Reaction of Alkyllithium Reagents with 2,2-Dialkyl-1,3-dioxolanes

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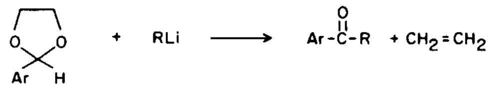
Several groups have recently called attention to the reaction of 2-aryl-1,3-dioxolanes with alkyllithium reagents to give aryl alkyl ketones (**1** → **2**) (3-5) and to the reaction of 2-alkyl- (6,7) and 2,2-dialkyl-1,3-dioxolanes (8-12) with Grignard reagents in hot benzene to give 1,2-ethanediol monoethers (**3** → **4**).

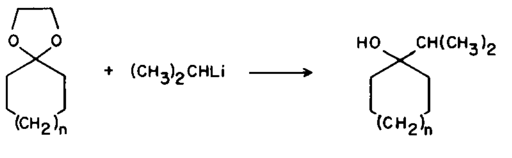


1 **2**

3 **4**

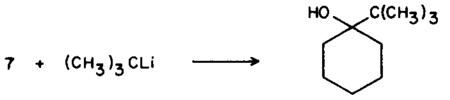
Since the dioxolane grouping is commonly employed to protect ketones against unwanted reactions with organometallic reagents (13), we felt it pertinent to call attention to a limitation on this practice when using highly reactive organolithium reagents.

Treatment of 1,1-ethylenedioxycyclopentane (**5**) with three equivalents of isopropyllithium in pentane at room temperature for 17 hours gave 1-isopropylcyclopentanol (**6**) in 64% yield. A similar reaction occurred with 1,1-ethylenedioxycyclohexane (**7**), affording 1-isopropylcyclohexanol (**8**) in 31% yield.



5: n = 0 **6**: n = 0
7: n = 1 **8**: n = 1

The more reactive *t*-butyllithium reacts with **7** under the same conditions to yield 1-(*t*-butyl)cyclohexanol (**9**) in 67% yield. The ketal **7** is much more stable to *n*-butyllithium, reacting to the extent of only 5% in the same period.



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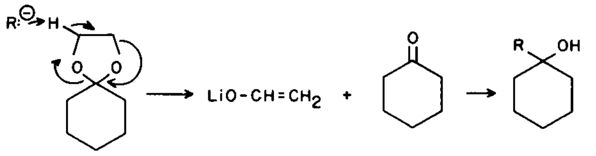
A probable mechanism for the reaction involves a concerted fragmentation of the ketal, leading to the lithium enolate of acetaldehyde and cyclohexanone, which reacts further with alkyllithium to yield the observed product (eq. 1). This hypothesis is supported by the observation that the ketal **10** is completely stable to *t*-butyllithium under the above conditions.



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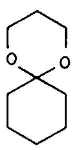

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EXPERIMENTAL

1-Isopropylcyclopentanol (6).

To a solution of 0.168 g. (2 mmoles) of cyclopentanone in 10 ml. of *n*-pentane under nitrogen was added 9.85 ml. of isopropyllithium in hexane (0.61 *M*., 6 mmoles). After 16 hours the mixture was quenched with 2 ml. of 50% aqueous isopropanol, extracted twice with 10 ml. portions of water, dried over calcium chloride and evaporated. There was obtained 0.112 g. of crude alcohol, which was purified by preparative vpc (10% Carbowax 20 M on Fluoropak at 167°).

Anal. Calcd. for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.67; H, 12.31.

1-Isopropylcyclohexanol (**8**).

The alcohol **8** was prepared in a strictly analogous manner from 0.196 g. (2 mmoles) of cyclohexanone.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.76. Found: C, 75.79; H, 12.77.

Reaction of 1,1-Ethylenedioxycyclopentane with Isopropyllithium.

To a solution of 0.256 g. (2 mmoles) of 1,1-ethylenedioxycyclopentane (14) in 10 ml. of pentane under nitrogen was added 9.85 ml. of isopropyllithium in hexane (0.61 *M*, 6 mmoles). After 17 hours the reaction mixture was quenched with 2 ml. of 50% aqueous isopropanol, extracted twice with 10 ml. portions of water, dried over calcium chloride and evaporated under reduced pressure to yield 0.145 g. of crude product. Analysis by vpc (150 ft. x 0.01 in. SF-96 capillary) showed it to consist of 36% of the unreacted ketal **5** and 64% of the alcohol **6**.

Reaction of 1,1-Ethylenedioxycyclohexane with Alkyllithium Reagents.

In a similar manner, 0.284 g. (2 mmoles) of 1,1-ethylenedioxycyclohexane (14) was treated with 6 mmoles of isopropyllithium for 17 hours. After workup, there was obtained 0.192 g. of crude product consisting of 69% of unreacted ketal **7** and 31% of alcohol **8**.

An identical reaction of 2.84 g. (20 mmoles) of the ketal **7** with 3 equivalents of 1.54 *M* *t*-butyllithium in pentane gave 2.57 g. of crude product containing 33% of unreacted ketal **7** and 67% of an alcohol, presumably 1-(*t*-butyl)cyclohexanol (**9**).

Analogous treatment of the ketal **7** with *n*-butyllithium for 17 hours gave a crude product consisting of greater than 95% of unreacted ketal. Approximately 5% of alcohol could be detected by capillary vpc.

Treatment of 1,1-Trimethylenedioxycyclohexane with *t*-Butyllithium.

Treatment of 0.292 g. (2 mmoles) of 1,1-trimethylenedioxycyclohexane (**10**) (14) with 3 equivalents of 1.54 *M* *t*-butyllithium in pentane for 17 hours, followed by normal workup gave a crude product consisting entirely of the unreacted ketal **10**.

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