# Reactions of Benzaldehyde Acetals with Butyl-lithium: a Stereospecific Olefin Synthesis

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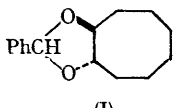
In the course of our work on medium ring compounds we wished to develop a stereospecific route to *trans*-cyclo-octenes which did not suffer from the disadvantages of Corey's thionocarbonate method,[1] namely, relative inaccessibility of starting material, and prolonged reaction time at elevated temperature. The hitherto neglected observation of Wharton *et al.*[2] that 2-phenyl-1,3-dioxolan underwent fragmentation to ethylene on reaction with phenyl-lithium prompted us to investigate the behaviour of the benzylidene derivative of *trans*-cyclo-octane-1,2-diol (I) towards alkyl-lithium derivatives. In the event, treatment of (I) in light petroleum with n-butyl-lithium in hexane (2·0 mol.) at 20° followed after 14 hours† by quenching with water gave *trans*-cyclo-octene (75%), shown to be uncontaminated with the *cis*-isomer by g.l.c., together with butyl phenyl ketone.

The success and high stereospecificity of this olefin-forming reaction led us to make a preliminary study of the reaction of a number of benzaldehyde acetals with butyl-lithium in order to delineate the gross mechanistic features of the process (see Table).

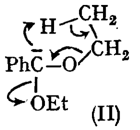
The main conclusions we deduce from this survey are: (i) the anion derived from benzaldehyde diethyl acetal decomposes predominantly by internal $E_2$ elimination‡ (II) and partly by a modified Wittig rearrangement§ involving (III) as an intermediate; (ii) the anion from 2-phenyl-1,3-dioxan partly undergoes a modified Wittig rearrangement‡ *via* (IV); (iii) the anions from 1,3-dioxolans react by cyclo-elimination to give olefin and benzoate ion *via* proton-abstraction from C-2, or benzaldehyde and an enolate ion by proton-abstraction from C-4 (or C-5) (where these positions bear an aryl group).¶

*Products from benzaldehyde acetals and huibutyl-litm in tetrahydrofuran*

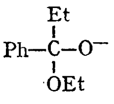
| Acetal | Products (yield %) |
|---|---|
| 1. Benzylidene derivative of (±)-hydrobenzoin | *trans*-stilbene (9), deoxybenzoin(66), 1-phenylpentan-1-ol (64) |
| 2. Benzylidene derivative of *meso*-hydrobenzoin (mixture of diastereoisomers) | deoxybenzoin (67), 1-phenylpentan-1-ol (70) |
| 3. Benzaldehyde diethyl acetal | 1-phenylpentan-1-ol (50), benzaldehyde (20), propiophenone (15), 3-phenyloctan-3-ol (5) |
| 4. 2-Phenyl-1,3-dioxan | 4-phenylnonane-1,4-diol (30), 1-phenylpentan-1-ol (17) |



(I)



(II)



$Ph-\overset{Et}{\underset{OEt}{C}}-O^-$

(III)

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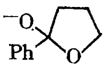
† The reaction is more rapid (complete in 1 hr.) with tetrahydrofuran as solvent; however, addition of butyl-lithium to *trans*-cyclo-octene occurs to a significant extent under these conditions.

‡ An intramolecular elimination in the reaction of benzyl ethyl ether with propylsodium (R. L. Letsinger and D. F. Pollart, *J. Amer. Chem. Soc.*, 1965, **78**, 6079) provides a precedent.

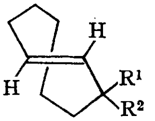
§ Wittig rearrangements of acetals do not appear to have been observed previously.

¶ The predominance of products derived from proton-abstraction at C-4 (or C-5) in the case of the dioxolans from the hydrobenzoins, may be ascribed to the lower stability of a carbanion adjacent to two rather than one oxygen atom (J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, 1967, **89**, 5911).

For 1,3-dioxolans the intramolecular *cis*-elimination and the modified Wittig rearrangement (4-ring transition state) are effectively prohibited for steric reasons, thus providing maximum opportunity for the cyclo-elimination to occur. We regard the latter as a symmetry-allowed process which is effectively the reverse of a 1,3-dipolar cyclo-addition reaction.[3]



(IV)



(V) $R^1$=OMe, $R^2$=H
(VI) $R^1$=H, $R^2$=OMe

The power of the dioxolan olefin synthesis can be further exemplified by the preparation of the diastereoisomerically pure *trans*-cyclo-oct-2-enyl methyl ethers (V) and (VI) by reaction of the benzylidene derivatives from *trans,cis*- and *cis,trans*-2,3-dihydroxycyclo-octyl methyl ether respectively with butyl-lithium in hexane–tetrahydrofuran. The methyl ether (V) was identical with the methylation product of the previously prepared *trans*-cyclo-oct-2-enol.[4]

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[1] E. J. Corey and J. I. Shulman, *Tetrahedron Letters*, 1968, 3655; E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, **87**, 934; E. J. Corey and R. A. E. Winter, *ibid.*, 1963, **85**, 2677.

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

[3] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 639; *J. Org. Chem.*, 1968, **33**, 2291.

[4] G. H. Whitham and M. Wright, *Chem. Comm.*, 1967, 294.