# **REACTION OF 1-METHYLCYCLOPROPENE**

### WITH METHYLMAGNESIUM IODIDE

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We found that 1-methylcyclopropene (I), in contrast to the previously studied cases [1, 2], when reacted with CH<sub>2</sub>MgI is capable of not only adding the starting Grignard reagent, but also the reaction product, namely 1,1-dimethylcyclopropylmagnesium iodide.

The reaction was run in ether at 0°C in a dry argon atmosphere and using an equimolar ratio of the reactants. The reaction products were identified by converting the formed organomagnesium compounds to the corresponding hydrocarbons and carboxylic acids. The decomposition of the reaction mixture with water gave a mixture of hydrocarbons (IIa) and (IIIa) in  $\sim 100\%$  yield, in a weight ratio of 5:4 (GLC data). Compound (IIa) was identified chromatographically by the retention time. Hydrocarbon (IIIa) was isolated by fractional distillation through a column, and its structure was confirmed by the elemental analysis, NMR, and mass spectral data. Carboxylation of the reaction mixture led to a mixture of acids (IIb) and (IIb), which without isolation were converted to methyl esters (IIc) and (IIIc) by treatment with CH<sub>2</sub>N<sub>2</sub>. Their ratio in the reaction mixture was 43:57 (GLC data). By fractional distillation in vacuo we isolated the pure (IIc) ester (the structure was confirmed by the elemental analysis and by the NMR and mass spectra) and a fraction that represented (IIIc). contaminated with 20% of (IIc) (NMR data).

An increase in the (I): CH<sub>3</sub>MgI ratio failed to lead to a substantial increase in the yield of (II). Thus, with a mole ratio of (I):  $CH_3MgI=2:1$  the yield of (IIa) was 52% (GLC data), but here the amount of the ene condensation products of (I) [3] increased substantially, which made it difficult to isolate compounds (II) and (III).

#### EXPERIMENTAL

The NMR spectra were taken on a Varian DA-60-IL instrument, using HMDS as the internal standard, and the chemical shifts are given in parts per million relative to TMS on the  $\delta$  scale. The mass spectra were taken on an MX-1303 spectrometer. The GLC analysis was run using a Pye-104 instrument. All of the operations were run in a dry argon atmosphere.

1-Methylcyclopropene (I) was obtained as described in [4], and the ratio of (I) and methylenecyclopropane (impurity less than 10%) was determined via the NMR spectrum and GLC. 1,1-Dimethylcyclopropane was obtained as described in [5].

Reaction of 1-Methylcyclopropene (I) with CH<sub>3</sub>MgI. a) Into 126 ml of an 0.92 N ether solution of CH<sub>3</sub>MgI (0.116 mole) at 0° was passed 6.7 g (0.125 mole) of (I), containing 6.0% of methylenecyclopropane. The reaction mixture was let stand overnight at  $\sim 20^{\circ}$ . Then it was decomposed with water. According to the GLC data, the yield of (IIa) and (IIIa) when based on reacted (I) was ~ 100%, and the ratio (IIa) : (IIIa) =5 :4. The gem-dimethylcyclopropane was identified by GLC using an authentic specimen. Fractional distillation through a column filled with glass packing, with an efficiency of 15 theoretical plates, gave a fraction with bp 52.1-53.0° (42 mm). which was distilled over Na to give the pure (IIIa) (based on the GLC data). Found: C 86.62; H 12.89%. C10H16. Calculated: C 87.02; H 12.98%.

The mass spectrum has the molecular ion m/e 124. NMR spectrum (in  $CHCl_3$ ): 1.13 s ( $C-C(CH_3)_2$ , 6H);

1.07 s (C C C H<sub>3</sub>, 3H); 0.22-0.27 w. m (H<sub>2</sub>C C H<sub>2</sub>, 4H); ABX spectrum c A A 0.125,  $\delta$  B 0.150,

 $\delta_X$  0.920 ppm,  $J_{AX}$  = 8.45,  $J_{BX}$  = 5.55,  $J_{AB}$  = 4.4 Hz, 3H.

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b) An ether solution of a mixture of (II) and (III), obtained as described above from 1.44 g (0.06 g-atom) of Mg. 8.52 g (0.06 mole) of CH<sub>3</sub>I, and 4.13 g (0.07 mole) of (I), was carboxylated at -78° with CO<sub>2</sub>, which had been dried by passage through conc. H<sub>2</sub>SO<sub>4</sub>. After distilling off most of the ether the residual product was treated at -27° with a 3-fold excess of  $CH_2N_2$ . Distillation gave 0.46 g of (IIc), bp 69-71° (64 mm),  $n_D^{20}$  1.4287. Found: C 65.36; H 9.33%. C7H12O2. Calculated: C 65.59; H 9.04%. NMR spectrum (in CCl4): 0.59-1.05 m CH<sub>2</sub>, 2H); **1.10s** (OOC--C с—сн<sub>3</sub> trans, 3H); 1.14 s (оос—с́--C-CH<sub>3</sub> cis, 3H); 1.35-1.59 m (ć CH-COO. 1H): 3.57 s (OCH<sub>3</sub>, 3H). NMR spectrum (in  $C_6H_6$ ): 0.50-1.58 m (protons of three-membered ring, 3H); 0.93 s CH<sub>a</sub> trans, 3H); 1.19 s (00C CH<sub>3</sub> cis, 3H); 3.45 s (OCH<sub>3</sub>, 3H). Scheme  $CH_3$ CH₃ CH<sub>3</sub>MgI  $CH_{3}$ (I) IMg CH CH₃ (II)(III)CH<sub>3</sub> H<sub>2</sub>O CO<sub>2</sub> CH3 CH3 CH<sub>3</sub>  $CH_3$ CH<sub>3</sub> CH<sub>3</sub> HOOC CH. ноос CH. CH₃  $CH_3$ (ПЪ) (lIa) (IIIa) (IIb) CH<sub>2</sub>N<sub>2</sub>  $CH_3$ CH₃ CH3 H<sub>3</sub>COOC H\_C00C CH<sub>3</sub>  $CH_3$ (IIIC) (11 c)

The fraction with bp 123-125° (64 mm) was (IIIc), contaminated with 20% of (IIc). NMR spectrum (in  $C_6H_6$ ): 0.13-1.58 m (protons of three-membered ring);  $\delta$  0.91, 1.02, and 1.12 ppm (singlets of three CH<sub>3</sub> groups on three-membered rings); 3.41 s (OCH<sub>3</sub>, 3H).

#### CONCLUSIONS

1. In contrast to the previously studied cases, 1-methylcyclopropene adds to the double bond not only  $CH_3MgI$ , but also the 1,1-dimethylcyclopropylmagnesium iodide that is formed during reaction.

2. 1-(1-methylcyclopropyl)-2,2-dimethylcyclopropane and 2-methyl-cis-1-r-carbomethoxy-2-(2,2-dimethylcyclopropyl) cyclopropane were obtained for the first time.

## LITERATURE CITED

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