denesulfonic acid, hydrogenation to 5-hydrindanol, nitric acid oxidation to 1-carboxy-2-cyclopentane-beta-propionic acid,[3] and cyclo-decarboxylation to the desired ketone over barium oxide.

To a 300-ml. Aminco hydrogenation bomb was charged 53 g. (0.43 mole) of purified *cis*-α-[0.3.3]bicycloöctanone, 43 g. (0.86 mole) of 100% hydrazine hydrate, 225 g. (4.0 moles) of potassium hydroxide and one liter of triethylene glycol.[4] The mixture was shaken at 195° for twenty-three hours in the sealed bomb. After cooling to room temperature, the reaction mixture was removed from the bomb (foaming), diluted with water, and the mixture steam-distilled. The two liters of steam distillate was acidified with 10% hydrochloric acid and extracted with 400 ml. of ethyl ether. The ether was removed from the separated, dried organic layer by distillation through a 20-plate fractionating column. To the residue was added 35 ml. of 2-octanone, and the mixture carefully fractionated through a 20-plate column to yield 32 g. of material boiling at 136–137° at 735 mm.

This product was combined with 19 g. of material prepared by the semicarbazone method[3] and distilled through a 25-plate column, yielding 49.5 g. of constant boiling, constant index *cis*-(0.3.3)bicycloöctane, b. p. 137° (735 mm.), $n^{20}\text{D}$ 1.4622. The hydrocarbon was filtered through a 2 × 20 cm. tube filled with activated silica gel (28–200 mesh), and the physical properties determined.

Acknowledgment.—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

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RECEIVED OCTOBER 19, 1948

The Preparation of α-Trifluoro-*p*-phenylacetophenone

BY J. H. SAUNDERS, R. J. SLOCOMBE AND EDGAR E. HARDY

Trifluoroacetic acid was converted to the acid chloride and this in turn to α-trifluoro-*p*-phenylacetophenone with an over-all yield of 53%. Recrystallization of this compound from methanol apparently gave the solvated ketone containing one molar equivalent of methanol.

Trifluoroacetyl Chloride.—A 1-liter 3-necked flask was equipped with a dropping funnel, stopper, and an 8-in. helix-packed column. A partial take-off still-head and a Hopkins type, Dry Ice-cooled condenser were attached to the column. The head and condenser gas outlet were then connected to a Dry Ice trap. Two hundred sixty grams (1.25 moles) of phosphorus pentachloride was placed in the flask and 96 g. (0.84 mole) of trifluoroacetic acid was added in 5-cc. portions. To ensure complete reaction the system was maintained under total reflux while the first 5 cc. of acid was added and for an additional ten minutes. Then all of the acid chloride produced from this portion of acid was distilled into the cold receiver before adding the next 5 cc. of acid. Proceeding in this manner about six hours were required for the entire reaction. When all of the acid had been added and had reacted the flask and its contents were warmed to 50° to drive out the last traces of acid chloride. The yield of the clear, straw-colored liquid, which contained some hydrogen chloride, was 119 g.

α-Trifluoro-*p*-phenylacetophenone.—The method of Simons and Ramler[1] was followed. From 205 g. (1.33 moles) of biphenyl, 178.5 g. (1.33 moles) of aluminum chloride, and the acid chloride from 96 g. (0.84 mole) of trifluoroacetic acid there was obtained 114 g. (55.6%) of recovered biphenyl and 112 g. (53.4% based on trifluoroacetic acid, 75.6% based on biphenyl consumed) of α-trifluoro-*p*-phenylacetophenone, b. p. 130–133° (3 mm.). After recrystallization from 60–70° petroleum solvent the compound melted at 51.2–51.4°.

Anal.[2] Calcd. for $C_{14}H_9OF_3$: C, 67.20; H, 3.62. Found: C, 67.48; H, 3.84.

When this product was recrystallized from methanol or methanol and water a new compound, m. p. 102.5–103.5°, was obtained. When this compound was heated above its melting point a condensable gas, presumably methanol, was evolved, and the residue again melted at 51.0–51.4°. Analysis indicated the presence of one mole of methanol per mole of ketone. The difficulty with which a solid of constant melting point was obtained indicated that this compound may have been unstable in methanol solution or that other states of solvation may have existed.

Anal. Calcd. for $C_{15}H_{13}O_2F_3$: C, 63.83; H, 4.64. Found: C, 64.03; H, 4.37.

The α-trifluoro-*p*-phenylacetophenone was insoluble in 10% sodium hydroxide solution but was rapidly hydrolyzed by warm alkali. The observed products were a gas, doubtless fluoroform,[1] and biphenyl-4-carboxylic acid, m. p. 226–228°. Gull and Turner reported m. p. 228° for this acid.[3]

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[1] Simons and Ramler, THIS JOURNAL, **65**, 389 (1943).

[2] Microanalyses were made by the Clark Microanalytical Laboratory, Urbana, Illinois.

[3] Gull and Turner, *J. Chem. Soc.*, 491 (1929).

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RECEIVED SEPTEMBER 24, 1948

Chlorination of *t*-Butylbenzene to 1-Chloro-2-methyl-2-phenylpropane

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The side chain of *t*-butylbenzene has been considered too inert to undergo reaction directly with the halogens. It was claimed that chlorination of *t*-butylbenzene in the presence of sunlight caused ring substitution only.[1] However, we chlorinated *t*-butylbenzene to 1-chloro-2-methyl-2-phenylpropane in 48% conversion. (This compound had been obtained previously by the peroxide-induced chlorination of *t*-butylbenzene with sulfuryl chloride.[2])

Proof of structure consisted of oxidizing the product to benzoic acid in small yield with alkaline potassium permanganate,[3] and carbonation of the corresponding Grignard reagent to the known 3-methyl-3-phenylbutyric acid[4] in 49% over-all conversion. The poor yield of benzoic acid in the above oxidation is to be anticipated for *t*-alkylbenzenes.[5] The preparation of the Grignard reagent was difficult to initiate. When the reaction started, it proceeded slowly but smoothly and an

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[1] Salibil, *Chem. Ztg.*, **35**, 97 (1911); *Chem. Zentr.*, **83**, 1581 (1912).

[2] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

[3] Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 163.

[4] Saboor, *J. Chem. Soc.*, 922 (1945); Hoffman, THIS JOURNAL, **51**, 2545 (1929).

[5] Legge, *ibid.*, **69**, 2079 (1947).