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## The Reaction of Phenylmagnesium Bromide with 2-Benzoyl-1-indanone and its Enol Methyl Ether

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Phenylmagnesium bromide undergoes conjugate 1,4-addition to 2-benzoyl-1-indanone and its enol methyl ether to give 2-benzoyl-3-phenylindene.

PHENYLMAGNESIUM bromide and phenyl-lithium react with 2-benzoyl-1-indanone (I) to give 2-benzoyl-3phenylindene (II), the structure of which has been established by ozonolysis to o-benzoylphenylacetic acid and benzoic acid.

Benzoylindanone can exist in equilibrium with two enol forms. The reaction of this compound with diazomethane does not indicate the proportion of the enols in the tautomeric mixture, since the reaction will disturb the equilibrium, and diazomethane will react with the more acidic enol to produce the methanediazonium ion which will then attack the more basic oxygen of the enolate anion formed. Diazomethane reacts with benzoylindanone to give 2-benzoyl-3-methoxyindene (III) indicating that the ring oxygen of the enolate anion is the more basic.<sup>1</sup>

bromide and phenyl-lithium would undergo normal 1,2-addition to the carbonyl of the benzoyl group of the enolate anion to give, after work up, the alcohol (IV) or 2-diphenylmethylene-1-indanone (V). In the phenyllithium reaction, indanone and benzophenone, the cleavage products of the alcohol (IV) were isolated. Similar cleavage reactions of tertiary alcohols are known.<sup>2-4</sup> A small quantity of diphenylmethyleneindanone was isolated from the Grignard reaction. That 2-benzoyl-3-phenylindene was the main product in these reactions indicates that conjugate 1,4-addition of the organometallic reagent to the enolate anion had occurred.

Conjugate 1,4-addition of Grignard reagents to the enolate anions of  $\beta$ -diketones may be a general reaction and not normal 1,2-addition as has been reported.<sup>2,5-10</sup>

It was assumed therefore that phenylmagnesium <sup>1</sup> R. D. Campbell and H. M. Gilow, J. Amer. Chem. Soc.,

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For example, Grignard reagents react with the enolate anion of benzoyl acetone to give the ketoalcohols (VI; R = Et or Ph) in quantitative yield.<sup>9</sup> The reactions of the enolate anion with methyl chloroformate to give the stereoisomeric O-carbomethoxyesters (VII; R = $CO_2Me$ <sup>11</sup> and with diazomethane to give the enol



ether (VII; R = Me)<sup>12</sup> demonstrate that the oxygen of the acetyl group is more basic than the oxygen of the benzovl group. Therefore the ketoalcohols (VI) must be formed by conjugate 1,4-addition of the Grignard reagent to the enolate anion

PhCO-CH=C 
$$\bigvee_{Me}^{OR}$$
  $\stackrel{IO}{\longleftarrow}$   $\stackrel{IO}{\longleftarrow}$   $\stackrel{IA-}{\longleftarrow}$  PhCO-CH<sub>2</sub>  $\stackrel{O-}{\longleftarrow}$   $\stackrel{IA-}{\longleftarrow}$  PhCO-CH<sub>2</sub>  $\stackrel{O-}{\longleftarrow}$   $\stackrel{OH}{\longleftarrow}$   $\stackrel{OH}{\longrightarrow}$   $\stackrel{OH}$ 

When 2-benzoyl-3-methoxyindene (III) is treated with phenylmagnesium bromide, conjugate 1,4-addition occurs, followed by loss of the elements of methanol, to give 2-benzoyl-3-phenylindene (II).

## EXPERIMENTAL

Ultraviolet spectra were measured for n-hexane solutions unless otherwise indicated.

Reaction of Phenylmagnesium Bromide with 2-Benzoyl-1-indanone.-Benzoylindanone (10 g.) in ether (200 ml.) with benzene (100 ml.) was added to phenylmagnesium bromide, prepared from bromobenzene (26.5 g.), magnesium (4 g.), and ether (80 ml.). The reaction mixture was boiled

(8 hr.) and poured on to ice and dilute sulphuric acid. The ethereal layer was dried  $(Na_2SO_4)$  and the solvent removed by distillation. Trituration of the residual oil with light petroleum gave crystals of 2-benzoyl-3-phenylindene, (4.0 g.), and a filtrate, which was concentrated and chromatographed on alumina with light petroleum as developer. The first yellow band ion gave 2-benzoyl-3-phenylindene (4.0 g.), yellow prisms (from light petroleum), m. p. 105-106°. Total yield 63% (Found: C, 89.0; H, 5.3.  $C_{22}H_{16}O$ requires C, 89.2; H, 5.4%);  $\nu_{max}$  1675 (C:O) and 1608 cm.<sup>-1</sup> (C:C);  $\lambda_{max}$  315 (log  $\varepsilon$  4.06) and 320 mµ (log  $\varepsilon$  4.06). The second yellow band yielded 2-diphenylmethylene-1-indanone (0.2 g.), yellow crystals (from ethanol), m. p. This compound was prepared by another 152—153°. method and its structure established.<sup>13</sup> A mixed m. p. with an authentic sample was not depressed.

Ozonolysis of 2-Benzoyl-3-phenylindene.-Ozone was passed through 2-benzoyl-3-phenylindene (1.0 g.) in carbon tetrachloride (50 ml.) until the ozonide separated. Steam distillation gave first solvent and then benzoic acid. The residual non-volatile solid was boiled with dilute sodium hydroxide solution and filtered. On acidification, a brown solid was obtained which was decolourised with charcoal and recrystallised from water to give o-benzoylphenylacetic acid.<sup>14</sup> The acids were identified by m. p. and mixed m. p.

Reaction of Phenyl-lithium with 2-Benzoyl-1-indanone.---Benzoylindanone (4.0 g.) in ether (50 ml.) was added to a filtered solution of phenyl-lithium, prepared from bromobenzene (10.7 g.), lithium (1.0 g.), and ether (50 ml.). The reaction mixture was boiled (7 hr.) and poured into dilute hydrochloric acid. The ethereal extract was dried (Na<sub>2</sub>SO<sub>4</sub>), the solvent removed, and the residual oil chromatographed on alumina with light petroleum as developer, to give benzophenone (0.6 g.), m. p. 46-47°, 2-benzoyl-3-phenylindene (2.6 g.), m. p. 101-102°, indanone (1.9 g.), m. p. 41°, and triphenylmethanol (0.1 g.), m. p. 161-162°. Slow inverse addition at room temperature gave the same products in approximately the same proportion.

Reaction of 2-Benzoyl-3-methoxyindene with Phenylmagnesium Bromide.-Crude 2-benzoyl-3-methoxyindene (1.9 g.) prepared by the method of Campbell and Gilow,<sup>1</sup> was treated with an excess of phenylmagnesium bromide in ether. After stirring for 5 hr., the orange reaction mixture was decomposed on ice and ammonium chloride. Work up gave an oil which was chromatographed on alumina with benzene as solvent and light petroleum as developer. A yellow band yielded 2-benzoyl-3-phenylindene (0.55 g.), m. p. 102-103°.

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