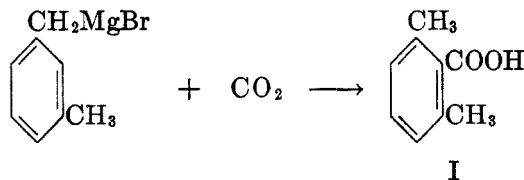


THE REACTION OF *m*-METHYLBENZYL MAGNESIUM BROMIDE
WITH CARBON DIOXIDE

CARL M. MOSER AND H. WILLIAM SAUSE

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Recently Musseron and Du (1) have carried out an extensive study on the reaction of methyl-substituted benzyl Grignard reagents with several reactants. The carbonation of the Grignard reagent formed from *m*-methylbenzyl bromide was among the reactions studied. The only product that was reported from this



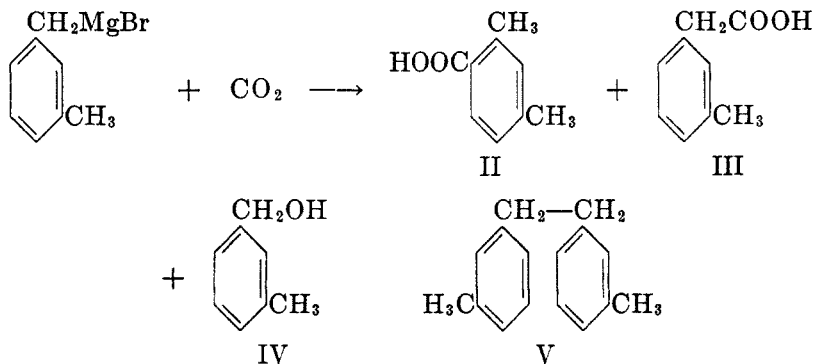
reaction was 2,6-dimethylbenzoic acid (I). The sole criterion for the identity of the product was a melting point, 115–116°, which is in good agreement with the melting point reported by other workers (2) for this acid.

The rearrangement observed in the course of this reaction was first discovered by Tiffeneau and Delange (3), who found that *o*-methylbenzyl alcohol rather than the expected β -phenylethyl alcohol is the product from the reaction of benzylmagnesium chloride and formaldehyde. The rearrangement most often observed is to the *ortho* position. However, in recent years rearrangement to the *para* position seems to have been definitely established. Austin and Johnson (4) have reported that 2,6-dichlorobenzylmagnesium chloride and acetyl chloride yield 3,5-dichloro-4-methylacetophenone, although the experimental details indicate that the reaction product may have been a mixture. More recently Burtle and Shriner (5) have definitely established the presence of about 5% *para* product in the reaction of benzylmagnesium chloride with diethyl sulfate. Musseron and Du (1) report that *o*-methylbenzylmagnesium bromide reacts with ethylene oxide to give 90% of the *para* product and 10% of the *ortho*.

In connection with another problem, we were in need of a quantity of I, and, as this procedure seemed convenient, the preparation of I as described by Musseron and Du was repeated.

The Grignard reagent from *m*-methylbenzyl bromide was prepared according to the usual procedure and also with the use of the "entrainment" procedure of Grignard (6) in which one mole of ethyl bromide is added to a mole of benzyl halide to enhance the formation of the benzyl Grignard reagent. The Grignard reagent was carbonated by bubbling dry carbon dioxide into the ethereal solution, and by pouring the ethereal solution on to Dry Ice. These variations in procedure produced no observable variation in the course of the reaction.

When the reaction mixture was worked up, the products were separated into acidic and neutral fractions. From the acidic fraction a solid acid could be readily



isolated, melting point 113–115° after one crystallization. Further recrystallization, however, raised the melting point to 122–123°. That this acid was not I but was instead 2,4-dimethylbenzoic acid (II) was definitely established by conversion of the acid to the amide. In addition to this acid there was also an oil in the acidic fraction that slowly solidified on standing in a desiccator. This was characterized as *m*-methylphenylacetic acid (III) through the amide. From the neutral fraction *m*-methylbenzyl alcohol (IV) was isolated along with a small quantity of higher-boiling material. This may have been the ditolylethane V, but there was insufficient material for complete characterization.

EXPERIMENTAL¹

m-Methylbenzyl bromide. The bromination of *m*-xylene was carried out according to the directions of Schramm (7) except that artificial illumination was used. On fractionation of the reaction mixture the following fractions were obtained: (a) recovered *m*-xylene (14%), b.p. 61° (23 mm.); (b) *m*-methylbenzyl bromide, b.p. 74° (4 mm.), $n_D^{25} 1.5545$, $d_4^{25} 1.373$ (74%); (c) crude solid *m*-xylene bromide (11%).

Reaction of m-methylbenzylmagnesium bromide with carbon dioxide. The following is a typical experiment. The *m*-methylbenzyl bromide (50 g.) was dissolved in dry ether (400 ml.) and was slowly dropped with vigorous stirring on to an excess (7.2 g.) of magnesium. The reaction proceeded during the addition of the halide and stopped soon after the last of the halide had been added. The reaction mixture was slowly poured over crushed Dry Ice (ca. 100 g.) and then allowed to stand at room temperature overnight. After hydrolysis with dilute hydrochloric acid, the layers were separated, and the aqueous layer was extracted once with ether. The ether solutions were combined and extracted with sodium carbonate solution. The carbonate solution was acidified and extracted with ether. The ether gave 26 g. of crude acid, m.p. 30–35°. Crystallization from dilute ethanol gave white needles, m.p. 113–115°. On further recrystallization material was obtained (6.4 g.) with m.p. 122–123° [reported (8) for 2,4-dimethylbenzoic acid, 125–126°]. A mixed m.p. of this acid with an authentic sample of 2,6-dimethylbenzoic acid (2) was 95–110°. The amide prepared from the acid in the usual manner melted at 182–183° [reported (9) for 2,4-dimethylbenzamide, 179–181°; reported (2) for 2,6-dimethylbenzamide, 138.5–139°]. On evaporation of the mother liquors a yellow oil remained that slowly solidified on standing in a desiccator, m.p. 40–50°. The melting point was not appreciably improved on crystallization. The amide

¹ Melting points are uncorrected.

prepared in the usual manner melted at 142–142.5°, and there was no depression on admixture of an authentic sample (10) of *m*-methylphenylacetamide.

The ethereal solution remaining after removal of the acidic material was dried and the ether evaporated. The residue was distilled and 2.1 g. of a pale yellow oil, b.p. 120–123° (26 mm.) [reported (1) for *m*-methylbenzyl alcohol 215° (740 mm.)] was obtained. Oxidation of this oil with permanganate gave *m*-toluic acid, m.p. 111–112°, undepressed when mixed with an authentic sample. A small quantity of a viscous, red-brown oil remained in the distillation flask. It did not appear to be either an alcohol or ketone. Attempts to oxidize this material did not lead to any recognizable products.

SUMMARY

1. The reaction of *m*-methylbenzylmagnesium bromide with carbon dioxide results in the formation of a mixture of 2,4-dimethylbenzoic acid, *m*-methylphenylacetic acid, and *m*-methylbenzyl alcohol. No 2,6-dimethylbenzoic acid could be isolated from the reaction mixture.

BALTIMORE 18, MARYLAND

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