

1227. *The Reaction of 2-Phenyl-1,3-dioxolan with Butyl-lithium*

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RECENT reports of the reaction of 2-substituted 1,3-dioxolans with Grignard reagents,¹ phenyl-lithium,² and butyl-lithium³ prompt us to record our own results. A protecting group was required for a carbonyl function, such that another group in the same molecule could undergo reaction with an alkyl-lithium reagent. To ascertain whether the cyclic ketal could be used, 2-phenyl-1,3-dioxolan was chosen as a model compound and its reaction with butyl-lithium at -5° investigated. The formation of benzaldehyde and valerophenone, characterised as their dinitrophenylhydrazones, indicated the instability of the cyclic ketal even at -5° . Benzaldehyde and valerophenone, in addition to other products, were also obtained when this reaction was carried out at the reflux temperature of cyclohexane.³ The ethylene thioketal of benzaldehyde is even less stable, reaction with butyl-lithium being sufficiently exothermic to cause the ether solvent to boil.

Experimental.—A solution of butyl-lithium in ether⁴ (56 ml., 1 mol.; 0.703N) was added to a solution of 2-phenyl-1,3-dioxolan⁵ (6.0 g.) in ether (50 ml.), cooled to -5° , in an atmosphere of nitrogen. After stirring for 10 min., aqueous ammonium chloride solution was added, and the ethereal layer washed with water and dried (MgSO_4). After removal of ether, the residue (5.6 g.) was distilled, b. p. $225-240^\circ$. Fractional distillation gave three fractions, of which the first (1.1 g.; b. p. up to $112^\circ/22$ mm.) had its main carbonyl peak at 1716 cm.^{-1} (liquid film; cf. benzaldehyde in solution,⁶ 1708 cm.^{-1}) and a minor peak at 1685 cm.^{-1} ; the second fraction (2.1 g.; b. p. $113-119^\circ/22$ mm.) had carbonyl peaks at 1715 and 1689 cm.^{-1} of approximately equal intensity; the third fraction (1.8 g.; b. p. $120^\circ/22$ mm.) had its main carbonyl peak at 1681 cm.^{-1} (cf. acetophenone,⁷ 1686 cm.^{-1}) and a minor peak at 1717 cm.^{-1} . Portions of the

¹ R. A. Mallory, S. Rovinski, and I. Scheer, *Proc. Chem. Soc.*, 1964, 416.

² P. S. Wharton, G. A. Hiegel, and S. Ramaswami, *J. Org. Chem.*, 1964, **29**, 2441.

³ K. D. Berlin, B. S. Rathore, and M. Peterson, *J. Org. Chem.*, 1965, **30**, 226.

⁴ T. L. V. Ulbricht, *Tetrahedron*, 1959, **6**, 225.

⁵ M. Sulzbacher, E. Bergmann, and E. R. Pariser, *J. Amer. Chem. Soc.*, 1948, **70**, 2827.

⁶ I. M. Hunsberger, *J. Amer. Chem. Soc.*, 1950, **72**, 5626.

⁷ H. W. Thompson and P. Torkington, *J.*, 1945, 640.

first and third fractions were converted into the dinitrophenylhydrazones, which were purified on a column of bentonite-kieselguhr (4 : 1), using chloroform as solvent. From fraction 1 was obtained benzaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 240—241° (from ethanol) (lit.,⁸ 239—240°). From fraction 3 was obtained valerophenone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 166—167° (from ethyl acetate) (lit.,⁸ 167—168°).

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⁸ G. D. Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 2720.
