

its identity) which upon standing in air was converted to III quantitatively. In view of this facile cleavage of the heterocyclic ring, further work is being carried out with other aromatic dihydroxy compounds and will be reported later.

#### Experimental<sup>9</sup>

**Reaction of Phenylphosphonous Dichloride with II.**—A solution of phenylphosphonous dichloride (17.9 g., 0.10 mole) in 50 ml. of bromobenzene was added dropwise with vigorous stirring at room temperature under nitrogen to a solution of catechol (11.0 g., 0.10 mole) in 350 ml. of bromobenzene. The resultant clear solution was then heated to reflux at which temperature hydrogen chloride was evolved quantitatively (0.20 mole). The mixture was refluxed for 6 hr. and the evolved hydrogen chloride was passed into water and titrated with 1.0 *N* sodium hydroxide. The clear yellow solution was distilled until nearly 300 ml. of bromobenzene was removed. The solution when cooled to 0° (nitrogen atmosphere) yielded 16.1 g. of 2-phenyl-1,3,2-benzodioxaphosphole (IV), m.p. 140–145°. It was collected by suction filtration and washed with bromobenzene. The filtrate which was concentrated to 80 ml. gave 4.0 g. of IV (total 20.1 g., 93%) which was stored in vacuum desiccator;  $\lambda_{\text{max}}^{\text{KBr}}$  6.23 and 6.7 (aromatic C=C), 6.92  $\mu$  (C<sub>6</sub>H<sub>5</sub>-P), besides other bands for substituted benzene rings.

In order to prepare the analytical sample, 2.09 g. of IV was subjected to repeated recrystallization from methylene chloride-petroleum ether (b.p. 40–60°). In spite of efforts to preserve anhydrous conditions (although nitrogen was used it was not rigorously deoxygenated and thus could cause oxidation of IV to VI) during this process, the ester IV was converted into *o*-hydroxyphenylhydrogen phenylphosphonate (III), m.p. 123.5–124.5°;  $\lambda_{\text{max}}^{\text{KBr}}$  2.95 (OH), 6.92 (C<sub>6</sub>H<sub>5</sub>-P), 7.8  $\mu$  (P→O); *pK<sub>a</sub>* 1.90 (methanol); neut. equiv. 253.2.

*Anal.* Calcd. for C<sub>12</sub>H<sub>11</sub>O<sub>4</sub>P: C, 57.3; H, 4.4; P, 12.4. Found: C, 56.8; H, 4.43; P, 12.36.

In other experiments, dropwise addition of phenylphosphonous dichloride to a stirred solution of an equimolar quantity of catechol in ether, tetrahydrofuran, or benzene containing triethylamine or pyridine at 0° in an atmosphere of nitrogen resulted in the immediate precipitation of the corresponding hydrochloride salt of the amine. Filtration of the precipitate gave a clear solution which on evaporation left an oil. This was purified by distillation, b.p. 139–141° (0.3 mm.);  $\lambda_{\text{max}}^{\text{film}}$  6.92 (C<sub>6</sub>H<sub>5</sub>-P), 7.8 (P→O), 8.2  $\mu$  (C-O-), besides other absorption bands. Immediate elemental analysis for carbon and hydrogen corresponded to VI.

*Anal.* Calcd. for C<sub>12</sub>H<sub>9</sub>O<sub>5</sub>P: C, 62.08; H, 3.9. Found: C, 61.80; H, 3.79.

**Reaction of Phenylphosphonic Dichloride with II.**—A solution of phenylphosphonic dichloride (19.5 g., 0.10 mole) in 50 ml. of bromobenzene was added dropwise under nitrogen over a period of 30 min. to a well-stirred solution of catechol (11.0 g., 0.10 mole) in 350 ml. of anhydrous bromobenzene. The mixture was boiled 6 hr., and the evolved hydrogen chloride (quantitative) was titrated. Removal of the solvent left an oil and immediate infrared analysis showed that VI was formed. Upon standing it solidified, m.p. 118–121°. Recrystallization from methylene chloride-petroleum ether or from bromobenzene gave sufficiently pure acid III, m.p. 123–124°.

**Hydrolysis of *o*-Hydroxyphenylhydrogen Phenylphosphonate (III).**—A mixture of 6.25 g. of III and 25 ml. of hydrochloric acid was boiled 16 hr. during which period the color of the solution turned from brown to pink. After cooling, the solution was diluted with water, neutralized with sodium bicarbonate, and extracted with ether. Evaporation of solvent gave 2.3 g. of catechol, m.p. 103.5–104.5°. The aqueous layer was acidified with hydrochloric acid and extracted with ether. From the ether extract 0.4 g. of crystalline phenylphosphonic acid (m.p. 158–160.5°) was isolated.

(9) All melting points are corrected and all boiling points are uncorrected. The microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

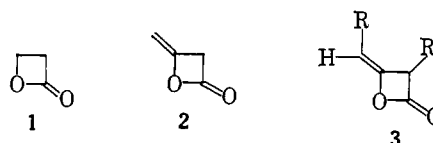
## Reactions of Aryl Grignard Reagents with 2,2,4-Trimethyl-3-hydroxy-3-pentenoic Acid $\beta$ -Lactone<sup>1</sup>

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The course of reaction of  $\beta$ -lactone systems with organometallic reagents is not well understood and appears to depend markedly upon the  $\beta$ -lactone employed.  $\beta$ -Propiolactone (1) has been reported to react with phenyl Grignard reagent by acyl-oxygen ring-opening, to give phenyl vinyl ketone and 3-bromopropanoic acid.<sup>3</sup> Phenyllithium yields phenyl vinyl ketone and



the diadduct, 1,1-diphenyl-1,3-propanediol.<sup>4</sup> However, benzyl and allyl Grignard reagents, as well as several organic cadmium reagents, have been reported<sup>4</sup> to produce alkyl-oxygen fission with concomitant ring opening to form the  $\beta$ -substituted carboxylic acids. Diketene (2) condenses with a variety of Grignard reagents,<sup>5</sup> adding 3 moles to give 1,1-disubstituted ethanol derivatives and methyl ketones. Aldoketene dimers (3) with Grignard reagents<sup>6</sup> give diadducts and the reverse aldol cleavage products of the diadducts. In all of these processes, yields of pure compounds were quite low and considerable polymeric material was reported.

We have investigated the reaction of the highly substituted  $\beta$ -lactone, 2,2,4-trimethyl-3-hydroxy-3-pentenoic acid  $\beta$ -lactone (4), with aryl Grignard reagents. In view of the geminal methyl groups on the  $\alpha$ -carbon of the  $\beta$ -lactone 4, we anticipated that the reaction might terminate after monoaddition to give a highly substituted  $\beta$ -diketone. If diaddition occurred, dehydration was not possible and a hydroxy ketone was a conceivable product, barring intervention of carbon-carbon cleavage in a retrograde aldol decomposition. The reactions were performed by normal addition of 4 in ether to the Grignard reagent followed by hydrolysis of the reaction mixture with ammonium chloride solution. Product analysis was completed by gas chromatography.

When excess phenyl Grignard reagent was allowed to react with 4 in ether, only benzophenone and diisopropyl ketone were obtained. This is analogous to the course of the same reaction with tetramethyl-1,2-cyclo-

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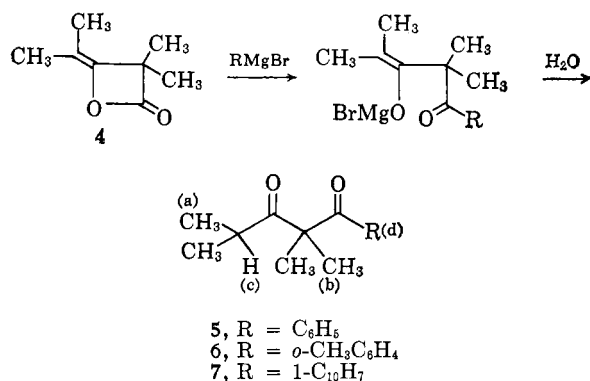
(3) T. L. Gresham, J. E. Jansen, F. W. Shaver, and R. A. Bankert, *J. Am. Chem. Soc.*, **71**, 2807 (1949).

(4) C. G. Stuckwisch and J. V. Bailey, *J. Org. Chem.*, **28**, 2362 (1963).

(5) A. Gibaud and A. Willemart, *Bull. soc. chim. France*, 432 (1956).

(6) D. V. Nightingale and R. H. Turley, *J. Org. Chem.*, **26**, 2656 (1961).

butanedione.<sup>7</sup> Diaddition of the Grignard reagent to the carbonyl group of **4** followed by immediate retrograde aldol cleavage seems reasonable. In spite of equimolar concentrations of phenyl Grignard reagent and lactone **4**, only a small quantity of monoaddition product **5** could be isolated along with cleavage products.



Small quantities of more than fifteen other compounds along with **4** were detected by gas chromatography. Compound **5** showed strong bands in the infrared region at 1718 and 1672 cm.<sup>-1</sup> for simple aliphatic and conjugated carbonyl functions, respectively, as well as a peak at 706 cm.<sup>-1</sup> for monosubstituted phenyl. Similarly, absorption for the twin carbonyl groups in **6** and **7** appeared at 1718 and 1671 cm.<sup>-1</sup> and at 1711 and 1671 cm.<sup>-1</sup>, respectively. Nuclear magnetic resonance spectrograms displayed signals as expected for methyl protons in an isopropyl group, the lone tertiary hydrogen, protons on equivalent geminal methyl groups, and the aromatic protons as shown in Table I.

TABLE I  
N.M.R. SPECTRA OF THE DIKETONES

Parent compound	— $\delta$ -Values of protons <sup>a</sup> ( $J$ in c.p.s.)—			
	a	b	c	d
<b>5</b>	0.91 d ( $J = 7$ )	1.43 s	2.72 m	7.55 m
<b>6</b> <sup>b</sup>	0.95 d ( $J = 7$ )	1.40 s	2.95 m	7.26 m
<b>7</b>	0.95 d ( $J = 7$ )	1.45 s	2.97 m	7.6 m

<sup>a</sup> d = doublet, s = singlet, m = multiplet. <sup>b</sup> The *ortho* methyl group displayed a singlet at  $\delta$  2.37.

In contrast, by increasing the size of the organometallic reagent by the use of *o*-tolyl and 1-naphthyl Grignard reagents, it was possible to prepare 1-(*o*-tolyl)-2,2,4-trimethyl-1,3-pentanedione (**6**) and 1-(1-naphthyl)-2,2,4-trimethyl-1,3-pentanedione (**7**), respectively. Although the yields were less than 50% in each case, considerable tars were produced which suggests polymerization is probably competitive. As proof of structure, **6** was treated with 20% aqueous sodium hydroxide. High yields of *o*-toluic acid and diisopropyl ketone were obtained.

Thus initial reaction of the Grignard reagent occurs at the carbonyl carbon, probably with concomitant ring opening. Benzophenone could be detected by infrared analysis in the reaction mixture within minutes after the addition of **4** to the phenyl Grignard reagent.

(7) J. L. E. Erickson and G. C. Kitchens, *J. Am. Chem. Soc.*, **68**, 492 (1946).

Apparently, introduction of a small amount of hindrance in the Grignard reagent permits survival of the monoaddition product, the  $\beta$ -diketone.

#### Experimental<sup>8-10</sup>

**Reaction of Excess Phenyl Grignard Reagent with 4.**—The phenyl Grignard reagent was prepared from 13.37 g. (0.55 g.-atom) of magnesium and 78.51 g. (0.5 mole) of bromobenzene in 100 ml. of anhydrous ether. The Grignard mixture was cooled to 5°, and a solution of 23.19 g. (0.165 mole) of **4** in an equal volume of ether was added dropwise with stirring to maintain the mixture temperature below 15°. When the addition was complete, the slurry was refluxed for 4 hr. The chilled mixture was hydrolyzed with cold 20% aqueous ammonium chloride and the aqueous phase was extracted with ether. Gas chromatographic analysis showed diisopropyl ketone and benzophenone as the only major products along with traces of other components. This was verified by additional experiments.

**Reaction of Phenyl Grignard Reagent with 4 (1:1). Preparation of 1-Phenyl-2,2,4-trimethyl-1,3-pentanedione (5).**—To the phenyl Grignard reagent (0.16 mole) was added a solution of 23.66 g. (0.16 mole) of **4** in an equal volume of ether in the manner described previously. The mixture was stirred for 6 hr. at room temperature, then boiled for 1 hr. The reaction mixture was then worked up as usual, and the resulting solution was concentrated to an oil. A mixture of the aforementioned oil, 17 g. of Girard-T reagent, 100 ml. of methanol, and 10 ml. of acetic acid was heated at reflux for 4 hr. The solution was cooled to room temperature, and 5% aqueous sodium hydroxide was added until the solution had a pH of 8. Water (100 ml.) was added and the resulting mixture was extracted with ether. When part of the ether had been distilled, a solid precipitated and was isolated by filtration. The filtrate was carefully chromatographed on acid-washed alumina. The small amount (1.7 g., 5%, based on **4**) of crude **5** was purified by preparative gas chromatography, using a 10% silicone rubber column, b.p. 81–84.5° (0.3 mm.).

*Anal.* Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>: C, 77.03; H, 8.31. Found: C, 77.15; H, 8.55.

**1-(*o*-Tolyl)-2,2,4-trimethyl-1,3-pentanedione (6).**—*o*-Tolyl Grignard reagent (0.4 mole) was prepared, and the mixture was cooled to 5°. A sample of **4** (18.48 g., 0.13 mole) dissolved in an equal volume of ether was added dropwise to the stirred Grignard reagent so that the temperature did not rise above 15°. The reaction mixture was worked up as before, and the organic phase was distilled *in vacuo* to give 1-(*o*-tolyl)-2,2,4-trimethyl-1,3-pentanedione (**6**), b.p. 158–160° at 15 mm. (12.0 g., 40%), and considerable residual tars.

*Anal.* Calcd. for C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>: C, 77.55; H, 8.68. Found: C, 77.67; H, 8.86.

One gram of pure diketone was refluxed in 10 ml. of 20% aqueous sodium hydroxide to give 0.584 g. (84%) of *o*-toluic acid. Diisopropyl ketone was identified in the reaction mixture by gas chromatography as the only other compound.

**1-(1-Naphthyl)-2,2,4-trimethyl-1,3-pentanedione (7).**—1-Naphthyl Grignard reagent (0.4 mole) was prepared in a manner as previously described.<sup>11</sup> The reagent was vigorously stirred to prevent solidification while cooling to 15°. An equal volume of ether was mixed with 12.6 g. (0.09 mole) of **4**, and the solution was added dropwise to the Grignard reagent (temperature was <15°). The slurry was worked up as described earlier to give an oil which was chromatographed three times on acid-washed alumina. The ketone, 1-(1-naphthyl)-2,2,4-trimethyl-1,3-pentanedione, distilled at 186–188° (4 mm.), 10.8 g. (44.8%).

*Anal.* Calcd. for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>: C, 80.56; H, 7.51. Found: C, 80.86; H, 7.51.

(8) All melting points are corrected; all boiling points are uncorrected. The lactone **4** was obtained from Eastman Chemical Products, Kingsport, Tenn., b.p. 170° (730 mm.).

(9) Gas chromatographic analyses were performed using an Aerograph Hy-Fi Model A-550 with a hydrogen flame ionization detector and an Aerograph A-350 unit. A 10% silicone rubber column on acid-washed Chromosorb W was satisfactory for the isolation of **4**.

(10) The nuclear magnetic resonance spectra were determined with a Varian Model A-60 high-resolution spectrometer fitted with a field-sensing stabilizer ("Super Stabilizer"). Carbon tetrachloride with tetramethylsilane as an internal standard was the solvent.

(11) See H. Gilman, N. B. St. John, and F. Schulze, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 425.