Experimental

Reactions of α^2-Chloroisodurene.—A solution of 16.9 g. (0.1 mole) of α^2-chloroisodurene[2] (b. p. 126–130° at 21 mm.) in 75 ml. of ether was added to 2.7 g. (0.11 atom) of magnesium foil (Merck, reagent grade) covered by 25 ml. of ether in the manner usually employed in the preparation of Grignard reagents. After refluxing one hour, the mixture (consisting of a suspension of white solid and much unreacted magnesium) was poured onto excess powdered Dry Ice. After coming to room temperature the resulting mixture was stirred with dilute hydrochloric acid with external cooling. The ether phase was combined with an ether extraction of the aqueous phase. The combined ether solution was extracted with excess sodium hydroxide solution. After drying over Drierite, the ether solution was fractionated yielding 7.9 g. (59%) of crude 1,2-dimesitylethane. Recrystallization from ethanol resulted in little loss; m. p. 116–117°; reported m. p. 117–118°.[3] This hydrocarbon yielded the tetrabromo derivative, 1,2-di-(3,5-dibromomesityl)-ethane, m. p. 177–179° after recrystallization from xylene; reported m. p. 178–180°.[3]

The sodium hydroxide extract, containing added ice, was acidified with hydrochloric acid and extracted several times with ether. The combined ether extractions were washed with water and dried over Drierite. An aliquot titrated with standard base indicated a yield of 13% of mesitylacetic acid. A blank indicated that no titratable hydrochloric acid was extracted in this manner. From a portion of the ether extract, there was obtained a sample of mesitylacetic acid, m. p. 166–168°; reported m. p. 167–168°.[1] Calcd. for $C_{11}H_{14}O_2$: neut. equiv., 178. Found: neut. equiv., 179.

When α^2-chloroisodurene was added to magnesium in ether during ten hours according to the procedure for preparing allylmagnesium chloride[4] and the reaction mixture worked up as described above, there were obtained a 40% yield of 1,2-dimesitylethane, m. p. 116–117°, and a 29% yield (determined by titration) of mesitylacetic acid, m. p. 167–168° (isolated sample).

Pentamethylbenzyl Chloride.—This compound was prepared by the chloromethylation of pentamethylbenzene (b. p. 118–120° at 30 mm.) by the general method of Vavon[5] except that a 20% excess of chloromethyl ether was employed. The chloride was isolated in 91% yield as a white solid, m. p. 80°[6] and b. p. 180–182° at 30 mm. Two recrystallizations from glacial acetic acid-water failed to raise the melting point.

Anal.[7] Calcd. for $C_{12}H_{17}Cl$: C, 73.27; H, 8.71; Cl, 18.03. Found: C, 73.26; H, 8.58; Cl, 18.17.

Reaction with Pentamethylbenzyl Chloride.—This halide (19.7 g., 0.1 mole) reacted with 2.7 g. (0.11 atom) of magnesium, followed by carbonation and treatment with acid. The ether phase on standing for half an hour precipitated 11.2 g. (70%) of 1,2-di-(pentamethylphenyl)-ethane, m. p. 241–243°. After three recrystallizations from dioxane, the product melted at 241.5–242°.

Anal.[7] Calcd. for $C_{24}H_{34}$: C, 89.37; H, 10.63. Found: C, 89.27; H, 10.57.

The sodium hydroxide extract of the ether phase yielded only a trace of white solid acid, presumably pentamethylphenylacetic acid.

Coupling of 2,4,6-Tribromobenzyl Bromide.—This halide[2] (5 g., 0.012 mole) was treated with methylmagnesium iodide by the method of Fuson[8] for coupling di-*o*-methylbenzyl chlorides. Crude 1,2-di-(2,4,6-tribromophenyl)-ethane, m. p. 216–220°, precipitated from the ether phase of the acidified reaction mixture. A further small quantity of product was obtained by fractionation of the ether; combined yield, 2.7 g. (69%). After recrystallization from 1500 ml. of ethanol, the product melted at 221°.

Anal.[7] Calcd. for $C_{14}H_8Br_6$: C, 25.64; H, 1.23; Br, 73.11. Found: C, 26.04; H, 1.40; Br, 73.10.

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[2] Hauser and Humphlett, *J. Org. Chem.*, **15**, 364 (1950).

[3] Wenzel, *Monatsh.*, **35**, 953 (1914).

[4] Kharasch and Fuchs, *J. Org. Chem.*, **9**, 364 (1944).

[5] Vavon, Bolle and Calin, *Bull. soc. chim.*, [5] **6**, 1025 (1939).

[6] Jacobsen [*Ber.*, **22**, 1217 (1889)] reported 99° as the melting point for this chloride prepared in unreported yield from hexamethylbenzene and phosphorus pentachloride.

[7] Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

[8] Fuson, Denton and Kneisley, THIS JOURNAL, **63**, 2652 (1941).

Pentaphenylacetone and Tetraphenylacetone[1]

BY SIMON W. KANTOR AND CHARLES R. HAUSER

In connection with another study, pure pentaphenylacetone[2] was synthesized conveniently in high yield by the acylation of potassium diphenylmethide with triphenylacetyl chloride.[3] The ketone was evidently converted to its potassium derivative in the reaction mixture and, in order to obtain maximum yield, two molecular equivalents of potassium diphenylmethide to one of the acid chloride were employed.

$$(C_6H_5)_3CCOCl + 2KCH(C_6H_5)_2 \longrightarrow K[(C_6H_5)_3CCOC(C_6H_5)_2] + KCl + CH_2(C_6H_5)_2$$

The two reactants were readily prepared. The potassium diphenylmethide was obtained from diphenylmethane by metalation with potassium amide[4] and the triphenylacetyl chloride, from the corresponding carboxylic acid[5] which was prepared by the carbonation of potassium triphenylmethide.[6]

In a similar manner, *sym*-tetraphenylacetone was synthesized conveniently in good yield by the acylation of potassium diphenylmethide with diphenylacetyl chloride.

$$(C_6H_5)_2CHCOCl + 2KCH(C_6H_5)_2 \longrightarrow K[(C_6H_5)_2CHCOC(C_6H_5)_2] + KCl + CH_2(C_6H_5)_2$$

In this case, there was also formed apparently a little of the O-acyl derivative of the ketone which was hydrolyzed with alkali, regenerating the ketone.

Both of these ketones are relatively unreactive. Vorländer and Rack[7] reported that tetraphenylacetone fails to undergo any carbonyl reactions and that it does not exhibit the properties of the

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[1] This work was carried out under contract N7 onr-455 with the Office of Naval Research.

[2] Wieland, Hintermaier and Dennstedt (*Ann.*, **452**, 23 (1927)) prepared this ketone by the thermal decomposition of diphenylacetylazotriphenylmethane but the method was tedious and the yield was low.

[3] An attempt to effect this acylation with methyl triphenylacetate failed to produce pentaphenylacetone. Instead, there was obtained triphenylacetic acid (56%), recovered diphenylmethane (63%) and considerable residual oil. The displacement of the triphenylacetate anion by the diphenylmethide anion might appear to have occurred but the diphenylethane, which would then have been formed, was not found.

[4] Yost and Hauser, THIS JOURNAL, **69**, 2325 (1947).

[5] Bistrzycki and Landtwing, *Ber.*, **41**, 687 (1908).

[6] Levine, Baumgarten and Hauser, THIS JOURNAL, **66**, 1230 (1944).

[7] Vorländer and Rack, *Ber.*, **56B**, 1125 (1923).

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.

CONTRIBUTION FROM THE
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[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.

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.

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

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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 $m\mu$ in acid solutions to 295 $m\mu$ 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 $m\mu$. 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

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[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).