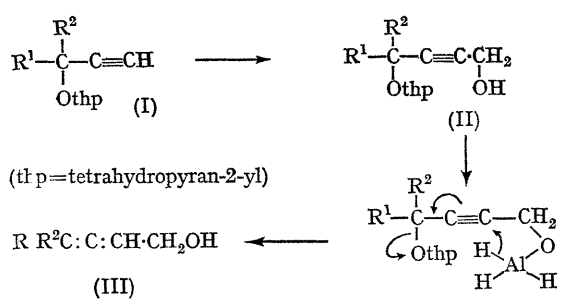
A New Method for the Preparation of Allenic Alcohols

By J. S. COWIE, PHYLLIS D. LANDOR, and S. R. LANDOR*
(*Department of Chemistry, Woolwich Polytechnic, London, S.E.*18)

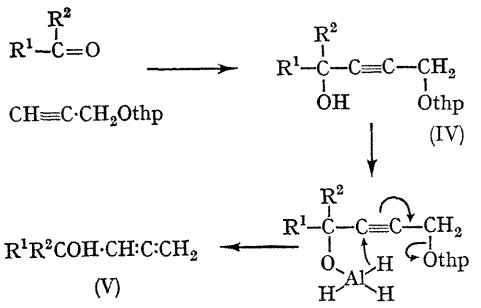
Summary Allenic alcohols are obtained in excellent yield by the ready elimination of the tetrahydropyranyloxy-group from the monotetrahydropyranyloxy-derivatives of butyne-1,4-diols with lithium aluminium hydride.

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



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%), ν_{max} 3330 (OH), 1965 (·C:C:C·) and 875 (·C:C:CH·)cm.$^{-1}$; τ($CDCl_3$) 9·1 (3H triplet, CH_3), 8·58 (2H multiplet, ·CH_2·CH_2·CH_3), 8·14 (1H singlet, OH), 8·08 (2H multiplet, :CH·CH_2·CH_2·), 5·9 (2H multiplet, ·CH_2·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%), ν_{max} 3325 (OH) 1970 and 875 (C:C:C)cm.$^{-1}$; τ($CDCl_3$) 9·05 (3H multiplet, CH_3·CH_2·) 8·32 [3H doublet of triplets, CH_3·C(Et):], 8·16 (2H quartet of doublets, CH_3·CH_2·), 8·11 (1H singlet, OH), 5·95 (2H doublet, CH_2·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%), ν_{max} 3350 (OH), 1960 (C:C:C), 845 (C:C:CH_2)cm.$^{-1}$; τ($CDCl_3$) 9·05 (3H multiplet, CH_3), 8·5 (4H multiplet, ·CH_2·CH_2·), 7·5 (1H singlet OH), 5·75 (1H multiplet, ·CHOH), 5·12 (2H multiplet, :CH_2), 4·72 (1H multiplet, :CH·), and 4-methylhexa-1,2-dien-4-ol[5] (V; R^1 = Et, R^2 = Me) (87%), ν_{max} 3380 (OH), 1965 (C:C:C), 845 (C:C:CH_2) cm.$^{-1}$; τ($CDCl_3$) 9·1 (3H triplet, CH_3·CH_2), 8·7 (3H singlet, CH_3·C), 8·45 (2H multiplet, CH_2·CH_3), 8·1 (1H singlet, OH), 5·12 (2H multiplet :CH_2), 4·77 (1H double doublet, CH:). 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 12th,* 1969; *Com.* 355.)

[1] H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *J. Chem. Soc.*, 1950, 3646; D. N. Robertson, *J. Org. Chem.*, 1960, **25**, 931.
[2] P. D. Landor, S. R. Landor, and E. S. Pepper, *J. Chem. Soc.* (*C*), 1967, 185.
[3] M. Bertrand and R. Maurin, *Compt. rend.*, 1965, **260**, 6122.
[4] M. Bertrand and J. Le Gras, *Compt. rend.*, 1962, **255**, 1305.
[5] H. Gutmann, O. Isler, G. Ryser, P. Zeller, and B. Pelmont, *Helv. Chim. Acta*, 1959, **42**, 718.
[6] A. C. Day and M. C. Whiting, *J. Chem. Soc.* (*B*), 1967, 991.
[7] S. R. Landor and N. F. H. Punja, unpublished results.