

spectrum (CDCl₃): δ 2.06 (s, 3 H); 2.27 (s, 3 H); 3.84 (s, 2 H); 7.1–7.35 (m, 6 H); 7.40–7.65 (m, 2 H). IR spectrum (KBr) cm⁻¹ (intensity): 2920 (w), 1745 (s), 1655 (m), 1445 (m), 1365 (ms), 1220 (s), 1155 (s), 1008 (m), 948 (m), 781 (s), 738 (s). Mass spectrum (*m/e* (%)): 264 (4), 222 (64), 179 (64), 178 (60), 43 (100).

4a+b, *Enolacetate of 9,10-diacetyl-9,10-dihydroanthracene*, 0–2% yield, m.p. 152–158°C (light petroleum), probably a mixture of the *cis* and *trans* forms. ¹H NMR spectrum (CDCl₃): δ 2.10 (s 6 H), 2.3 (two closely spaced singlets, 6 H), 7.1–7.6 (m 8 H). Mass spectrum (*m/e* (%)): 348 (1.5), 306 (10), 264 (28), 263 (38), 246 (17), 221 (16), 203 (17), 178 (22), 73 (68), 43 (100).

9-Acetyl-9,10-dihydroanthracene, (4). **3** was hydrolyzed in aqueous ethanolic 1 N HCl by boiling for 3 h under nitrogen. After cooling the mixture was diluted with water and extracted with ether, which was washed with an aqueous sodium bicarbonate solution and dried. Evaporation of the ether left a residue which was purified on a column of alumina using 5/95 ethyl acetate/light petroleum as eluent. **4** (liquid),^{8,9} ¹H NMR (60 HMz, CDCl₃): δ 1.96 (3 H, s), 3.89 (1 H, d, *J* 18.5 Hz), 4.14 (1 H, d, *J* 18.5 Hz), 4.93 (1 H, broad s) 7.1–7.5 (8 H, m). Besides the couplings recorded, small unresolved long-range couplings between the 9 and 10 protons are found. **4** semicarbazone, m.p. 222–224°C (224–226°C).⁹

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The Reaction of 2-Methylphenylmagnesium Bromide with Ethyl 3-Coumarincarboxylate. Addition of Three Reagent Molecules Followed by a Ring Opening

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The reaction of 2-methylphenylmagnesium bromide with ethyl 3-coumarincarboxylate (**1**) has recently been studied in this laboratory.¹ The reaction product proved to be ethyl 4-(2-methylphenyl)-3,4-dihydrocoumarin-3-carboxylate (**2**), formed by a fast conjugate addition.

It has earlier been established that phenylmagnesium bromide to some extent can react further with the primarily formed 1,4-adduct giving slowly 3-(2-hydroxyphenyl)3-phenylpropionophenone on saponification.²

When 2-methoxyphenylmagnesium iodide was allowed to react with ethyl 3-coumarincarboxylate, several higher boiling products appeared if the reaction time was extended.³

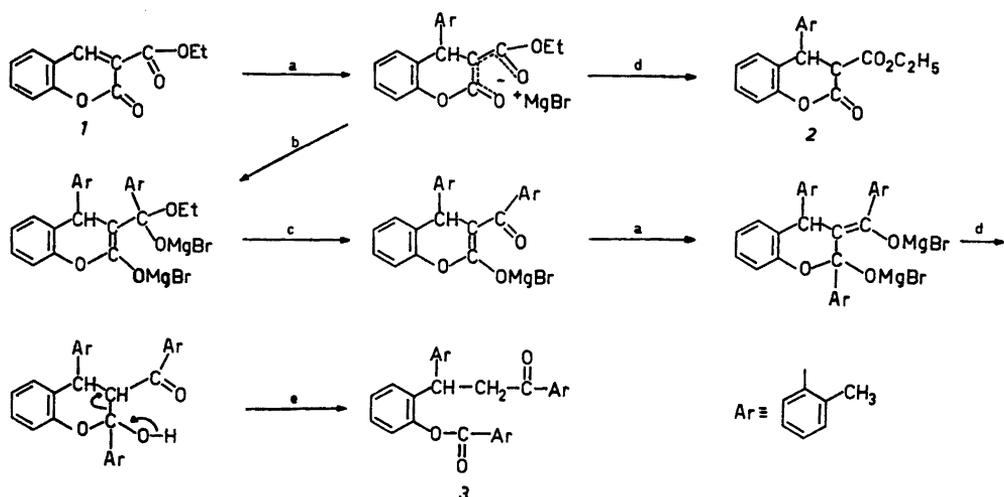
Because 2-methylphenylmagnesium bromide can be considered to have a reactivity between that of phenylmagnesium bromide and 2-methoxyphenylmagnesium iodide it seemed interesting to look more closely at the reaction between 2-methylphenylmagnesium bromide and ethyl 3-coumarincarboxylate.

When the ratio of reagent to substrate was raised to 5 in the reaction of 2-methylphenylmagnesium bromide with ethyl 3-coumarincarboxylate and the reaction time was prolonged to 48 h, mainly one new product (GLC yield ca. 25%) appeared. This compound, which was isolated by column chromatography, was formed rather slowly. By spectroscopic methods it was shown to be 1,3-di(2-methylphenyl)-3-[2'-(2-methylbenzoyloxy)phenyl]propan-1-one (**3**).

This compound is obviously formed by addition of three molecules of the Grignard reagent followed by a ring opening reaction during and after hydrolysis of the primarily formed magnesium complexes (Scheme 1). The ring opening reaction can be considered as an example of the reverse aldol condensation, where the equilibrium lies far towards the free ester and ketone.

The missing reactivity of the magnesium complex, which is formed by the first 1,4-addition, is explained by the lack of a well-defined carbonyl group. The actual reagent in

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Scheme 1. a. 1,4-Addition; b. 1,2-addition; c. elimination of C_2H_5OMgBr ; d. hydrolysis; e. ring opening.

the slow addition may be di(2-methylphenyl)-magnesium, which is present in equilibrium with the Grignard reagent and is more reactive.⁴

Experimental. Reaction of 2-methylphenyl-magnesium bromide with ethyl 3-coumarincarboxylate.⁵ A solution of ethyl 3-coumarincarboxylate (5.79 g) in dry benzene (40 ml) was added to the Grignard reagent prepared from 2-bromotoluene (22.7 g), magnesium (3.2 g), and dry diethyl ether (110 ml). The reaction was worked up after 48 h. The yield of products was 10.4 g.

On treatment of the sirupy reaction product with ethanol, the 1,4-adduct (2) crystallized (4.4 g, from ethanol). The residue weighed 4.03 g and consisted mainly of one component (GLC analysis; column 1.5 m 1% SE-30).

Chromatography. The column, Pharmacia SR-25/100, was packed with 428 ml alumina (Merck 1097). The height of the packing was 840 mm. A part of the residue (250 mg) was dissolved in 1.0 ml benzene and applied at the lower end of the column. The speed of the liquid phase (benzene) was 21.6 ml/h regulated by a peristaltic pump, Desaga 131900. The eluate was divided into fractions of 5.4 ml. The fractions 55–75 contained the pure substance (3). Yield: 15.2 mg (from ethanol), m. p. 93–94°C. MS [IP 70 eV; m/e (% rel. int.): 438 (1, M), 329 (2 [M - C₈H₆O]), 312 (15, [M - C₈H₆O₂]), 119 (100, C₈H₇O), 91 (26, C₇H₇), 65 (5, C₆H₅). ¹H NMR (60 MHz, CDCl₃): δ 1.98 (3 H, s), 2.02 (3 H, s), 2.53 (3 H, s), 3.49 (2 H, d, J 8.0 Hz), 5.00 (1 H, t), 6.7–8.2 (16 H, m). IR (CCl₄): 1750 (s), 1700 (s).

Hydrolysis. The substance (13 mg) was hydrolyzed with 5 drops of KOH in H₂O (1:1) and a small amount of ethanol. The mixture

was boiled for 30 min and 5 drops of dimethyl sulfate was added during 30 min. After 2 h the mixture was dissolved in water and extracted with ether. The mass spectra (combined GC/MS; LKB 9000) of the two compounds in the ether extract revealed that the expected products had been formed, methyl 2-methylbenzoate and 1,3-di(2-methylphenyl)-3-(2-methoxyphenyl)propan-1-one.

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