

REGIOSELECTIVE ALKYLATION OF ALLYLIC GRIGNARD REAGENTS .
A NEW SYNTHESIS OF GERANIOL.

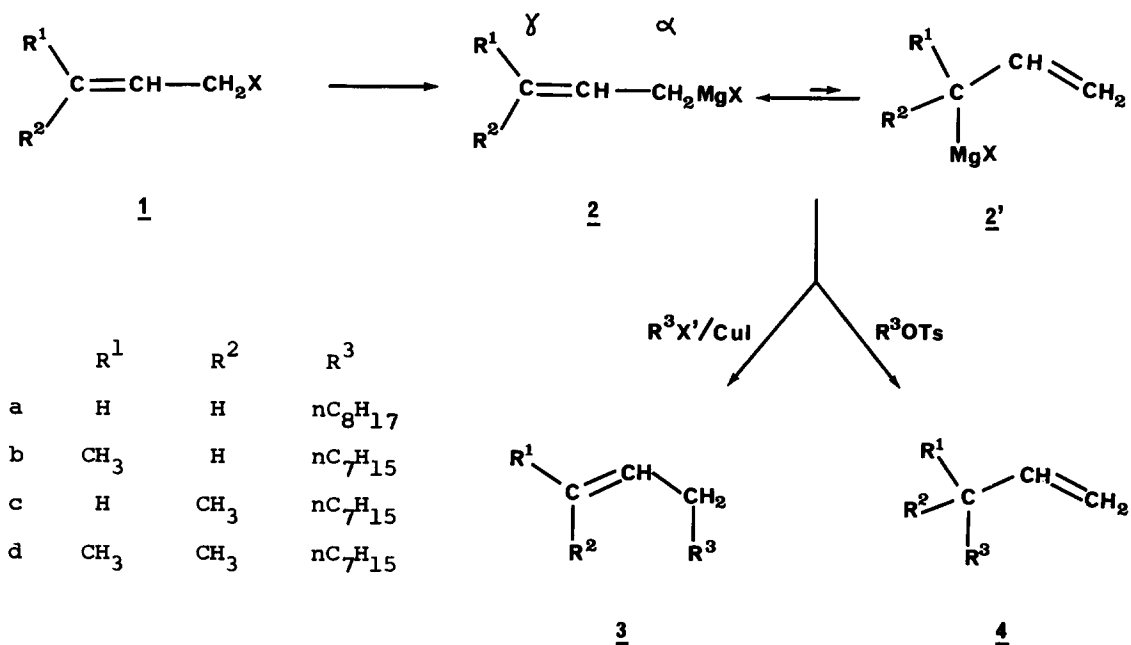
Fadila Derguini-Boumechal, Robert Lorne and Gerard Linstrumelle

E.R. 12 du C.N.R.S., Laboratoire de Chimie de l'Ecole Normale Supérieure
24, rue Lhomond, 75231 Paris Cedex 05.

(Received in UK 8 February 1977; accepted for publication 21 February 1977)

The allylic Grignard reagents^{1,2} provide a useful method of introducing a double bond into a molecule. However, the synthetic utility is often impeded by the formation of both isomers when an unsymmetrical substrate is utilized.

We wish to report the copper catalyzed alkylation³ of such species and the selective coupling reaction in the α or γ position.



We are continuing our investigations on the extension and applications of the cross coupling method reported here.

NOTES AND REFERENCES

- (1) R.A. Benkeser, Synthesis, 347 (1971)
- (2) G. Courtois and L. Miginiac, J. Organometal. Chem., **69**, 1 (1974)
- (3) Without copper salts, the alkylation of allylic Grignard reagents has been reported, by reactive halides : G. Stork, P.A. Grieco and M. Gregson, Tetrahedron Letters, 1393 (1969); A.F. Thomas and W. Pawlak Helv. Chim. Acta, **54**, 1822 (1971), and by an alkyl bromide (65 hr in refluxing ether) : R.L. Letsinger and J.G. Traynham, J. Amer. Chem. Soc., **72**, 849 (1950)
- (4) These compounds are identical to samples prepared by known procedures, G. Linstrumelle, Tetrahedron Letters, 3809 (1974); J. Millon, R. Lorne and G. Linstrumelle, Synthesis, 434 (1975); F. Derguini-Boumechal and G. Linstrumelle, Tetrahedron Letters, 3225 (1976)
- (5) All yields are based upon distilled products.
- (6) Containing 13% of 3-bromo-1-butene. There is no need to remove this impurity since both of these bromo isomers produce the same Grignard reagent^{1,2}
- (7) Without copper iodide, 4 hr from -40° to room temperature, a mixture (10:10:80) of 3b, 3c, 4c was obtained in 83% yield.
- (8) Without copper iodide, at 0° for 3 hr, a mixture (70:30) of 4d and 3d was obtained in 88% yield.
- (9) In this case, some 3-3-dimethyl -1-decene (2%) could also be detected.
- (10) The influence of the leaving group on sodium and lithium mesomeric carbanion alkylations has been reported : W.S. Murphy, R. Boyce and E.A. O'Riordan, Tetrahedron Letters, 4157 (1971); W. Oppolzer and R.L. Snowden, Tetrahedron Letters, 4187 (1976)
- (11) All new compounds were identified by satisfactory analytical and spectral data.
- (12) In tetrahydrofuran, this reaction was very slow : 60% of a mixture (8:92) of 3d and 4d and 40% of unreacted tosylate after 28 hr at 0°.
- (13) An attempted synthesis of geraniol with a similar procedure, without copper salts, failed : H. Kwart and R.K. Miller, J. Amer. Chem. Soc., **76**, 5403 (1954)

- (14) Prepared by hydrolysis of (E) -4-chloro-3-methyl-2-buten-1-ol acetate, W. Oroshnik and R.A. Mallory, J. Amer. Chem. Soc., 72, 4608 (1950); A. Allais, D. Bertin and G. Nominé, Bull. Soc.Chim. Fr., 209 (1955)
- (15) The reaction of (E) -4-bromo-3-methyl-2-buten-1-ol with 5 molar equivalents of lithium di-n-butyl-copper in ether has been reported: J.H. Babler and W.J. Buttner, Tetrahedron Letters, 239 (1976). We have found that (E) -4-chloro-3-methyl-2-buten-1-ol 5, (1 equiv.) with butylmagnesium bromide (2.4 equiv.) and copper iodide (0.24 equiv.), 1.5 hr from -50° to room temperature, in tetrahydrofuran, gave 65% of (E) -3-methyl-2-octen-1-ol.