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]bicyclooöctanone, 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)bicyclooöctane, b. p. 137° (735 mm.), $n^{20}{}_D$ 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.

THE WHITMORE LABORATORY
DEPARTMENT OF CHEMISTRY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.
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]

---

[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).

RESEARCH LABORATORY
PHOSPHATE DIVISION
MONSANTO CHEMICAL COMPANY
ANNISTON, ALABAMA
RECEIVED SEPTEMBER 24, 1948

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

BY WILLIAM E. TRUCE, E. T. MCBEE AND C. C. ALFIERI

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

---

[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).

82% conversion of halide to Grignard reagent was achieved as determined by titration.[6]

Experimental

Three moles (402 g.) of *t*-butylbenzene was placed in a long reaction tube which was strongly illuminated. Chlorine, which was first bubbled through a sulfuric acid absorption tube, was slowly bubbled through the hydrocarbon over a period of three hours until a total of three moles had passed. Subsequent rectification yielded 90 g. (0.67 mole) of *t*-butylbenzene, 240 g. (1.42 moles) of 1-chloro-2-methyl-2-phenylpropane, 45 g. of polychlorinated material and 70 g. of still residue. The physical constants of 1-chloro-2-methyl-2-phenylpropane are b. p. 111–112° (18 mm.), $n^{20}\text{D}$ 1.5245, and $d^{20}{}_4$ 1.047.

Anal. Calcd. for $C_{10}H_{13}Cl$: Cl, 21.02. Found: Cl, 21.0, 21.0.

We gratefully acknowledge the financial support of this work by the Procter and Gamble Company.

---

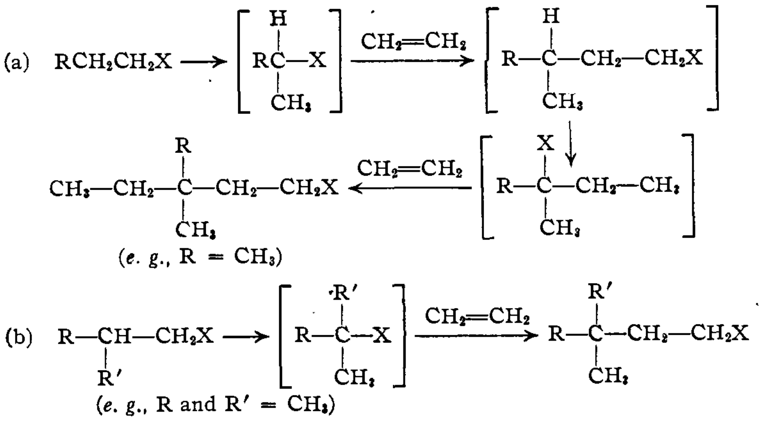
[6] Gilman, *et al.*, THIS JOURNAL, **45**, 150 (1923).

DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY
AND PURDUE RESEARCH FOUNDATION
LAFAYETTE, INDIANA
RECEIVED AUGUST 5, 1948

Condensation of Saturated Halides with Unsaturated Compounds. VII. Condensation of Neopentyl Chloride with Ethylene[1]

BY LOUIS SCHMERLING AND E. E. MEISINGER

The metal halide catalyzed condensation of ethylene with alkyl halides (particularly chlorides and bromides) containing at least three carbon atoms offers a means of preparing 1-halo-3,3-dialkylalkanes.[2] The reaction of typical primary alkyl halides may be illustrated as:



$$\text{(a)}\quad RCH_2CH_2X \longrightarrow \left[R\underset{CH_3}{\overset{H}{C}}-X\right] \xrightarrow{CH_2=CH_2} \left[R-\underset{CH_3}{\overset{H}{C}}-CH_2-CH_2X\right]$$

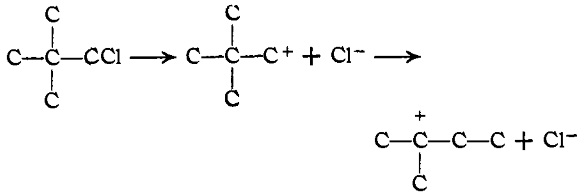
$$CH_3-CH_2-\underset{CH_3}{\overset{R}{C}}-CH_2-CH_2X \xleftarrow{CH_2=CH_2} \left[R-\underset{CH_3}{\overset{X\downarrow}{C}}-CH_2-CH_3\right]$$

(*e. g.*, R = CH$_3$)

$$\text{(b)}\quad R-\underset{R'}{CH}-CH_2X \longrightarrow \left[R-\underset{CH_3}{\overset{R'}{C}}-X\right] \xrightarrow{CH_2=CH_2} R-\underset{CH_3}{\overset{R'}{C}}-CH_2-CH_2X$$

(*e. g.*, R and R′ = CH$_3$)

An example of the reaction of ethylene with a third type of primary alkyl halide, namely, a 1-halo-2,2-dialkylalkane, will now be described. The condensation of neopentyl chloride with ethylene proceeded smoothly at −14 to −20° in the presence of aluminum chloride. There was obtained a 38% yield of chloroheptane which was identified as 1-chloro-3,3-dimethylpentane which is also the product of the condensation of ethylene with *t*-pentyl chloride. Isomerization of the neopentyl group to *t*-pentyl apparently occurred



$$C-\underset{C}{\overset{C}{C}}-CCl \longrightarrow C-\underset{C}{\overset{C}{C}}-C^+ + Cl^- \longrightarrow C-\underset{C}{\overset{+}{C}}-C-C + Cl^-$$

The dissociation of the neopentyl chloride into the unstable positive neopentyl ion and the negative chloride ion is probably brought about by formation of a complex with the catalyst, $(CH_3)_3CCH_2^+AlCl_4^-$.

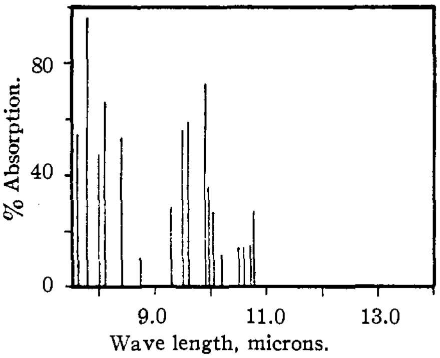


Fig. 1.—Infrared absorption spectrum of 1-chloro-3,3-dimethylpentane.

Experimental

Condensation of Neopentyl Chloride with Ethylene.—A mixture of 40 g. (0.37 mole) of neopentyl chloride,[3] 50 g. of *n*-pentane diluent and 5 g. of aluminum chloride was placed in a three-necked flask immersed in a Dry Ice-acetone-bath. Ethylene was bubbled into the stirred mixture while the temperature was permitted to rise from −70 to −15° at which point absorption began (determined by difference of gas rates in inlet and outlet bubblers). The temperature was maintained at −14 to −20° for the duration of the addition of ethylene (three quarters of an hour) during which time the catalyst gradually coagulated. The liquid product was decanted from the 12 g. of yellow sludge and powder, washed with water, dried and distilled. There was obtained 19 g. (0.14 mole) of product b. p. 50–51° at 20 mm. pressure (150–151° at 760 mm.); $n^{20}\text{D}$ 1.4300. There was also obtained 22 g. of unidentified higher-boiling material which apparently consisted largely of chlorononane and chlorohendecane.

The product boiling at 50–51° at 20 mm. was shown to be 1-chloro-3,3-dimethylpentane by converting it to β-*t*-pentylpropionanilide by the method of Schwartz and Johnson[4]: m. p. 95–96°. This anilide did not depress the melting point of the analogous derivative of 1-chloro-3,3-dimethylpentane prepared by the condensation of *t*-pentyl chloride with ethylene.[2]

---

[1] Preceding paper in this series, THIS JOURNAL, **71**, 107 (1949).

[2] L. Schmerling, *ibid.*, **67**, 1152 (1945).

[3] Obtained by the chlorination of neopentane according to the method of F. C. Whitmore and G. H. Fleming, *ibid.*, **55**, 4161 (1933). We wish to thank Dr. Vladimir Haensel for the sample of neopentane which was prepared by the demethylation of neohexane: V. Haensel and V. N. Ipatieff, *Ind. Eng. Chem.*, **39**, 853 (1947).

[4] A. M. Schwartz and J. R. Johnson, THIS JOURNAL, **53**, 1063 (1931); see also H. W. Underwood, Jr., and J. C. Gale, *ibid.*, **56**, 2117 (1934).