Synthesis of a 5,6-Dienol

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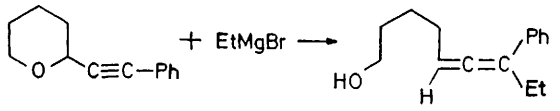
Summary Treatment of 2-(phenylethynyl)tetrahydropyran with ethylmagnesium bromide gives 7-phenylnona-5,6-dien-1-ol.

INTRAMOLECULAR additions of organometallic centres to isolated carbon–carbon multiple bonds have been well studied as potential routes to cycloalkanes,[1] but syntheses of allenic counterparts by use of olefinic and acetylenic



(I) (II)

precursors are limited. In particular, low yields are obtained of allene derivatives with several CH_2 units between the allenic triad and the organometallic centre, since multistep processes are necessary.[2] We required new synthetic routes to substituted 5,6-allenic alcohols, and report here a new synthesis of such allenols.

Coupling of 2-chlorotetrahydropyran with phenylethynylmagnesium bromide gives the racemic tetrahydropyran (I) (65%) [ν_{max} (film) 2220, 1600, 1490, 1440, 1080, 1030, 750, and 685 cm^{-1}; δ (CCl_4) 7·22 (5H, m, Ph), 4·42 (1H, m) 3·84 (1H, m), 3·5 (1H, m), and 1·6 (6H, m)].[3] Treatment of an ethereal solution of (I) with EtMgBr (2 mol. equiv.) for 24 h at room temperature affords the dienol (II) quantitatively in high purity [*m/e* 216·15; δ (CCl_4) 7·3 (5H, m, Ph), 5·5 (1H, m, C=C*H*), 3·5 (2H, t, OCH_2), 2·7 (1H, m, OH), 2·3 (2H, m), 2·05 (2H, m), 1·5 (4H, m), and 1·09 (3H, t, Me)].

The reaction has been extended to 2-(alkylethynyl)tetrahydropyrans. Rearrangement of (I) to allenols with other Grignard reagents has been observed; the scope of this reaction, and the possibility of using $LiAlH_4$ is being investigated.

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[1] Recent reports include: A. Maercker and K. Weber, *Annalen*, 1972, **756**, 20; J. K. Crandall and D. J. Nelson, to be published.
[2] J. K. Crandall and G. L. Tindell, *Chem. Comm.*, 1970, 1411; G. L. Tindell, Ph.D. Dissertation, Indiana University, Bloomington, Indiana, 1971.
[3] Other physical data were in agreement with those reported by R. Zelinski and J. Louvar, *J. Org. Chem.*, 1958, **23**, 807.