Reaction of Phenylmagnesium Bromide with 3,4-Epoxybut-1-ene

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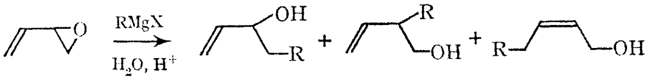
WE have observed anomalous behaviour in the reaction of organomagnesium compounds with 3,4-epoxybut-1-ene (I). The so-called 'conjugate addition' reaction of an organomagnesium reagent to an unsaturated system[1] has been of great value for the alkylation of specific sites,[2] particularly for systems with $\alpha\beta$-unsaturated aldehyde, ketone, or ester functions. We have extended this reaction to unsaturated systems which contain neither carbonyl or carboxyl functions. Three unsaturated alcohols can arise from direct reaction[3] of (I) and organomagnesium reagents:



(I) (II) (III) (IV)

Earlier investigations of this reaction give conflicting reports,[4–7] and the reaction of (I) with phenylmagnesium bromide was claimed to give either 4-phenylbut-2-enol (IV; R = Ph)[4] or 2-phenylbut-3-enol (III; R = Ph).[7] Our results conflict with both these reports.

Reaction of (±)-3,4-epoxybut-1-ene (I) (10·0 mmole) with phenylmagnesium bromide (11·0 mmole) in gently refluxing sodium-dried diethyl ether for 1 hr. gave a mixture of isomeric phenylbutenols (90%) which was analysed by v.p.c. Three compounds were separated by preparative v.p.c.:[†] compound (A) (II; R = Ph) 8·4 ± 1·5%, compound (B) (III; R = Ph) 84·0 ± 0·6%, and compound (C) (IV; R = Ph) 7·6 ± 1·4%. Although the i.r. spectra of compounds (A), (B), and (C) are very similar, ^{1}H n.m.r. spectroscopy with double-irradiation techniques and allyl alcohol as a model system[8] allows unambiguous structural assignments. In addition, compound (B) was hydrogenated with Pd–C and H_2 at 30 lb./in.^{2}, to give 2-phenylbutan-1-ol which was identical with an authentic sample (n.m.r. and v.p.c.).

We suggest that (II; R = Ph) arises from attack of the organomagnesium reagent at the unsubstituted oxiran ring position of 3,4-epoxybut-1-ene.

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[†] The products are stable to the v.p.c. conditions employed and no isomerization was observed.

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[2] See e.g.: J. Munch-Petersen, *J. Org. Chem.*, 1957, **22**, 170; H. O. House, W. L. Respess, and G. M. Whitesides, *ibid.*, 1966, **31**, 3128; H. O. House and R. W. Bashe, jun., *ibid.*, 1967, **32**, 784.

[3] Other products resulting from rearrangement of (I) prior to addition with the organomagnesium reagent have been observed: R. W. Freedman and E. I. Becker, *J. Org. Chem.*, 1951, **16**, 1701.

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[7] H. Gurien, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1955.

[8] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution Nuclear Magnetic Resonance Spectra Catalog," Varian Associates, Palo Alto, California, 1962, no. 34.