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Synthesis and Reactions of 2-Cyclopenten-1-ylmagnesium Chloride

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The preparation of 2-cyclopenten-1-ylmagnesium chloride is described. 2-Cyclopentene-1-carboxylic acid and other 2-cyclopenten-1-yl compounds are thus readily prepared. The acid is isomerized in sodium hydroxide solution to the α,β-isomer and the equilibrium concentration has been determined by NMR-spectroscopy.

The successful preparation of 2-cyclopentene-1-carboxylic acid (Ic) by the most obvious way, *viz.* carbonation of 2-cyclopenten-1-ylmagnesium chloride (Ib), has never been achieved owing to the difficulty in obtaining the allylic Grignard reagent. It has only been brought to reaction, with carbon dioxide[1] and formaldehyde,[2] respectively, in the Barbier modification, *i.e.* generation of the Grignard reagent in the presence of the other reactant. Minute amounts of the acid Ic and a 20 % yield of 2-cyclopenten-1-ylcarbinol (If) could be isolated.

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R	R
a. Cl	e. CO_2CH_3
b. MgCl	f. CH_2OH
c. COOH	g. CH_2Cl
d. COCl	h. $C(OH)Ph_2$
	i. CH_2COOH

We now report the preparation, in tetrahydrofuran (THF) at low temperature, of 2-cyclopenten-1-ylmagnesium chloride. Reaction conditions must be very accurately controlled (see experimental part) in order to obtain good yields (about 60 %, judged by carbonation). The Grignard reagent, when formed, is quite stable as shown by the fact that refluxing the solution for 40 h did not depress the yield of acid Ic.

In no case has the isomeric acid, 1-cyclopentene-1-carboxylic acid, been found. This acid is formed by isomerisation of 2-cyclopentene-1-carboxylic acid under alkaline conditions. This behaviour is in accordance with that of other β,γ-unsaturated acids. The rather slow isomerisation was followed by means of NMR-spectroscopy. The equilibrium mixture contained 80 % α,β-unsaturated acid.

The coupling product, di-(2-cyclopenten-1-yl), is found as a by-product. It can be made the major product, when the reaction is run in diethyl ether at reflux temperature.[1] Presumably, it is a mixture of stereoisomers, the composition depending on reaction temperature.

The conditions found optimal in THF was tried in diethyl ether and in methylal. In the former case a Grignard reagent was formed, and an 18 % yield of acid Ic resulted from carbonation. In the latter case, however, only the dimer was isolated (57 %).

With benzophenone the Grignard reagent (in THF) gave 2-cyclopenten-1-yldiphenylcarbinol (Ih).

Treatment of acid Ic with diazomethane gave the methyl ester (Ie) which is also formed from the acid chloride (Id) and methanol. This ester has previosuly been prepared from the nitrile.[2] The acid chloride is easily obtained from the acid and thionyl chloride.

It has been reported [2] that reduction of methyl and ethyl 2-cyclopentene-1-carboxylate with lithium aluminum hydride gives very poor yields (6 and 8 %) of 2-cyclopenten-1-ylcarbinol (If). We encountered no difficulty with this reaction. In several runs yields from the methyl ester varied between 90 and 97 %.

When the carbinol was treated with thionyl chloride in pyridine by the method of Frazer *et al.*[4] 2-cyclopenten-1-ylcarbinyl chloride (Ig) was formed. This chloride gave a Grignard reagent which yielded, after carbonation, the known 2-cyclopenten-1-ylacetic acid (Ii)

The structures of the cyclopentenyl compounds are confirmed by their NMR-spectra which show complex multiplets. Recently, Chapman and King [5] found that the splitting of the proton signal from alcoholic hydroxyl groups could be observed in dimethyl sulfoxide. This was found also for the carbinol If, which shows a triplet (τ 5.5 ppm), indicating a primary alcohol group.

EXPERIMENTAL

A typical preparation of the Grignard reagent follows.

2-Cyclopenten-1-ylmagnesium chloride (Ib). A four-necked reaction flask is fitted with a mechanical stirrer, a reflux condenser with its top connected to a by-pass nitrogen lead, a graduated separatory funnel (250 ml) with pressure-equalizing tube, and a thermometer reaching into the reaction mixture. The whole apparatus should be completely dry and flushed with purified nitrogen. Dry magnesium turnings (19.5 g, 0.8 at.) and purified THF (250 ml) are placed in the flask, and 3-chlorocyclopentene (Ia) (82 g, 0.8 mole), diluted with THF to 250 ml, in the separatory funnel. The flask, with the stirrer started, is cooled in a dry ice-acetone bath (−12° external), and when the temperature of the flask content has reached −10° the addition of the chloride is started and kept at a rate of about 50 ml/h. Normally, the reaction will start (indicated by beginning rise of temperature) after 20−30 min and will be almost finished when all the chloride has been added (5−6 h). The temperature must be kept near −10° all the time by adjusting the external cooling. After stirring for one additional hour the reagent is ready for use.

2-Cyclopentene-1-carboxylic acid (Ic). The Grignard solution, prepared as described above, is forced with nitrogen pressure into a slurry of dry ice (*ca.* 250 g) and THF (100 ml) contained in a beaker (2 l). Working up is conventional and includes continuous extraction with ether of the acidified aqueous layer. From the amounts of reactants mentioned there resulted: 2-cyclopentene-1-carboxylic acid, 50 g (55 %), b.p. 103−104°/11 mm, n_D^{25} 1.4667, and di-(2-cyclopenten-1-yl), 15 g (28 %), b.p. 52−57°/9 mm, n_D^{24} 1.4857.

In one instance where the Grignard solution was refluxed (temperature 70°) for 40 h before carbonation, the yield of the acid rised to 61 % and that of the dimer was 24 %.

2-Cyclopenten-1-yldiphenylcarbinol (Ih). Benzophenone (44 g, 0.24 mole) in THF (100 ml) was added (15 min) to the Grignard reagent from 0.4 mole of chloride at −5° and left overnight at room temperature. 38.7 g (64.5 %) of carbinol were isolated. B.p. 143.5−146°/0.2 mm, n_D^{24} 1.5930. (Found: C 86.5; H 6.97. Calc. for $C_{18}H_{18}O$: C 86.4; H 7.25).

Isomerisation of 2-cyclopentene-1-carboxylic acid. The acid (11.2 g, 0.1 mole) was dissolved in 400 ml of 10 % sodium hydroxide and the solution refluxed for 22 h. 8.72 g (78 %) of 1-cyclopentene-1-carboxylic acid were isolated. M.p. 119°, uncorr. (Ref. 6, 120−121°).

In another experiment 2.0 g (0.018 mole) were refluxed for 8 days with a 5% solution of sodium hydroxide. Aliquots were withdrawn, acidified and extracted twice with ether. After drying over magnesium sulphate the ether was evaporated and the residue was dissolved in deuteriochloroform and the NMR-spectrum was recorded. The relative amounts of the two isomeric acids were evaluated from the signals at τ 4.2 ppm (two olefinic protons in the β,γ-acid) and 3.1 ppm (one olefinic proton in the α,β-acid). Equilibrium was reached in 4−5 days and the equilibrium mixture contained 80 ± 2 % of the α,β-acid.

2-Cyclopentene-1-carboxylic acid chloride (Id). The acid (27.2 g, 0.24 mole) was added (30 min) to refluxing purified thionyl chloride (58 g). After reflux for one additional hour the reaction mixture was worked up. Yield of acid chloride was 27 g (85 %). B.p. 59−60°/22 mm; n_D^{25} 1.4740. (Found: C 55.3; H 5.36; Cl 26.8. Calc. for C_6H_7OCl: C 55.2; H 5.41; Cl 27.1).

Methyl 2-cyclopentene-1-carboxylate (Ie). a) From diazomethane (5 g, 0.12 mole) and acid Ic (11.2 g, 0.10 mole) in ether at −5° was obtained 13.0 g (99.5 %) of the methyl ester. B.p. 44−45°/9 mm, n_D^{25} 1.4479.

b) The acid chloride Id (25. 4 g, 0.20 mole) was added (50 min) to methanol (8 g) at 0°. The reaction mixture was left for an hour before working up. Yield 24.4 g (99 %). B.p. 46°/10 mm (b.p. 156°/760 mm), n_D^{25} 1.4490. (Found: C 65.9; H 7.75. Calc. for $C_7H_{10}O_2$: C 66.6; H 7.98).

2-Cyclopenten-1-ylcarbinol (If). To lithium aluminum hydride (7 g) in ether (200 ml) was added in the course of 45 min methyl 2-cyclopentene-1-carboxylate (40 g, 0.32 mole) dissolved in ether (200 ml). Stirring was maintained for additional 30 min before hydrolysis. Yield 28.7 g (92 %). B.p. 58−59°/9 mm, n_D^{22} 1.4737.

In one experiment, where lithium aluminum hydride was extracted into the ethereal solution of the ester, a 97 % yield of the carbinol was obtained.

2-Cyclopenten-1-ylcarbinyl chloride (Ig). Carbinol If (28.3 g, 0.29 mole) and pyridine (22.7 g, 0.29 mole) in ether (100 ml) was cooled to −10° and thionyl chloride (33. 6 g, 0.15 mole) was added according to Frazer *et al.*[4] The distilled product (25.2 g, 75.5 %), b.p. 66−90°/80 mm, was rather impure. It was purified with bicarbonate solution and redistilled: 18.8 g (56 %), b.p. 70−72°/80 mm, n_D^{23} 1.4733. (Found: C 62.2; H 7.69; Cl 29.6. Calc. for C_6H_9Cl: C 61.8; H 7.78; Cl 30.4).

2-Cyclopenten-1-ylacetic acid (Ii). 2-Cyclopenten-1-ylcarbinyl chloride (3.6 g, 0.03 mole) in ether (25 ml) was added (25 min) to magnesium (0.84 g, 0.034 at.) and ether (10 ml). A crystal of iodine was added from the start. Afterwards, the reaction mixture was heated and refluxed overnight. After carbonation 2.44 g (62 %) of distilled product were isolated. B.p. 117−118°/12 mm, n_D^{26} 1.4681.

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