NOTES.

The Behaviour of Keten in the Friedel–Crafts Reaction. By F. S. Spring and T. Vickerstaff.

Hurd (*J. Amer. Chem. Soc.*, 1925, **47**, 2777) examined the reaction of keten with benzene in the presence of aluminium chloride and concluded that acetophenone was a product, though he was unable to isolate it in a pure state. Packendorff, Zelinsky, and Leder-Packendorff (*Ber.*, 1933, **66**, 1069) isolated from the product of the same reaction a ketonic fraction and reduced it catalytically; fractionation then gave ethylbenzene (representing the acetophenone present in the ketonic mixture) and a liquid ketone which they believed to be 2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, since the oxime had m. p. 74° (they quote m. p. 77·5—78° as the literature constant; Bamberger and Voss, *Ber.*, 1894, **27**, 1547, and Bamberger and Lodter, *Annalen*, 1895, **288**, 115, give m. p. 87·5—88°).

We have re-examined the reaction and isolated acetophenone and some *p*-ethylacetophenone, the formation of which is no doubt due to the presence of ethylene in the keten.

Keten was prepared by the thermal decomposition of acetone (Hurd, " Organic Syntheses," IV, 39), an electrically heated furnace being used instead of coal gas; the furnace was wired with three independent heating sections. The best yields of keten were obtained when only the centre section was heated, this being adjusted to give a constant temperature of 850°, and when the acetone was passed through the system quickly (4—5 c.c. min.). These observations are in accord with those of Rice, Greenberg, Waters, and Vollrath (*J. Amer. Chem. Soc.*, 1934, **56**, 1760), who found that the main condition for high percentage yield of keten was a small fractional decomposition of the acetone.

Keten was passed slowly into a suspension of aluminium chloride (120 g.) in benzene (100 c.c.), maintained at 0° and rapidly stirred until the evolution of hydrogen chloride ceased. The product was poured on ice and extracted with benzene, and the extract washed with water, dried, and distilled. After removal of the benzene the following fractions were collected: (a) 15 g., b. p. 80—100°/15 mm.; (b) 7 g., b. p. 110—120°/15 mm.; (c) 6 g., b. p. 120—180°/15 mm.; (d) 4 g., b. p. 180—220°/15 mm.

Acetophenone. When fraction (a) was redistilled, the bulk passed over at 90°/15 mm. This fraction was converted quantitatively into acetophenonesemicarbazone, which, crystallised once from methyl alcohol, formed needles, m. p. and mixed m. p. 201° (Found : N, 23·7. Calc. : N, 23·7%).

p-*Ethylacetophenone.* Fraction (b) on redistillation gave a main fraction, b. p. 110°/15 mm. (237°/767 mm.; Beilstein gives b. p. 236°/760 mm. for *p*-ethylacetophenone). The semicarbazone, after two crystallisations from methyl alcohol, had m. p. 196°, undepressed by p-*ethylacetophenonesemicarbazone* prepared in the usual manner from *p*-ethylacetophenone (Klages and Lickroth, *Ber.*, 1899, **32**, 1558); this semicarbazone separated from methyl alcohol in needles, m. p. 196° (Found : C, 63·9; H, 7·1; N, 20·4. $C_{11}H_{15}ON_3$ requires C, 64·4; H, 7·3; N, 20·5%). Oxidation of the fraction, b. p. 110°/15 mm., with chromic acid mixture gave terephthalic acid (methyl ester, m. p. 140°).

When fraction (c) was redistilled, the boiling point rose steadily. No definite product was isolated.

The Reaction of Phenol with Keten.—In view of Van Alphen's statement (*Rec. trav. chim.*, 1924, **43**, 861) that phenol is not acetylated by means of keten we re-examined the reaction: quantitative acetylation occurred when keten was passed into liquid phenol at 80° (cf. Rice, Greenberg, Waters, and Vollrath, *loc. cit.*).—The University, Manchester. [*Received, July 16th,* 1935.]

Apparent Cases of Liquid-crystal Formation in p-*Alkoxybenzoic Acids.* By Brynmor Jones.

Two apparent cases of liquid-crystal formation have already been recorded (Bradfield and B. Jones, J., 1929, 2660); *p*-*n*-propoxy- and *p*-*n*-butoxy-benzoic acids melt sharply to milky liquids which at somewhat higher temperatures suddenly become clear. The same phenomenon is now observed with other members of this series. The temperatures at which the solid changes into the cloudy liquid, and the individual m. p.'s are recorded below, together with analytical data for the new compounds.

Acid.	Transition pt.	M. p.	Found.*		Calc.	
			C, %.	H, %.	C, %.	H, %.
p-*n*-Propoxybenzoic	146°	156°	—	—	—	—
p-*n*-Butoxybenzoic	147	160	—	—	—	—
p-n-*Amyloxybenzoic*	122	148	69·0	7·8	69·2	7·8
p-n-*Hexyloxybenzoic*	105	150	70·3	8·1	70·3	8·2
p-n-*Heptyloxybenzoic*	91	145	70·9	8·4	71·1	8·5
p-n-*Octyloxybenzoic*	100	145	71·6	8·8	71·9	8·9
p-*Cetyloxybenzoic*	99	131	76·5	10·6	76·2	10·6

* Micro-determinations by Dr. A. Schoeller.

The corresponding *meta* series would not be expected to exhibit this phenomenon, and this is borne out by examination of the propoxy-, butoxy-, and amyloxy-acids.

The observations are best made with a narrow capillary tube containing three or four times the amount of material usually taken for a m. p. determination, any artificial illumination being cut off when the solid changes to the opalescent liquid. As the temperature is raised, the milkiness diminishes slightly, and then suddenly disappears completely. If the temperature is allowed to fall 0·5—1·0° at this point, the clear liquid *appears* to become a mass of fine crystals, which disappear when the temperature is again raised.

The acids, with one exception, were prepared by boiling under reflux for 2—3 hours 1 mol. of *p*-hydroxybenzoic acid, dissolved in 2 mols. of aqueous potassium hydroxide, with 1·1 mols. of the alkyl iodide. Under these conditions little or no esterification takes place, and the free acids, liberated by the addition of concentrated hydrochloric acid, were crystallised thrice from small volumes of glacial acetic acid. All five acids crystallise from this solvent in aggregates of colourless prisms. Freshly crystallised, they appear under the microscope as radiating blades. For the preparation of *p*-*n*-heptyloxybenzoic acid from *n*-heptyl chloride prolonged heating was necessary.—The University, Sheffield. [*Received, October, 17th,* 1935.]

An Improved Preparation of Diacetone-glucose. By D. J. Bell.

The condensation of glucose with acetone has been the subject of much investigation. Previous workers have found that, owing to its greater solubility, the β-form of the sugar is almost essential to obtaining an appreciable yield when the following catalysts are employed : hydrogen chloride (Fischer and Rund, *Ber.*, 1916, **49**, 93; Levene *et al.*, *J. Biol. Chem.*, 1921, **48**, 236, and later papers), anhydrous copper sulphate (Ohle, *Ber.*, 1924, **57**, 1566), and phosphoric oxide (Smith and Lindberg, *Ber.*, 1931, **64**, 505). The yields obtained by these methods are indifferent and variable, and the reaction requires a considerable time (48 hours). Levene and Meyer (*J. Biol. Chem.*, 1931, **91**, 617), using acetone containing 0·5% of sulphuric acid and anhydrous copper sulphate, obtained diacetone-glucose in 70% yield, starting from α-glucose, but here, again, the reaction requires 24 hours (cf. also Freudenberg and Smeykal, *Ber.*, 1926, **59**, 107).

By the use of 4% of sulphuric acid, the author has, in 5 hours, obtained diacetone-glucose in 72% yield (in repeated experiments): 100 g. of α-glucose are shaken with 2 l. of acetone (B.P.) containing 80 ml. of concentrated sulphuric acid. In 4—5 hours, only a trace of undissolved material remains. Without filtration, the acid is neutralised with anhydrous sodium carbonate, the solids removed, and the filtrate evaporated to dryness. The residue is taken up in cold water (a small amount of dark yellow oil remains undissolved), the solution extracted three times with benzene to remove acetone auto-condensation products, and the extract washed twice with a little water, which is united with the original aqueous layer. The combined aqueous extracts (1 vol.) are shaken with norit, filtered, and extracted six times with chloroform (1/5 vol.); the chloroform extract, after dehydration over anhydrous sodium sulphate and evaporation to dryness in a vacuum, yields 102—106 g. of almost pure diacetone-glucose. The aqueous layer, after evaporation in a vacuum and crystallisation of the residue from alcohol, yields about 20 g. of monoacetone-glucose.

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3-*Nitro*-4-*aminodiphenylmethane and its Derivatives.* By WILLIAM A. WATERS.

THE smooth mononitration 4-acetamidodiphenylmethane, which cannot be effected with nitric acid, either alone or in acetic acid solution (J., 1933, 1064), proceeds quantitatively by Menke's method (*Rec. trav. chim.*, 1925, **44**, 141).

3-*Nitro*-4-*acetamidodiphenylmethane*.—(a) 3 G. of 4-acetamidodiphenylmethane were added with shaking to 2 g. of copper nitrate crystals (trihydrate) in 8 c.c. of acetic anhydride; after being kept for 1 hour at 25°, the green solution was poured into water.

(b) 18 G. of 4-aminodiphenylmethane were treated with 20 c.c. of acetic anhydride; after 10 minutes the warm solution was poured into 12 g. of copper nitrate crystals in 25 c.c. of acetic anhydride, and a further 20 c.c. of acetic anhydride were then added. The mixture was kept for 1 hour at 25° and poured into water.

Both processes yielded one pure *mononitro*-compound, which crystallised from dilute methyl alcohol in yellow plates, m. p. 99° [Found (micro-analyses by Dr. G. Weiler): C, 66·5; H, 5·1; N, 10·1. $C_{15}H_{14}O_3N_2$ requires C, 66·6; H, 5·2; N, 10·4%].

3-*Nitro*-4-*aminodiphenylmethane* was obtained by refluxing the acetyl derivative (6 g.) with sulphuric acid (5 c.c.) in alcohol (50 c.c.) for an hour. It formed deep orange plates from concentrated solutions in methyl alcohol, and fine needles from more dilute solutions; m. p. 78° (Found: N, 12·3. $C_{13}H_{12}O_2N_2$ requires N, 12·3%). On treatment with bromine in glacial acetic acid solution it yielded 5-*bromo*-3-*nitro*-4-*aminodiphenylmethane*, which crystallised from dilute methyl alcohol in bright orange-yellow needles, m. p. 71° (Found: Br, 26·2. $C_{13}H_{11}O_2N_2Br$ requires Br, 26·0%).

Further Nitration of 3-*Nitro*-4-*acetamidodiphenylmethane*.—(a) 3 G. of the mononitro-compound, dissolved in a mixture of concentrated sulphuric and glacial acetic acids (equal vols.), were treated with 1 c.c. of fuming nitric acid and maintained at 30—40° for an hour. 2·5 G. (yield, 80%) of 3 : 4′-dinitro-4-acetamidodiphenylmethane, m. p. 150° (Waters, *loc. cit.*), were isolated from the solid produced when the mixture was poured into water.

(b) 6 G. of the mononitro-compound were added to 4 g. of copper nitrate crystals in 15 c.c. of acetic anhydride; the mixture was maintained at 25° for an hour and poured into water. The product, fractionally crystallised from methyl alcohol, yielded 0·9 g. (30%) of 3 : 4′-dinitro-4-acetamidodiphenylmethane and 0·6 g. (20%) of an isomeride, separating as fine bright yellow needles, m. p. 81—82° (Found: N, 13·5. $C_{15}H_{13}O_5N_3$ requires N, 13·3%). This is almost certainly 3 : 5-*dinitro*-4-*acetamidodiphenylmethane*, since Menke's nitration process favours the production of *o*-derivatives.—UNIVERSITY CHEMICAL LABORATORIES, DURHAM. [*Received, September 21st, 1935.*]