# A New Method for the Preparation of Allenic Alcohols

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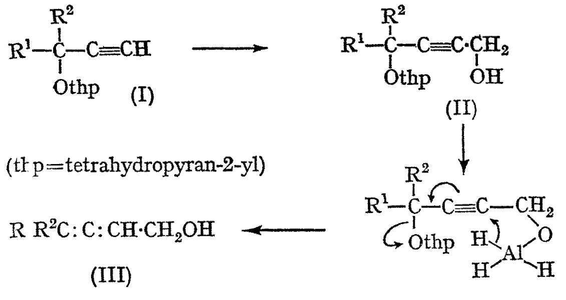
*Summary* Allenic alcohols are obtained in excellent yield by the ready elimination of the tetrahydropyranyloxy-group from the monotetrahydropyranyloxy-derivatives of butyne-1,4-diols with lithium aluminium hydride.

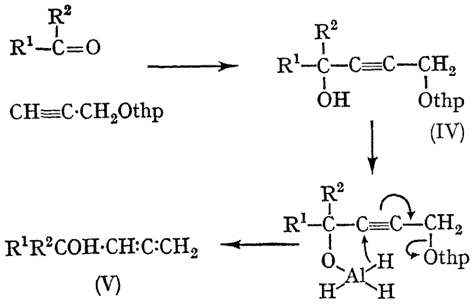
WE report a new general method for the synthesis of allenic alcohols from the monotetrahydropyranyloxy-derivatives of substituted butyne-1,4-diols (II),



(thp=tetrahydropyran-2-yl)

These are readily prepared from prop-1-yn-3-ols and dihydropyran,[1] followed by reaction with ethylmagnesium bromide and gaseous formaldehyde;[2] reduction with an excess of lithium aluminium hydride in ether gave the allenic alcohols (III) as the sole products (g.l.c. and elemental analysis) in excellent overall yields. For example, 4-tetrahydropyran-2′-yloxyhept-2-yn-1-ol (II; $R^1 = Pr$, $R^2 = H$) gave hepta-2,3-dien-1-ol (III; $R^1 = Pr$, $R^2 = H$) (95%), $\nu_{max}$ 3330 (OH), 1965 (·C:C:C·) and 875 (·C:C:CH·)cm.$^{-1}$; $\tau(CDCl_3)$ 9·1 (3H triplet, $CH_3$), 8·58 (2H multiplet, $\cdot CH_2 \cdot CH_2 \cdot CH_3$), 8·14 (1H singlet, OH), 8·08 (2H multiplet, $:CH \cdot CH_2 \cdot CH_2 \cdot$), 5·9 (2H multiplet, $\cdot CH_2 \cdot OH$), 4·72—4·66 (2H multiplet ·CH:C:CH·) and 4-methyl-4-tetrahydropyran-2′-yloxyhex-2-yn-1-ol (II; $R^1 = Et$, $R^2 = Me$) gave 4-methylhexa-2,3-dien-1-ol[3] (III; $R^1 = Et$, $R^2 = Me$) (73%), $\nu_{max}$ 3325 (OH) 1970 and 875 (C:C:C)cm.$^{-1}$; $\tau(CDCl_3)$ 9·05 (3H multiplet, $CH_3 \cdot CH_2 \cdot$) 8·32 [3H doublet of triplets, $CH_3 \cdot C(Et):$], 8·16 (2H quartet of doublets, $CH_3 \cdot CH_2 \cdot$), 8·11 (1H singlet, OH), 5·95 (2H doublet, $CH_2 \cdot OH$), 4·71 (1H octet :CH).

The synthesis is equally successful for terminal allenic alcohols,



starting from substituted butyne-1,4-diols with a protected primary hydroxy-group (IV) which are readily obtained from aldehydes or ketones and 3-tetrahydropyran-2′-yloxyprop-1-yne.[2] Thus, by reduction with lithium aluminium hydride we have prepared hepta-1,2-dien-4-ol[4] (V; $R^1$ = Pr, $R^2$ = H) (78%), $\nu_{max}$ 3350 (OH), 1960 (C:C:C), 845 (C:C:$CH_2$)cm.$^{-1}$; $\tau$($CDCl_3$) 9·05 (3H multiplet, C$H_3$), 8·5 (4H multiplet, ·C$H_2$·C$H_2$·), 7·5 (1H singlet O*H*), 5·75 (1H multiplet, ·C*H*OH), 5·12 (2H multiplet, :C$H_2$), 4·72 (1H multiplet, :C*H*·), and 4-methylhexa-1,2-dien-4-ol[5] (V; $R^1$ = Et, $R^2$ = Me) (87%), $\nu_{max}$ 3380 (OH), 1965 (C:C:C), 845 (C:C:$CH_2$) cm.$^{-1}$; $\tau$($CDCl_3$) 9·1 (3H triplet, C$H_3$·$CH_2$), 8·7 (3H singlet, C$H_3$·C), 8·45 (2H multiplet, C$H_2$·$CH_3$), 8·1 (1H singlet, OH), 5·12 (2H multiplet :C$H_2$), 4·77 (1H double doublet, C*H*:). The tetrahydropyranyloxy-group is much more easily displaced than a hydroxy-group as is shown by reduction of but-2-yn-1,4-diol with lithium aluminium hydride; this, under similar conditions, gave only 2% of buta-2,3-dien-1-ol and 98% of but-2-en-1,4-diol. However, under forcing conditions, 2,5-dimethylhex-3-yn-2,5,-diol gives the allene, 2,5-dimethylhexa-2,3-dien-5-ol,[6] in 54% yield, the displaced hydroxy-group being tertiary in this case.

Application of this reaction to the monotetrahydropyranyloxy-derivatives of enyne diols should give a cumulene alcohol. However, this is further reduced by an excess of hydride ion to a mixture of allenic and acetylenic alcohols[7] and therefore the method cannot be used for the synthesis of a cumulene.

(*Received, March* 12*th*, 1969; *Com.* 355.)

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