87. *The Action of Grignard Reagents on Esters of Optically Active Carboxylic Acids.*

By A. Campbell and J. Kenyon.

When methylmagnesium iodide and phenylmagnesium bromide react with (—)methyl hydratropate, the resulting tertiary alcohols are optically active.

Two different suggestions have been advanced as to the course of the reaction which occurs when a tertiary alcohol is produced by the interaction of a Grignard reagent and a carboxylic ester (Grignard, *Compt. rend.*, 1901, **132**, 336; Boyd and Hatt, *J.*, 1927, 898), but they have this in common—they both restrict the reactivity of the ester to the $\cdot CO_2R$ part of the molecule $R'\cdot CO_2R$.

It follows from this view of the mechanism of the reaction that when the reacting ester is derived from an optically active carboxylic acid the resulting tertiary alcohol will itself be optically active since the four bonds of the asymmetric atom present in the radical R′ remain undisturbed.

On the other hand it is stated by Bergmann and Hartrott (*J.*, 1935, 1218) that when the methyl ester of (—)-1-methylbutane-1-carboxylic acid reacts with phenylmagnesium bromide the resulting 1 : 1-diphenyl-2-methylpentan-1-ol is optically inactive. The authors recognise that this result is unexpected and to account for it they put forward several suggestions, one of which is that " the carbinol (or its bromomagnesium derivative) when formed undergoes spontaneously reversible dehydration $CHMePr\cdot CPh_2\cdot OH \rightleftharpoons CMePr{:}CPh_2$ which must be accompanied by racemisation ".

Although we considered this explanation inherently improbable we decided to investigate the reaction in case it could throw light on the failure of attempts to resolve racemic tertiary alcohols by the hydrogen phthalic ester procedure which has proved successful for the resolution of the less easily dehydrated secondary alcohols. (—)Methyl hydratropate reacts readily with methylmagnesium iodide and with phenylmagnesium bromide to yield the corresponding tertiary alcohols, both of which are optically active.

If Bergmann and Hartrott (*loc. cit.*) are right in supposing that tertiary alcohols which contain two phenyl radicals are capable of undergoing reversible dehydration when produced in the presence of excess of a Grignard reagent and subsequently of isolation as virtually pure alcohols, it seems reasonable to suppose that the equilibrium may be approached from the other side, and that the ethylenic dehydration product dissolved in the same excess of a Grignard reagent should, on addition of a molecular proportion of water, yield the virtually pure alcohol.

To test this hypothesis 1 : 1 : 2-*triphenylpropylene*, dissolved in four molecular proportions of phenylmagnesium bromide, was mixed with one molecular proportion of water : the mixture was then heated under reflux for two hours and decomposed in the usual manner, but no trace of tertiary alcohol was found and the unsaturated hydrocarbon was recovered unchanged.

It seems unlikely therefore that the optically active ester used by these authors underwent racemisation as a result of the reaction they describe. It may have been racemised by some undescribed agency : the ready racemisation of carboxylic esters under alkaline conditions (cf. Kenyon and Young, *J.*, 1940, 216) may be noted in this connexion.

EXPERIMENTAL.

(−) + *dl*-Methyl hydratropate, prepared from incompletely resolved hydratropic acid [15 g. of α_{5461} − 21·45° (*l*, 0·5)] (yield, 14 g.), had b. p. 109—110°/14 mm.; $d_{4^\circ}^{18^\circ}$ 1·0353; $n_{\mathrm{D}}^{18^\circ}$ 1·5008; α_{5893}^{20} − 19·28°, $\alpha_{5461}^{20^\circ}$ − 23·55° (*l*, 0·5).

(+) + *dl*-1 : 1-*Dimethyl*-2-*phenylpropan*-1-*ol*.—The methyl hydratropate (5 g.) was added dropwise to a solution of methylmagnesium iodide (Mg, 3 g.; MeI, 17·5 g.) and the mixture, after being heated under reflux for 2 hours, was decomposed with ammonium chloride solution. The resulting tertiary *alcohol*, b. p. 135—136°/15 mm. (yield, 5 g.), had $d_{4^\circ}^{20^\circ}$ 1·0372; $n_{\mathrm{D}}^{22^\circ}$ 1·5162; $\alpha_{5893}^{20^\circ}$ + 3·44°, $\alpha_{5461}^{20^\circ}$ + 4·02° (*l*, 0·5) (Found : C, 80·3; H, 9·9. $C_{11}H_{16}O$ requires C, 80·5; H, 9·7%).

(+) + *dl*-1 : 1 : 2-*Triphenylpropan*-1-*ol*.—Prepared as described above from the methyl ester (5 g.) and Grignard reagent (Mg, 3·2 g.; PhBr, 23·4 g.), this *alcohol* had b. p. 180—183°/15 mm. (yield 4 g.), and formed prisms from light petroleum, m. p. 90°; $[\alpha]_{5893}$ + 35°, $[\alpha]_{5461}$ +49° (*l*, 0·5; *c*, 2·40 in methanol); $[\alpha]_{5893}$ + 34°, $[\alpha]_{5461}$ + 53 (*l*, 0·5; *c*, 2·10 in chloroform) (Found : C, 87·5; H, 6·7. $C_{21}H_{20}O$ requires C, 87·5; H, 6·9%).

1 : 1 : 2-*Triphenylpropylene*.—A solution of 1 : 1 : 2-triphenylpropanol (10 g.) and iodine (0·1 g.) in benzene (10 c.c.) was heated under reflux for 24 hours, washed with sodium thiosulphate solution, and dried. The resulting *triphenylpropylene* had b. p. 174—177°/15 mm. (yield 7 g.) and separated from light petroleum in prisms, m. p. 93° (Found : C, 93·6; H, 6·8. $C_{21}H_{18}$ requires C, 93·3; H, 6·7%).

Attempted Hydration of 1 : 1 : 2-*Triphenylpropylene*.—The hydrocarbon (5 g.) was added to phenylmagnesium bromide (4 mols.); no visible reaction occurred. Water (0·3 c.c.) was then added dropwise to the stirred solution and the whole heated under reflux for 2 hours. Decomposition of the reaction mixture in the usual manner yielded unchanged 1 : 1 : 2-triphenylpropylene (4·5 g.), m. p. 93°, alone and when mixed with the untreated material.

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