benzophenone)[7] in a range suitable for spectrophotometric analysis. Using a blank comparable with the solution solvent, the optical density at 290 mμ was measured and from this was calculated the concentration of product. Results are shown in Fig. 1.

Reaction of Resorcinol Dimethyl Ether with Methyl Acrylate.—A mixture of 15.0 g. of resorcinol dimethyl ether (I) and 150 g. of pyrophosphoric acid was placed in a flask equipped with a stirrer and drying tube and heated to 65°. While stirring, there was added during 1 hr. 18.8 g. of methyl acrylate. Ice and water (400 ml.) were added and the mixture was extracted with several portions of ether. The combined extract was washed twice with water and dried (sodium sulfate). Evaporation of solvent left 28.1 g. of liquid product (IIa) which was hydrolyzed by refluxing for 6 hr. in 200 ml. of 2 *M* potassium hydroxide in methanol. Water was added and the resulting mixture washed several times with ether. Acidification of the aqueous phase followed by ether extraction and processing as described above gave a crystalline residue. Recrystallization from ethyl acetate–petroleum ether gave 24.0 g. (77%) of 1,3-dimethoxy-4,6-bis(2-carboxyethyl)benzene (IIb), m.p. 120–121°.

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.60; H, 6.38; neut. equiv., 286. Found: C, 59.90; H, 6.38; neut. equiv., 284.

A reaction identical with the preceding except for the substitution of commercial polyphosphoric acid for pyrophosphoric acid gave 10.5 g. (34%) of the diacid (IIb).

Condensation of Resorcinol Dimethyl Ether with Ethyl Acetoacetate.—A mixture was prepared comprised of 15.0 g. of resorcinol dimethyl ether (I) and 150 g. of pyrophosphoric acid. To this was added during 30 min., with stirring, (20°) 15.5 g. of ethyl acetoacetate. After 1 hr., 300 ml. of ice and water were added and the resulting mixture was extracted with three portions of ether. The combined extracts were dried and distilled through a short-path system. There was obtained 10.1 g. of liquid, b.p. 130–144° (0.3 mm.), and 4.0 g., b.p. 145–240° (0.3 mm.). Crystallization of the former from ethyl acetate–petroleum ether gave 7.2 g. (35%) of 7-methoxy-4-methylcoumarin (III), m.p. 155–156°. A sublimed sample had m.p. 157–158° (lit.,[21] m.p. 159°).

The smaller fraction was heated under reflux for 12 hr. in 50 ml. of 3 *M* methanolic potassium hydroxide. Processing in the usual way gave 1.5 g. (6%) of β-methyl-2,4-dimethoxycinnamic acid (IVb), m.p. 148–149° (lit.,[22] m.p. 145°).

An attempt to effect this condensation with commercial polyphosphoric acid failed; neither of the products described could be isolated from the mixture.

Condensation of Resorcinol Dimethyl Ether with 2-Carbethoxycyclohexanone.—A well stirred mixture of 15.0 g. of resorcinol dimethyl ether (I) and 150 g. of pyrophosphoric acid was heated to 65° and during 15 min. 20.5 g. of 2-carbethoxycyclohexanone was added. After an additional 5 min. the mixture was poured into 400 ml. of ice and water (stirring) and the product was extracted with several portions of ether. The combined extracts were washed twice with water and dried. The residue remaining from evaporation of solvent crystallized. Recrystallization from ethyl acetate–petroleum ether gave 12.8 g. (53%) of 3-methoxy-7,8,9,10-tetrahydrodibenzo[*b,d*]pyran-6-one (V), m.p. 119–120°. A sublimed sample melted sharply at 121°.

Anal. Calcd. for $C_{14}H_{14}O_3$; C, 73.04; H, 6.09. Found: C, 72.91; H, 5.98.

Methyl *cis*-2-Methoxycinnamate (VI).—This substance was prepared by a modification of the method described by Stoermer.[23] A solution of 20.0 g. of *trans*-2-methoxycinnamic acid in 1700 ml. of methanol was irradiated through a Pyrex filter with a 200-w. high-pressure mercury vapor lamp. The process was monitored by the periodic withdrawal of samples and a measurement of the ultraviolet spectrum of each. It was discontinued when no further spectral changes were observed (6 hr.). Methanol was removed at an aspirator and the residual solid fractionally crystallized from ethanol. There was obtained 12.0 g. of crude *cis* acid, m.p. 84–87°, and 6.0 g. of recovered *trans* acid, m.p. 181°. Several recrystallizations of the former gave 10.0 g. (50%) of colorless *cis* acid, m.p. 90° (lit.,[24] m.p. 88–89°).

cis-2-Methoxycinnamic acid (6.0 g.) was converted to the methyl ester by treatment of an ethereal solution with excess diazomethane. After 15 min., the excess was destroyed by the dropwise addition of acetic acid. Ether was removed under reduced pressure and the residue distilled through a short-path system to give 6.0 g. of the ester (VI), b.p. 84–88° (0.1 mm.), $n^{23}\text{D}$ 1.5646, $\lambda_{\max}^{\text{EtOH}}$ 273 mμ, ε 14,800 (lit.,[24] b.p. 277°, $n^{10}\text{D}$ 1.5718).

Conversion of Methyl *cis*-2-Methoxycinnamate to Coumarin.—The ester (VI) (2.0 g.) was stirred into 15 g. of pyrophosphoric acid. The vessel was cooled during the early stages of reaction so as to maintain room temperature. After 3 hr. (occasional stirring) 25 ml. of water was added and the resulting mixture was extracted with three portions of ether. Evaporation of solvent from the dried solution left 1.20 g. (79%) of pale yellow solid, m.p. 65–70°. Recrystallization from ethanol raised the m.p. to 69–70°, undepressed with a sample mixed with authentic coumarin (VII).

An attempt to cyclize the *trans* ester under essentially identical conditions gave a 95% recovery of starting material. Similarly, ethyl β-(2,4-dimethoxyphenyl)propionate gave starting material.

Acknowledgment.—The authors are indebted to the Robert A. Welch Foundation for the financial support of this work.

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[21] H. von Pechmann and C. Duisberg, *Ber.*, **16**, 2119 (1883).

[22] H. von Pechmann and J. B. Cohen, *ibid.*, **17**, 2129 (1884).

[23] R. Stoermer, *ibid.*, **42**, 4865 (1909); **44**, 637 (1911).

[24] W. H. Perkin, *J. Chem. Soc.*, **31**, 388 (1877).

The Course of the Mannich Reaction with Isopropyl Methyl Ketone. Preparation of Isopropyl Vinyl Ketone

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In connection with another problem, the hitherto unknown isopropyl vinyl ketone was required. A potentially promising precursor of this substance, namely 1-(N,N-dimethylamino)-4-methylpentanone-3 (I), has been reported[1,2] as the product of the Mannich reaction between isopropyl methyl ketone, formaldehyde, and dimethylamine hydrochloride. Evidence for the structure of this product was provided by condensation of the amine with ethyl acetoacetate to afford 3-isopropyl Δ^2-cyclohexenone, but the yield was unspecified.

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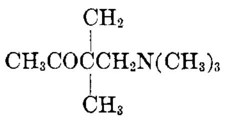
[1] R. Jacquier, M. Mousseron, and S. Boyer, *Bull. soc. chim. France*, **23**, 1653 (1956).

[2] R. Jacquier and S. Boyer, *ibid.*, **21**, 442 (1954).

$(CH_3)_2NCH_2CH_2COCH(CH_3)_2$

I



$CH_3COC(CH_3)_2CH_2N(CH_3)_2$

II

When this Mannich reaction was carried out according to the published procedure, we obtained a 39% yield of basic material, b.p. 66–69° (31–33 mm.), reported,[1] 86° (20 mm.). The picrate melted at 137–139°, after several recrystallizations, as compared with the reported value[1] of 118–119°. The n.m.r. spectrum of our specimen of the amino ketone indicated the presence of 6 protons at δ = 2.15 p.p.m. [$-N(CH_3)_2$], 2 protons at 2.11 (CH_2—N), 3 protons at 2.07 (CH_3CO), and 6 protons as a singlet at 1.07 (2 unsplit CH_3), and was clearly inconsistent with the proposed structure for this product. This spectrum, on the contrary, is entirely compatible with the structure of the product arising from condensation at the methine rather than the methyl position of isopropyl methyl ketone, namely 3,3-dimethyl-4-(N,N-dimethylamino)butanone-2 (II), which we therefore believe to be the major constituent of the previously described base. Since there seems to be no reliable information recorded on the course of the Mannich reaction in such instances,[3] we considered it imperative to confirm the structure in the present case by preparing the authentic amino ketone I.

1-(N,N-Dimethylamino)-4-methylpentanone-3 (I) was produced in 64% yield by the aluminum chloride-catalyzed addition of isobutyryl chloride to ethylene, followed by treatment of the resulting 1-chloro-4-methylpentanone-3 with dimethylamine. The n.m.r. spectrum of this product showed absorption for 4 protons at δ = 2.48 p.p.m. (2 methylenes), 6 protons at 2.12 (—$N(CH_3)_2$), and a doublet of 6 protons centered at 1.01 (J_{AB} = 6 c.p.s.) (2 split CH_3), which is entirely consistent with the structure I. The picrate of this amine melted at 146–147°; thus the melting point of the previously reported picrate (see above) does not correspond with that of this product either. It is difficult to see how the previous workers obtained the isopropylcyclohexenone from their Mannich base, unless it was produced in very low yield as the result of the presence of a small proportion (undetected by the n.m.r. spectrum) of the isomeric base I.

Isopropyl vinyl ketone was prepared in 49% yield from the amino ketone I by conversion to the hydrochloride followed by pyrolysis of the salt under reduced pressure.

Experimental

3,3-Dimethyl-4-(N,N-dimethylamino)-butanone-2.—The reported procedure[1] was employed. Thus from 86 g. of isopropyl methyl ketone, 80 g. of dimethylamine hydrochloride, 50 g. of trioxane, 1 ml. of concentrated hydrochloric acid, and 400 ml. of absolute ethanol there was obtained 56.0 g. (39% yield) of colorless liquid, b.p. 66–69° (31–33 mm.), n^{25}_{D} 1.4285. The n.m.r. spectrum, reported above, was determined at 60 Mc. Deuteriochloroform was employed as solvent, and tetramethylsilane was used as an internal standard.

The **picrate**, after several recrystallizations from absolute ethanol, was obtained as yellow needles, m.p. 137–139°.

Anal. Calcd. for $C_{14}H_{20}O_8N_4$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.4 H, 5.6; N, 14.9.

1-(N,N-Dimethylamino)-4-methylpentanone-3.—The following is an adaptation of the excellent procedure of Wilds, McCaleb, and Inglett[4] for the preparation of ethyl vinyl ketone. Ethylene was passed into a solution of 47.0 g. of isobutyryl chloride and 63 g. of anhydrous aluminum chloride in 300 ml. of anhydrous chloroform while the temperature of the solution was maintained at about 5° by means of an ice bath. After 2 hr. the absorption of ethylene had ceased, and the mixture was stirred overnight. The solution was poured into cracked ice containing 100 ml. of concentrated hydrochloric acid, and the aqueous phase was extracted with chloroform. The combined chloroform solutions were washed well with water and dried over anhydrous sodium sulfate. The solution was concentrated to 150 ml. under reduced pressure and then cooled to 0°. Dimethylamine (60 g.) was slowly added to this solution with stirring. After 16 hr. at room temperature, the solution was diluted with 300 ml. of chloroform, then extracted with cold 10% hydrochloric acid. The combined aqueous acidic layers were cooled in ice, made basic with excess 10% sodium hydroxide solution, and extracted thoroughly with ether. The combined ether layers were washed with water, followed by saturated brine, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue distilled through a short Vigreux column to afford 40 g. (64% yield) of colorless liquid, b.p. 74–75° (17 mm.), n^{25}_{D} 1.4255. The n.m.r. spectrum (see discussion) was determined under the conditions described in the preceding experiment.

Anal. Calcd. for $C_8H_{17}ON$: C, 67.09; H, 11.96; N, 9.78. Found: C, 66.8; H, 11.7; N, 9.5.

The **picrate** was obtained from absolute ethanol as yellow plates, m.p. 146–147°.

Anal. Calcd. for $C_{14}H_{20}O_8N_4$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.3; H, 5.4; N, 14.8.

Isopropyl Vinyl Ketone.—A 15-g. portion of 1-(N,N-dimethylamino) 4-methylpentanone-3, prepared as described above, was dissolved in 500 ml. of anhydrous ether, and hydrogen chloride gas was passed through the solution until all of the hydrochloride had been precipitated. The white solid was collected by filtration and dried in a desiccator. The dried hydrochloride was heated with 0.5 g. of hydroquinone under reduced pressure (200 mm.), and the liquid which was distilled from the mixture was dried over anhydrous sodium sulfate and distilled through a short Vigreux column to afford 5.0 g. (49% yield) of colorless liquid, b.p. 50° (90 mm.), n^{25}_{D} 1.4148, $\lambda_{max}^{CHCl_3}$ 5.87, 5.97 μ (split carbonyl).

Anal. Calcd. for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.1; H, 10.6.

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(4) A. L. Wilds, K. E. McCaleb, and G. E. Inglett, unpublished work. We wish to thank Professor Wilds for making this procedure available to us.