

SYNTHESIS OF ALLYLIC HALIDES AND
1,5-DIENES FROM ALLYLIC ALCOHOLS

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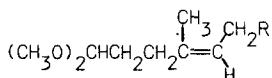
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The use of allylic alcohols as precursors of a variety of olefinic systems presents a problem, especially in the case of γ,γ -disubstituted derivatives, since it is essential to maintain the structure of the molecule.

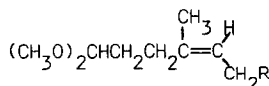
The most recent efforts (1) at producing trisubstituted olefins of known stereochemistry via the transformation of allylic alcohols involve formation of mesitoates (2) (e.g. from geraniol and nerol) followed by coupling with grignard reagents. The method was only reasonably successful with geraniol, although appreciable tertiary coupling took place, but it failed completely with the more hindered neryl isomer.

The chlorides should obviously be more generally useful, provided that they can be made without rearrangement and under conditions allowing the retention of sensitive groups.

Initial attempts using thionyl chloride in the presence of tributylamine (3) led, in our hands, to appreciable amounts of rearranged (tertiary) halides from γ,γ -disubstituted allyl alcohols, but we have found that the latter may readily be transformed into the corresponding chlorides by a procedure which we illustrate here with the sensitive acetal alcohol 1, R=OH, which has the nerol geometry: A solution of 3.48 g of 1, R=OH, in 10 ml of ether and 5 ml of hexamethylphosphoramide was treated at room temperature with one equivalent of commercial



II



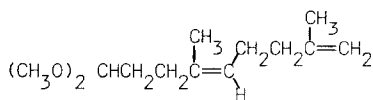
I

methyl lithium in ether, followed by 4 g of p-toluenesulfonyl chloride and 2.4 g of LiCl in 10 ml of ether and 5 ml of hexamethylphosphoramide. The mixture after standing overnight at room temperature and usual work up gave directly the desired chloride (4), 1, R=Cl, bp 66-69° (0.4 mm), δ (CDCl₃), 1.72 (3H,s), 3.25 (6H,s), 4.0 (2H,d,J-7), 4.25 (1H,t,J-7), 5.35 (1H,J-7).

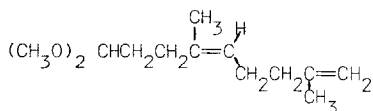
There was no detectable amount of terminal vinyl group. The trans isomer II, R=OH, could be converted in the same manner to the corresponding chloride II, R=Cl, and, similarly, pure geranyl chloride, bp 64-65° (0.05 mm), could be obtained from geraniol in 80% yield.

The transformation of nerol and geraniol into the chlorides I, R=Cl and II, R=Cl makes possible the synthesis of a variety of trisubstituted olefins via the usual SN₂ displacements on the pure halides. There are, however, substances which might more easily be obtained via coupling of grignard reagents. This is especially true of 1,5-dienes which we required in connection with other work, and which are represented by structures III and IV. Initial attempts at coupling I and II, R=Cl, with methallyl magnesium chloride led to considerable tertiary coupling, as might have been expected from published observations (5). We have found, however, that methallylmagnesium chloride readily couples in very high yield, and essentially without rearrangement, with either I or II, R=Cl, provided the coordination effectiveness of magnesium ion is decreased by the use of hexamethylphosphoramide as a co-solvent: A solution of methallylmagnesium chloride (from 40 g of methallyl chloride) in 250 ml of tetrahydrofuran was added slowly to a mixture of 10 g of I, R=Cl, in 75 ml of tetrahydrofuran and 75 ml hexamethylphosphoramide and kept overnight. This gave in 95% yield III, bp 75-78° (0.55 mm) λ film 6.08, 11.30 μ , δ (CDCl₃), 1.7 (6H,m), 3.30 (6H,s), 4.36 (1H,t), 4.72 (2H,s,broad), 5.20 (1H,t).

The trans chloride II, R=Cl, similarly gave IV in high yield. The main spectral difference between III and IV is that in the former the methyl on the trisubstituted double bond comes at the same place as the isopropenyl methyl (δ 1.7) whereas it is at δ 1.6 in the isomeric IV, as expected. (6).



IV



III

Acknowledgement.

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References.

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- (3) Cf. V. G. Young, F. F. Caserio, Jr., and D. D. Brandon, Jr., ibid., 82, 6163 (1960).
- (4) The direct formation of a chloride by this type of reaction was first observed with a propargylic alcohol by F. P. Darmory, in this laboratory.
- (5) E. J. Corey, S. W. Chow, and R. A. Scherrer, J. Am. Chem. Soc., 79, 5773 (1957).
R. M. Magid, and J. G. Welch, ibid., 90, 5211 (1968).
- (6) Cf. R. B. Bates and D. M. Gale, ibid., 82, 5749 (1960).