

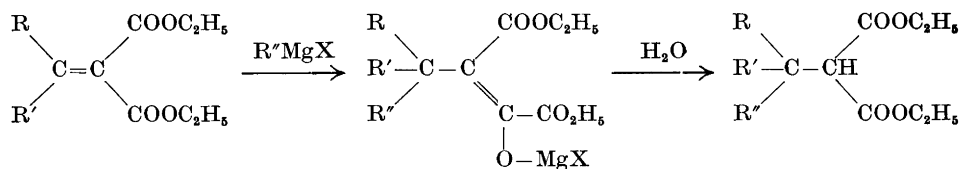
The Action of Phenylmagnesium Bromide on Diphenylmethylenemalonic Ester

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α -Benzoyl- β,β -diphenyl- β -ethoxypropionic ester is formed in the reaction between phenylmagnesium bromide and diphenylmethylenemalonic ester.

The action of Grignard reagents on alkylidenemalonic^{1,2} and arylidenemalonic³ esters usually results in 1,4-addition to the conjugated double bond system $C=C-C=O$:



Reactions involving diphenylmethylenemalonic ester ($R = R' = \text{phenyl}$) have not been studied, however. When the investigations were extended to the reaction between this substance and phenylmagnesium bromide, a compound melting at $164.5\text{--}165.5^\circ$ was obtained in a low yield. A single 1,4-addition is not possible since this reaction would have resulted in triphenylmethylmalonic ester, m.p. 133° . Combustion analysis and molecular weight determination pointed to the composition $\text{C}_{26}\text{H}_{26}\text{O}_4$, *i.e.* one molecule of diphenylmethylenemalonic ester had taken up one phenyl group and one hydrogen atom.

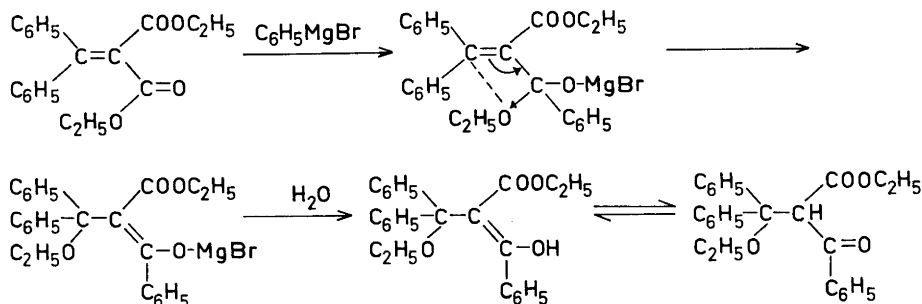
In order to study the changes in structure, the IR spectra of diphenylmethylenemalonic ester and the reaction product dissolved in tetrachloromethane were compared with each other. The most dominant feature of the former spectrum is a strong and broad band at $1750\text{--}1700\text{ cm}^{-1}$ due to the conjugated double bond system $C=C(C=O)_2$. After the reaction with the Grignard reagent, this band is replaced by two bands at 1755 and 1720 cm^{-1} . Further, the bands in the neighbourhood of 3000 cm^{-1} are slightly broadened and new,

distinct bands appear at about 1 640 (strong), 1 595—1 560 (strong), 1 140 (sharp), and 1 120 (sharp) cm^{-1} .

The change in the band at about 3 000 cm^{-1} and the new and strong band at 1 640 cm^{-1} implies an enolized β -keto ester containing a hydrogen bond (II)⁴. The additional absorption in the usual ketone region supports the hypothesis that even in this case an equilibrium between the keto form (I) and the enol form (II) exists.

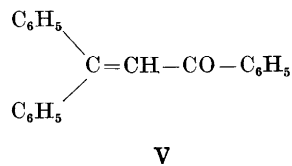
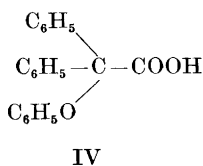
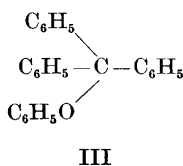


These circumstances and the composition $\text{C}_{26}\text{H}_{26}\text{O}_4$ suggest a 1,2-addition to the double bond between the carbon and oxygen atoms in one of the carboethoxy groups of the malonic ester followed by an allylic type rearrangement for the formation of the compound:



The two phenyl groups and the readily removed hydrogen atom in the vicinity should make the ethoxy group labile in both acid and alkaline solution. This prediction is in harmony with the experimental observations.

Further, asymmetrical C—O—C stretching vibrations of an open chain ether occur usually near 1 100 cm^{-1} . IR spectra of triphenylmethyl ethyl ether (III) and ethoxydiphenylacetic acid (IV) show absorption bands at 1 115 cm^{-1} which well correspond to the band of the present substance at 1 120 cm^{-1} .



Owing to the instability of the substance, it was not possible to isolate in the pure state a simple fragment of the molecule containing the phenyl groups and the ethoxy group attached to the same carbon atom. The properties of the substance on saponification and oxidation may, however, be interpreted as proof of the suggested structure. When the substance is saponified with alkali, it may be expected that besides the reactions which occur with β -keto esters the ether group will be partly split off as ethanol. On oxidation of the alkaline solution, a part of the compound should therefore give benzophenone and a part a mixture of ethoxydiphenylacetic acid and benzoic acid. Experiments proved that benzophenone is formed (isolated as its 2,4-dinitrophenylhydrazone), and when the acids were chromatographed on paper, spots with the same R_F values as ethoxydiphenylacetic acid and benzoic acid were obtained in addition to spots with lower R_F values. When the ether group was split off by treating with hydrochloric acid before the saponification, the results were similar but the spot corresponding to ethoxydiphenylacetic acid was lacking.

It may be pointed out that even the reaction between phenylbenzylideneacetone (V) and phenylmagnesium bromide proceeds as a 1,2-addition⁵.

EXPERIMENTAL

Diphenylmethylenemalonic ester was prepared according to Wideqvist⁶.

Action of phenylmagnesium bromide on diphenylmethylenemalonic ester. To the Grignard reagent prepared from magnesium (3.60 g), bromobenzene (23.56 g) and dry ether (55 ml) a solution of diphenylmethylenemalonic ester (16.20 g) in dry ether (50 ml) was gradually added in the course of 15 min. After the brown mixture had been refluxed for one hour, it was cooled and poured into a mixture of ice and dilute hydrochloric acid. The ether phase was washed with water and a dilute solution of potassium carbonate. When it was dried with sodium sulphate, crystals began to separate on the surface of the drying agent. After standing overnight, the precipitate was filtered off and treated with warm water until free from sodium sulphate. When the ether filtrate was allowed to evaporate slowly, another smaller sample was obtained. The total yield of α -benzoyl- β,β -diphenyl- β -ethoxypropionic ester was 25.5 % (5.12 g). After being dissolved in benzene and precipitated with ethanol it melted at 164.5–165.5°. (Found: C 77.53; H 6.46; Mol.wt. (Rast) 387 ± 15 . Calc. for $C_{26}H_{26}O_4$: C 77.59; H 6.51; Mol.wt. 402).

Saponification and oxidation of the substance. A small sample (0.30 g) was dissolved in ethanol (30 ml). A solution of potassium hydroxide (0.80 g) in water (1 ml) was added and the mixture heated on a boiling water bath for 2 h. The alcohol was evaporated under reduced pressure and the residue dissolved in water. A 5 % potassium permanganate solution was then added until the red colour persisted. After the manganese dioxide had been dissolved by adding sodium hydrogen sulphite and dilute sulphuric acid, the organic substances were extracted with ether. Organic acids were removed by shaking with a dilute potassium hydroxide solution. From the residue (0.05 g) of the neutral ether solution, benzophenone was isolated as its 2,4-dinitrophenylhydrazone, m.p. 238–239°.

The alkaline aqueous solution containing the organic acids was acidified and extracted with ether. The residue (0.19 g) of the ether phase was examined chromatographically on paper (Schleicher & Schüll 2043 b GI) and aqueous ammonium carbonate and propanol as the mobile phase. After spraying with an acid solution of bromophenol blue, spots with the following R_F values were obtained: 0.92, 0.77, 0.69 and 0.60. Under the same conditions ethoxydiphenylacetic acid and benzoic acid had R_F values of 0.92 and 0.76, respectively.

When a sample of the substance (0.55 g) was first boiled with a mixture of ethanol (125 ml), water (5 ml) and hydrochloric acid (6 ml) for 2 h and then treated as above after addition of potassium hydroxide (6 g) in water (6 ml), the spot with the R_F value 0.92 was absent.

The elementary analysis was carried out by Dr. A. Bernhardt, Mühlheim, and the IR spectra were taken by Mr. B. C. Fogelberg, Centrallaboratorium Ab., Helsingfors.

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