

equilibrium then becomes unnecessary and confusing.

Two solid phases, A and B, ground to particles of radius  $r_A$  and  $r_B$ , respectively, may coexist in phase equilibrium if

$$G_{A\infty} + (2\gamma_A V/r_A) = G_{B\infty} + (2\gamma_B V/r_B) \quad (4)$$

provided that (2) is valid.

If experimentally determined equilibrium values of  $1/r_B$  are plotted against the corresponding values of  $1/r_A$ , a straight line should come out. Extrapolation of the plot to  $1/r_A = 0$  (or  $1/r_B = 0$ ), ( $G_{A\infty} - G_{B\infty}$ ) and  $V$  being known from other experiments, should yield values for  $\gamma_A$  and  $\gamma_B$ .

A numerical estimate. To estimate the magnitude of the contribution  $2\gamma V/r$  to the chemical potential, one must know the surface tension  $\gamma$ . For solid sodium chloride and solid magnesium oxide one calculates, from the experimental results of Nicolson,<sup>3</sup>  $\gamma = 0.4 \text{ N m}^{-1}$  and  $\gamma = 2-4 \text{ N m}^{-1}$ , respectively, in agreement with measurements of the surface enthalpy of these substances (for a discussion see Tosi<sup>4</sup>). Aragonite and calcite being somewhat harder than sodium chloride but not as hard as magnesium oxide (hardness<sup>5</sup> of aragonite 3.5-4, calcite 3, halite 2.5, periclase 5.5 on the Mohs scale), it seems reasonable to put  $\gamma = 1 \text{ N m}^{-1}$  for the former solids.

Assuming the vapour phase to consist of carbon dioxide, one calculates for aragonite (density<sup>5</sup> 2950  $\text{kg m}^{-3}$ , molar mass 84.1  $\text{kg kmol}^{-1}$ )  $V = 2.85 \times 10^{-2} \text{ m}^3 \text{ kmol}^{-1}$ , and thus

$$G(r) - G_\infty \approx \frac{0.06 \text{ J kmol}^{-1} \text{ m}}{r}$$

Inserting  $r = 10^{-7} \text{ m}$  (0.1  $\mu\text{m}$ ) one finds  $G(r) - G_\infty \approx 6 \times 10^6 \text{ J kmol}^{-1}$ , i.e. of the same order of magnitude as  $\Delta G$  of reaction (II). Thus, for aragonite and calcite ground to fine particles, the phase equilibrium (I) may come out as a case of energetical equilibrium.

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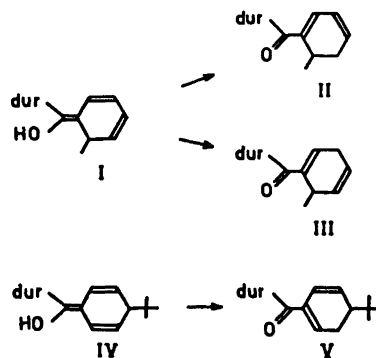
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## The Reaction of Benzoyldurene with Methylmagnesium Bromide and *t*-Butylmagnesium Chloride

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The reactions of benzoyldurene with methylmagnesium and *t*-butylmagnesium halides have been studied by Fuson *et al.*<sup>1-3</sup> (see review<sup>4</sup>) and by the present authors.<sup>5</sup> Previous uncertainty<sup>1-4</sup> regarding the nature of the primary reaction products has now been clarified by the observation that the Grignard-benzophenone adducts on protonation produce rather labile enols (I and IV, dur=2,3,5,6-tetramethylphenyl) (*cf.* Experimental). Prototropic rearrangements, and other reactions of the latter, give rise to the secondary products which were partly identified by Fuson *et al.*<sup>1-3</sup> NMR data (*cf.* Experimental) support the structures



(I–V) and suggest that several of the reaction products formerly isolated were, in fact, mixtures.

The purity and stereochemical character of the enol (I) remain unknown.

*Experimental.* NMR spectra were obtained on a Varian A-60 or a Varian HA-100 instrument. The solvent was deuteriochloroform containing TMS when not otherwise indicated. Melting points are uncorrected.

*Enol (I).* A mixture of benzoyldurene<sup>3,5</sup> (2 mmol) and methylmagnesium bromide (2 ml, 2.5 M in ether) was kept at 90°C for 20 h (ampoule). The mixture was cooled to –80°C and poured onto ammonium chloride and ice. The ether phase was concentrated *in vacuo* and in turn subjected to NMR spectroscopy (60 MHz, in CCl<sub>4</sub>). The spectrum revealed the presence of a methyl group (*d*,  $\delta$  1.21,  $J=7.0$ ), an allylic proton (an apparent double *q*,  $\delta$  3.72,  $J=7.0$  and 4.0), a hydroxy group ( $\delta$  4.24, exchangeable), and 4 vinylic protons (two 2H-multiplets, one at  $\delta$  5.31–5.45, the other at  $\delta$  5.66–5.85). The coexistence of the corresponding 1,2-adduct (1-duryl-1-phenylethanol) in the crude reaction mixture was inferred, *inter alia*, from signals at  $\delta$  7.27 (phenyl).

*Ketone formation (in acid).* By addition of acetic acid (0.1 ml) to the ethereal solution of the enol (I) or, alternatively, by decomposition of the Grignard adduct with 2 N hydrochloric acid, followed by removal of the ether, an oil separated which, according to NMR data, contained the ketone (II) in admixture with 1-duryl-1-phenylethanol. The oil was triturated with ethanol, when the crude ketone (II) crystallised slowly at –20°C. Recrystallisation, once from ethanol and twice from petroleum ether, gave colourless crystals, m.p. 122–124°C (reported<sup>1</sup> m.p. 123–124°C). NMR (CCl<sub>4</sub>) (100 MHz) showed an aliphatic methyl group (*d*,  $\delta$  1.03,  $J=7.0$ ), aromatic CH<sub>3</sub>-groups (*s*,  $\delta$  1.97 and 2.19, 6 H each), an allylic methylene group (*m*,  $\delta$  2.9–*ca.* 2.0), a methine proton (*m*,  $\delta$  3.12, an apparent quintet,  $J=ca.$  7, further split by allylic coupling,  $J<1$ ), vinylic protons (*m*, 2 H at 5.99 and 1 H at  $\delta$  6.22), and an aromatic proton (*s*,  $\delta$  6.83). (II) (in 2,2,4-trimethylpentane) showed an absorption maximum at 302 nm ( $\epsilon$  *ca.* 10<sup>4</sup>).

*Ketone formation (in alkali).* Addition of triethylamine (0.1 ml) to the ethereal solution of the enol (I) gave (according to NMR) the ketone (III), also resulting from addition of ethanol to the Grignard adduct. The ketone was prepared from benzoyldurene (50 mmol) and methylolithium (60 mmol) in ether (80 ml)

kept at reflux temperature for 1 h. Slow decomposition with water, removal of ether, trituration with methanol and recrystallisation, once from petroleum ether and five times from methanol, gave colourless crystals of (III), (4.0 mmol, m.p. 121–123°C). (Found: C 84.72; H 8.70. Calc. for C<sub>18</sub>H<sub>22</sub>O: C 84.99; H 8.72.) The NMR-spectrum (100 MHz) showed a methyl group (*d*,  $\delta$  1.23,  $J=7$ ), aromatic CH<sub>3</sub>-groups (*s*,  $\delta$  1.95 and 2.17, 6 H each), an allylic methylene group (*m*,  $\delta$  2.66–2.87), a methine proton (*m*, 3.20–3.62), two vinylic protons (*m*, apparently an AB system subject to further coupling,  $\delta$  5.55 and 5.77,  $J=10$ ), a vinylic proton (*m*,  $\delta$  6.24–6.37), and an aromatic proton (*s*,  $\delta$  6.82). (III) (in 2,2,4-trimethylpentane) showed an absorption maximum at 247 nm ( $\epsilon$  *ca.* 4200).

*Enol (IV) and ketone (V).* The *t*-butylmagnesium chloride-durophenone adduct<sup>5</sup> was treated with water until the ether phase became clear. NMR analysis (60 MHz) of the oily residue (crude enol IV) showed the presence of a *t*-butyl group (*s*,  $\delta$  0.90), four aromatic methyl groups ( $\delta$  2.0–2.3), an allylic proton (*m*,  $\delta$  2.65–2.86), three vinylic protons (*m*,  $\delta$  5.49–6.00), one half of a signal (an apparent triplet,  $\delta$  6.80,  $J\sim 1.5$ ) from a vinylic proton, the other half of the signal hidden under that of the aromatic proton ( $\delta$  6.98), suggesting a coupling constant of *ca.* 11. The enolic proton was generally observed near  $\delta$  4. The enol did not crystallise. When dissolved in ethanol containing 5 % hydrochloric acid conc., the ketone (V) crystallised. Recrystallisation from ligroin (80/110°C) gave colourless crystals (yield 70 % from benzoyldurene; m.p. 148–150°C, reported<sup>3</sup> 150–151°C). NMR (100 MHz) showed a *t*-butyl group (*s*,  $\delta$  0.90), four aromatic methyl groups ( $\delta$  1.95 and 2.18), three allylic protons (*m*,  $\delta$  2.0–2.6), three vinylic protons (*m*,  $\delta$  5.7–6.9), and an aromatic proton (*s*,  $\delta$  6.86), consistent with the structure presented in Ref. 3, but not with that proposed in the review article.<sup>4</sup>

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