New Cyclisation Reaction of Aryl-lithium Species; *X*-Ray Crystal Structure of (2,3-dihydro-3-benzofuryl)acetanilide

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Summary Direct metallation of 3-allyloxybenzanilides gave the 2-lithioderivatives, which underwent a cyclisation process to yield (2,3-dihydrobenzofuryl)acetanilides; the structure of (2,3-dihydro-3-benzofuryl)acetanilide has been determined by *X*-ray crystallography.

Recently we demonstrated the synthetic utility of the aryl-lithium reagents (**1**), obtainable by direct metallation of 3-alkoxy-substituted benzanilides.[1,2] In an attempt to extend the utility of these accessible reagents we examined the corresponding 3-allyloxy-derivatives and discovered they undergo an unusual cyclisation reaction, in which two new carbon–carbon bonds are formed. Thus treatment of (**2**,R = H) in tetrahydrofuran and tetramethylethylenediamine (THF, TMEDA, 1:1 v/v) with s-butyl-lithium (2 equiv.) at −60 °C for 2 h followed by 0 °C for 20 min caused partial isomerism to the *Z*-enol ether (**3**), a reaction which could be achieved in quantitative yield with lithium di-isopropylamide in tetrahydrofuran at 25 °C for 8 h.[3] However, when the reaction was conducted at a higher temperature [*i.e.* to a mixture of THF and TMEDA (1:1 v/v) at −60 °C was added n-butyl-lithium (2 equiv.), and the mixture was warmed briefly to 0 °C, recooled to −60 °C, and then treated with a solution of (**2**,R = H) (1 equiv.) in THF and then warmed to 20 °C for 24 h] the usual work-up (aqueous NH_4Cl) gave an isomer, recrystallised from chloroform, m.p. 132—133 °C. The structure (**4**), was assigned to this isomer based on its i.r. spectrum ν_{max} 1685 and 3430 cm^{-1}, and n.m.r. spectrum ($CDCl_3$), δ 2·73 (2H, octet, AB of ABX, J_{AB} = 15, J_{AX} = 8, J_{BX} = 6·5 Hz), 3·95 (1H, m, H_X), 4·25 (1H, d of d, H_C, J_{CD} = 9, J_{CX} = 5 Hz), 4·71 (1H, t, H_D, J_{CD} = J_{DX} = 9 Hz), 6·83 (2H, t, aromatic, J = 7·5 Hz), and 7·0—7·8 (8H, m, aromatic and NH, after D_2O exchange, 7H, m). Acid hydrolysis gave aniline and an acid, presumed to be (**5**). Final proof of these conclusions was obtained by an *X*-ray diffraction analysis of (**4**).

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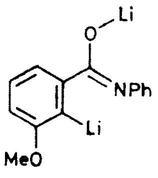
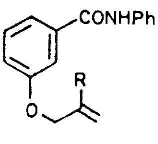
† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available from the British Library as supplementary publication No. SUP 22947 (11 pp.). For details of obtaining this material, see *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index issues, Notice to Authors No. 7.



(1)



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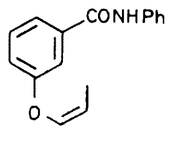

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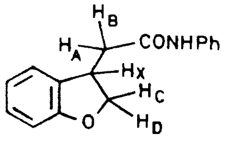

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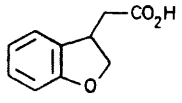

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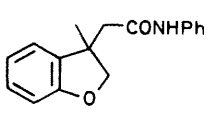


(6)

Crystal data: compound (**4**), $C_{16}H_{15}NO_2$, triclinic, a = 4·934(3), b = 9·607(1), c = 13·743(2) Å, α = 88·82(1), β = 84·65(2), γ = 89·26(2)°; Z = 2, space group $P\bar{1}$ (C_i^1, No. 2); four-circle diffractometer data, Mo-K_α radiation, 1251 independent reflections, structure solution by MULTAN,[4] final R 0·0376. The conformation of the molecule in the crystal is shown in the Figure.

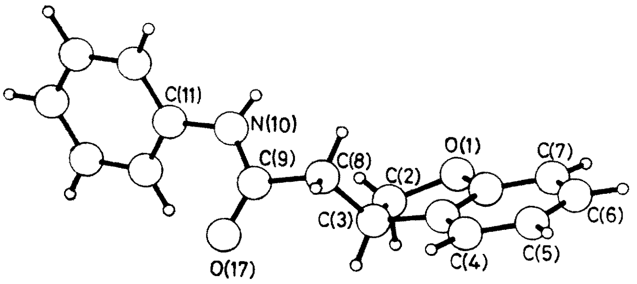
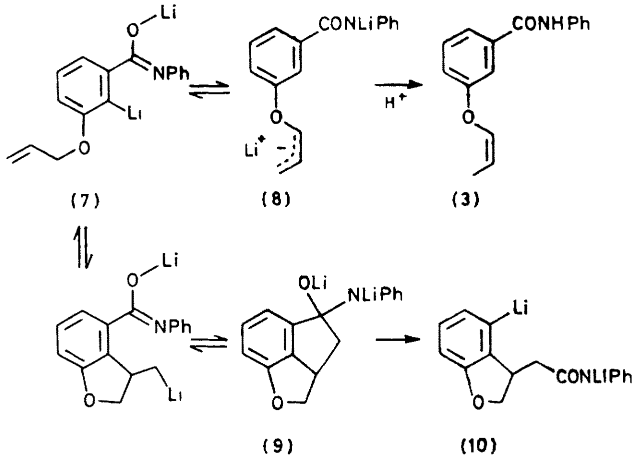


FIGURE. Structure of (2,3-Dihydro-3-benzofuryl)acetanilide.

Similarly when (**2**, R = Me) was subjected to the same conditions the cyclisation product (**6**) was obtained. Attempts to achieve this conversion with the *O*-cinnamyl or prop-2-ynyl ethers gave only the respective double bond-isomerised compounds.



SCHEME

The most likely explanation of these observations is depicted in the Scheme. Thus the initially formed dilithio species[1] (**7**) is isomerised at low temperatures to (**8**), the precursor after quenching of the *Z*-enol ether (**3**), whereas at room temperature cyclisation occurs, in two stages, to the tricyclic (**9**) which subsequently undergoes Haller–Bauer type cleavage.[5]

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[1] J. E. Baldwin and K. W. Bair, *Tetrahedron Lett.*, 1978, 2559.

[2] I. Forbes, R. A. Pratt, and R. A. Raphael, *Tetrahedron Lett.*, 1978, 3965; J. N. Reed, S. O. de Silva, and V. Snieckus, *ibid.*, p. 5099; S. O. de Silva and V. Snieckus, *ibid.*, p. 5103.

[3] This reaction has precedent, *e.g.* C. C. Price and W. H. Synder, *J. Am. Chem. Soc.*, 1961, **83**, 1773; D. A. Evans, G. C. Andrews, and B. Buckwalter, *ibid.*, 1974, **96**, 5560.

[4] G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, 1971, **27**, 368.

[5] Ring opening and closing reactions of organolithium and Grignard reagents containing double bonds are well known: *cf.* E. A. Hill, H. G. Richey, and T. C. Rees, *J. Org. Chem.*, 1963, **28**, 2161; S. A. Kandil and R. E. Dessy, *J. Am. Chem. Soc.*, 1966, **88**, 3027.