(1-phenylpentyl-oxy)phenol (3) (800 mg, 30%) (Found: C, 79.95; H, 7.8. C₁₇H₂₀O₂ requires C, 79.65; H, 7.85%), ν_{\max} (film) 700, 740, 1220, 1258, 1598, 3030, 3060, 3080, and 3520 cm⁻¹, τ 2.5–2.9 (5H, m, aromatic), 3.0–3.5 (4H, m, aromatic) 4.48 (1H, s, exchangeable OH), 4.96 (1H, dd, CH), and 7.6–9.2 (9H, m, Buⁿ), *m/e* 256 (weak *M*⁺) and 91 (base peak). Product B was rechromatographed on a column of silica gel; its spectra remained unchanged.

The reaction was repeated on 1/100 molar scale concurrently with the similar reaction between *n*-butyl-lithium and 10-phenyl-9,11-dioxabicyclo[6.3.0]undecane, the two reactions being carried out under identical conditions. The reaction involving the dioxolan (5) was complete within 24 h (n.m.r.), whereas that involving (1) took 38 h to reach completion (t.l.c.).

Reaction between *n*-Butyl-lithium and *o*-(1-Phenylpentyl-oxy)phenol (3).—The catechol monoether (3) (250 mg) was treated with *n*-butyl-lithium at 20° for 48 h. The products were isolated in the usual way; t.l.c. showed the presence of a little 1-phenylpent-1-ene (2).

I thank Dr. G. H. Whitham for help and encouragement.

[3/833 Received, 17th April, 1973]

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⁷ K. D. Berlin and B. S. Rathore, *Tetrahedron Letters*, 1964, 2547.

⁸ C. G. Overberger and L. P. Hern, *J. Org. Chem.*, 1962, **27**, 417.

⁹ M. Schlosser and K. F. Christmann, *Annalen*, 1967, **708**, 1.

⁴ T. H. Fife, *J. Amer. Chem. Soc.*, 1967, **89**, 3228.

⁵ H. Meerwein, in Houben-Weyl, 'Methoden der Organischen Chemie,' G. Thieme Verlag, Stuttgart, 1965, vol. 6, part 3, p. 199; S. Cabiddu, G. Gelli, and E. Marongiu, *Ann. Chim. (Italy)*, 1970, **60**, 580.