isomeric enol form. We have been unable to convert pentaphenylacetone to its oxime and to effect reduction of the ketone by the Clemmensen method or by lithium aluminum hydride in refluxing ether. Neither have we been able to acylate the ketone with benzoyl chloride in pyridine or with a mixture of acetic anhydride and sodium acetate, indicating the presence of no appreciable amount of the enol form of the ketone.

Experimental

Pentaphenylacetone.—Potassium triphenylmethide,[6] prepared from 0.2 mole of triphenylmethane (m.p. 92.5–93°) and 0.22 mole of potassium amide in 250 ml. of ether, was carbonated[6] giving triphenylacetic acid, m.p. 262–264° (reported m.p. 263–265°)[6] in 94% yield. This acid (0.105 mole) was gently refluxed with a mixture[5] of 30 g. of phosphorus pentachloride and 90 ml. of phosphorus oxychloride giving triphenylacetyl chloride, m.p. 124–126° (reported m.p. 128–129°)[5] in 99% yield. After two recrystallizations from benzene or ligroin (b.p. 60–90°) the acid chloride melted at 126–128°; yield 89%.

To a suspension of 0.1 mole of potassium diphenylmethide in 250 ml. of dry ether,[4] immersed in a Dry Ice–acetone-bath, was added rapidly a solution of 15.3 g. (0.05 mole) of triphenylacetyl chloride (m.p. 126–128°) in 125 ml. of dry benzene. After refluxing twenty-four hours, the mixture was poured into 300 ml. of water. More ether and benzene were added and, after shaking, the aqueous-alkaline phase was separated. The ether–benzene phase was washed with water, dried over sodium sulfate and the solvents distilled. The residue was stirred with approximately 100 ml. of methanol and the solid filtered off yielding 19 g. (87%) of crude pentaphenylacetone, m.p. 174–177°. One recrystallization from a benzene–ethanol mixture gave the pure ketone, m.p. 180–181° cor. (reported m.p. 180°[2]); yield 70%.

Anal.[8] Calcd. for $C_{33}H_{26}O$: C, 90.37; H, 5.98. Found: C, 90.48, 90.75; H, 6.28, 6.17. Acidification of the aqueous alkaline phase, yielded 10% of triphenylacetic acid, m.p. 262–265°.

Tetraphenylacetone.—Potassium diphenylmethide, prepared from 0.25 mole of diphenylmethane and 0.275 mole of potassium amide in 250 ml. of ether, was carbonated[4] giving diphenylacetic acid, m.p. 146–147° (reported m.p. 147–148°)[4] in 92% yield. This acid (0.108 mole) was refluxed[9] with thionyl chloride (0.2 mole) to form diphenylacetyl chloride, m.p. 53–55° (reported m.p. 55°)[10] in 93% yield. After two recrystallizations from ligroin (b.p. 70–90°) the acid chloride melted at 54–55°; yield 61%.

To a suspension of 0.1 mole of potassium diphenylmethide in 200 ml. of ether, immersed in a Dry Ice–acetone-bath, was added rapidly a solution of 0.05 mole of diphenylacetyl chloride in 125 ml. of ether. After refluxing twelve hours, the mixture was worked up essentially as described above for pentaphenylacetone. The residue obtained on removing the solvent from the dried ether phase was stirred with 150 ml. of methanol and the remaining solid filtered off and washed with 50 ml. of methanol giving essentially pure tetraphenylacetone, m.p. 133–134° (reported m.p. 134°[7]); yield 52%. The combined methanol filtrate was steam distilled until no more diphenylmethane came over. The residue was stirred with 25 ml. of methanol giving 4.5 g. of crude tetraphenylacetone, m.p. 124–127°. This crude solid, which gave a positive hydroxamic acid test for esters,[11] was refluxed with 50 ml. of 5% sodium hydroxide solution for one hour, diluted with 200 ml. of water and the solid filtered off. In this manner there was obtained more (20%) tetraphenylacetone, m.p. 129–131° after one recrystallization from glacial acetic acid.

Acidification of the original aqueous alkaline phase yielded 19% of diphenylacetic acid, m.p. 146–147° after one recrystallization from water. Acidification of the alkaline filtrate from the refluxed mixture yielded 6% of diphenylacetic acid; this acid resulted evidently from hydrolysis of the O-acyl derivative of the ketone.

(8) Analyses by Clark Microanalytical Laboratory, Urbana, Ill.; Micro-Tech Laboratories, Skokie, Ill.

(9) Staudinger, *Ber.*, **44**, 1620 (1911).

(10) Staudinger, *ibid.*, **38**, 1737 (1905).

(11) Feigl, "Spot Tests," Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 358.

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8-Methoxyhydrocoumarin

BY C. F. KOELSCH AND C. R. STEPHENS, JR.

When 8-methoxycoumarin is hydrogenated, and the product is dissolved in alkali and then precipitated with acid, there is obtained a substance, m. p. 107–108°. It has been reported[1] that this substance is 8-methoxyhydrocoumarin.

It has now been found, however, that the substance is soluble immediately in dilute sodium bicarbonate, and that its composition agrees with that calculated for **2-hydroxy-3-methoxyhydrocinnamic acid**. The compound shows no tendency to lose water when it is crystallized from ethyl acetate–ligroin or from water.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.2; H, 6.1. Found: C, 61.5; H, 6.4.

The true **8-methoxyhydrocoumarin**, obtained in 70% yield when the hydrogenation product is isolated directly, and not dissolved in alkali, forms colorless needles from ether–ligroin, m. p. 76–77°.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.6. Found: C, 67.7; H, 5.7.

(1) Rupp and Linck, *Arch. Pharm.*, **253**, 41 (1915).

SCHOOL OF CHEMISTRY
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Effect of *p*H on the Far Ultraviolet Absorption of Tyrosine[1]

BY N. KRETCHMER AND R. TAYLOR[2]

Crammer and Neuberger[3] in their study of the shift in the absorption maximum of tyrosine from the wave length of 274 mμ in acid solutions to 295 mμ in alkaline solutions observed an increase in molecular extinction coefficients from 1290 to 2300. The usefulness of this absorption band in the analysis of intact proteins for tyrosine was mentioned. Sizer and Peacock[4] have also examined the effect of a few *p*H changes on the absorption band of tyrosine. At a *p*H of 12 there was observed an additional maximum in the tyrosine spectrum at a wave length of 240 mμ. These authors indicated that the complete ionization of the phenol group was responsible for the maximum.

In this report, a more complete study of the

(1) Aided by a grant from the Life Insurance Medical Research Fund.

(2) Chas. Pfizer and Co., Brooklyn, New York.

(3) J. L. Crammer and A. Neuberger, *Biochem. J.*, **37**, 302 (1943).

(4) I. W. Sizer and A. C. Peacock, *J. Biol. Chem.*, **171**, 767 (1947).