Removal of the benzene filtrate under vacuum below 50° yielded 28 g. of a white crystalline residue. Recrystallization from alcohol yielded 22 g. (calcd. 24 g.) of cyclopentamethylene-thiuram disulfide[10]; m. p. 129–130°. An insoluble residue of 2 g. (Crop 2) remained which on recrystallization from chloroform melted at 137°.

The theoretical yields recorded above are calculated on the assumption that all of the sulfur from the piperidine monosulfide reacted to produce the hexasulfide. This assumption is further substantiated by the yields which are obtained on treating piperidine disulfide[11] (0.1 mole; m. p. 64–65°) in a like manner. The corresponding yields of the hexasulfide were: Crop 1, 17.5 g., m. p. 138–140°; Crop 2, 3.5 g. (calcd. 22.4 g.). On removal of the benzene filtrate as before, a crystalline residue of 21.5 g. was obtained. Recrystallization from alcohol gave 15 g. (calcd. 16 g.) of the disulfide; m. p. 128–129°.

Cyclohexyl Isothiocyanate.—N-Cyclohexyl-2-benzothiazole-sulfenamide[12] (167 g., m. p. 100–102°) was dissolved in 2500 cc. of ether, treated with 96 g. of carbon disulfide and the solution stirred for seventy-two hours. After removal of the solvent under vacuum, the crystalline residue was filtered off and washed with petroleum ether.

The precipitated 2-mercaptobenzothiazole was separated from the sulfur by solution in dilute sodium hydroxide (3%). Precipitation by acidification yielded 96.2 g. (90.9%) of 2-mercaptobenzothiazole; m. p. 178–179°.

Distillation of the residue after evaporation of the petroleum ether yielded 77 g. (86%) of cyclohexyl isothiocyanate,[13] b. p. 97–98° (11–12 mm.) or 222° (749 mm.).

Action of Carbon Disulfide on 2-Benzothiazole-sulfen-piperidide.—2-Benzothiazole-sulfen-piperidide[14] (0.2 mole; m. p. 79–80°) was dissolved in 700 cc. of ether containing 45 g. of carbon disulfide and the solution was allowed to stand for thirty days. The crystalline precipitate which formed was filtered off; yield 59.5 g. Evaporation of the ether yielded 7 g. of additional material.

The combined precipitate was treated with 1500 cc. of acetone and filtered, leaving a residue of 2,2′-dithiobisbenzothiazole; yield 22.8 g. (68.6%); m. p. 178–179°. Evaporation of the acetone and repeated recrystallization of the residue from alcohol after treatment with decolorizing charcoal yielded 15.8 g. (49.3%) of cyclopentamethylene-thiuram disulfide; m. p. 130–131°.

Summary

1. A new reaction, that of carbon disulfide on amine sulfides and on sulfenamides, has been demonstrated; the course of the reaction is determined by the substituents present in the amine and in the amide group.

2. Four new compounds: dimethylamine monosulfide, morpholine monosulfide, morpholine disulfide, and di-(morpholyl-N-thiocarbamyl) trisulfide, have been synthesized.

3. A new method has been reported for the preparation of cyclohexyl isothiocyanate, and for tetra substituted thiuram disulfides and hexasulfides.

---

[10] Ehrenberg, *J. prakt. Chem.*, [2] **36**, 129 (1887).

[11] Michaelis and Luxembourg, *Ber.*, **28**, 166 (1895).

[12] Harman, U. S. Patent 2,191,656.

[13] Skita and Rolfes, *Ber.*, **53**, 1247 (1920).

[14] Tschunkur and Kohler, U. S. Patent 2,045,888.

NITRO, WEST VA. RECEIVED MARCH 13, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. XVII. The Addition of an Alkyl Chloride to the Double Bond[1]

BY J. H. SIMONS AND A. C. MEUNIER

As a continuation of the investigation of the catalytic activity of hydrogen fluoride, we have studied the reactions of an alkyl chloride with olefins. Hydrocarbons, phenols, alcohols, and acids have previously been added to olefins by the catalytic influence of hydrogen fluoride; but we have found in this investigation that an alkyl halide can be added to an unsubstituted olefin.

Tertiary butyl chloride reacted with cyclohexene to produce a number of products. Cyclohexyl chloride and cyclohexyl fluoride were produced in large amounts. The chloride was probably formed by direct addition to cyclohexene of hydrogen chloride, which was split out from the *t*-butyl chloride. A large intermediate fraction, consisting of an inseparable mixture of aliphatic chlorides and olefins, was very similar to the product obtained in this Laboratory[2] by the reaction of *t*-butyl chloride itself with hydrogen fluoride. A higher boiling chloride, obtained in an 11% yield, subsequently was identified as 1-chloro-3-*t*-butylcyclohexane.

With trimethylethylene, *t*-butyl chloride reacted to produce no isolatable addition product, because of the similarity of such an addition product to the components of the inseparable aliphatic mixture obtained from *t*-butyl chloride itself.

The secondary chloride, isopropyl chloride,

---

[1] For the previous paper of this series, see THIS JOURNAL, **64**, 1356 (1942).

[2] Simons, Fleming, Whitmore and Bissinger, *ibid.*, **60**, 2267 (1938).

treated with cyclohexene, resulted in considerable cyclohexyl chloride and a sizeable residue, but no intermediate aliphatic fraction, as in the case of *t*-butyl chloride.

The formation of 1-chloro-3-*t*-butylcyclohexane instead of the 1,2 compound indicates that hydrogen fluoride may have the same effect in this reaction as aluminum chloride has in another. Nenitzescu and co-workers[3] have made 1-substituted-3-phenyl and 1-substituted-4-phenyl-cyclohexanes by treating 1-chloro-2-substituted-cyclohexanes with benzene in the presence of aluminum chloride.

The identification of 1-chloro-3-*t*-butylcyclohexane was made by dehydrohalogenating in alcoholic potassium hydroxide and oxidizing the resulting olefin to a substituted adipic acid, which proved to be β-*t*-butyladipic acid. The position of the chloro group was indicated as 3, as the 3,5-dinitrobenzoate of 4-*t*-butylcyclohexanol depressed the melting point of the 3,5-dinitrobenzoate of the alcohol made from the oxidation of the Grignard reagent of the chloride in question.

Experimental

General Method.—The technique and apparatus was similar to that previously used in other hydrogen fluoride catalyzed reactions in this Laboratory.

One mole of olefin was added dropwise to a solution of 1 to 2 moles of alkyl chloride in 2 to 6 moles of liquid hydrogen fluoride at 0 to 5°. After complete addition, the reactants were allowed to warm to room temperature and stirred until hydrogen chloride evolution was not detectable. This required about twenty-four hours. The organic layer was treated in the usual manner, and a crude separation by distillation made to obtain a middle fraction, which contained the identifiable products. This procedure was necessary because of the decomposition of fluorides and chlorides, when heated, unless in a fairly pure state. The middle fraction was then carefully distilled to obtain the various products, which were in turn redistilled to obtain the pure compound.

The identified products of the reaction between *t*-butyl chloride and cyclohexene were cyclohexyl chloride, cyclohexyl fluoride, and 1-chloro-3-*t*-butylcyclohexane in yields of 65, 11.5 and 11.1% based on the cyclohexene used. The cyclohexyl chloride was identified by its b. p. 143° (760 mm.), n^{20}_D 1.4626, its anilide m. p. 146°, and its α-naphthalide m. p. 188°. The cyclohexyl fluoride, b. p. 42.5° (98 mm.), m. p. 13°, and n^{20}_D 1.4147. The 1-chloro-3-*t*-butylcyclohexane, b. p. 98° (20 mm.), $n^{19.5}_D$ 1.4630, $d_{19.5}$ 0.9389 (pycnometer).

Identification of 1-Chloro-3-*t*-butylcyclohexane

This compound was shown to have the empirical formula of $C_{10}H_{19}Cl$ by its *Anal.* Calcd. for $C_{10}H_{19}Cl$: Cl, 20.3; M_R 51.05; mol. wt., 174. Found: Cl, 19.9; M_R 51.23; mol. wt. (cryoscopic), 177.

Dehydrohalogenation of $C_{10}H_{19}Cl$.—Between 40 and 64.5 g. (0.27–0.37 mole) of chloride was added dropwise to a solution of 50 to 63 g. of potassium hydroxide (c. p. sticks dried in a vacuum desiccator for several hours) in 218 to 268 g. of absolute ethanol under reflux over a period of three and one-half to six hours. Stirring and heating were continued for twenty-four to sixty-one hours. After separation and distillation a 36% yield of olefin was obtained, b. p. 60° (15 mm.), n^{20}_D 1.4581. Molecular weight (cryoscopic) (observed) 136 (calculated for $C_{10}H_{18}$), 138; d^{20} 0.8313, M_R (obs.) 45.35, M_R calcd. 45.71. *Anal.* Calcd. for $C_{10}H_{18}$: C, 86.9; H, 13.1. Found: C, 86.97; H, 13.37. These data indicate the olefin to have the formula $C_{10}H_{18}$.

Oxidation of $C_{10}H_{18}$—Isolation of β-*t*-Butyladipic Acid.—To a suspension of 40 g. of potassium permanganate in 300 cc. of water, was added 17 g. of olefin, the mixture was vigorously stirred at 0 to 10° for seventeen hours, and an additional six and one-half hours at room temperature. The products were filtered and the filtrate acidified with an excess of concentrated sulfuric acid. The product of an ether extraction was recrystallized several times from water to a constant melting point of 114°. Recrystallization from benzene did not raise the melting point. Neutral equivalent (observed), 103.5; (calculated for *t*-butyladipic acid), 101.

β-*t*-Butyladipic acid was synthesized by the method of Perkins and Dietzler,[4] from 4-*t*-butylcyclohexanol. A solid was obtained, which was recrystallized to a constant melting point of 113°. Perkins and Dietzler reported 115° for the melting point of this compound. A mixture of this acid with that of the acid prepared from $C_{10}H_{18}$ melted at 113.5–114.5.

The di-anilides of the two acids were prepared. The one obtained from the olefin, m. p. 206°, the one from 4-*t*-butylcyclohexanol 205.0–205.5°; and mixed m. p. 205–206°. These data indicate the olefin to be *t*-butylcyclohexene-$\Delta^{3,4}$ and the chloride, $C_{10}H_{19}Cl$, to be either 1-chloro-3-*t*-butylcyclohexane or 1-chloro-4-*t*-butylcyclohexane.

Oxidation of the Grignard Reagent of $C_{10}H_{19}Cl$.—A Grignard reagent of $C_{10}H_{19}Cl$ was prepared. It was then oxidized with molecular oxygen. The complex (R–O–Mg–Cl) was then decomposed by ice and ammonium chloride, and the ethereal layer dried over magnesium sulfate. The ether was removed by evaporation and the residue, which did not crystallize on cooling, was distilled through a Claisen flask to yield 3.5 g. material, b. p. 119 to 129° (29 mm.), 1.4 g. low boiling material, and 1 g. residue. The intermediate fraction did not crystallize, but its boiling point was in the right range for that of a *t*-butylcyclohexanol.

The 3,5-Dinitrobenzoate Derivatives of the Alcohols.—From the intermediate fraction obtained from the distillation above (b. p. 119 to 129°) the 3,5-dinitrobenzoate was prepared, m. p. 144°. *Anal.* Calcd. for $C_{17}H_{18}O_6N_2$: N, 8.14. Found: N, 7,99.

A similar 3,5-dinitrobenzoate made from 4-*t*-butylcyclo-

---

[3] (a) Nenitzescu and Gavat, *Ann.*, **519**, 260 (1935); (b) Nenitzescu and Cureaveanu, *Ber.*, **70B**, 346 (1937).

[4] Perkins and Dietzler U. S. Patent 1,960,211; *Chem. Abs.*, **28**, 4435 (1934).

hexanol had m. p. 157.5°. *Anal.* Calcd. for $C_{17}H_{16}O_6N_2$: N, 8.14. Found: N, 8.10.

Mixed melting point of the two 3,5-dinitrobenzoates 125 to 136°. This indicates the chloride to be not the 1,4, but the 1,3 compound.

Summary

Tertiary butyl chloride was found to react with cyclohexene in hydrogen fluoride to produce a 65% yield of cyclohexyl chloride, 11.5% cyclohexyl fluoride and an 11% yield of a chloride identified as 1-chloro-3-*t*-butylcyclohexane.

Reactions of *t*-butyl chloride with trimethylethylene and of isopropyl chloride with cyclohexene produced no isolable addition product of the chloride to the olefin.

STATE COLLEGE, PA. RECEIVED JULY 10, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Addition of Hydrogen Fluoride to Halo-olefins

BY ALBERT L. HENNE AND EDWIN P. PLUEDDEMAN

The individual cases of hydrogen fluoride addition to halo-olefins previously reported[1,2,3] are here supported by more examples and extended to a generalized study. The technique outlined in the three papers cited has been used, with minor adjustments for specific cases.[4]

All but two of the compounds were already known: these are described with analysis in the table. The large quantities of material prepared made it possible to purify all samples adequately, and two sets of physical properties were found to be improvements over previously reported values. They are also listed in the table.

Monohalo-olefins RHC=CHX did not react well and did not yield clean cut products. At room temperature there was no apparent combination with hydrogen fluoride. After four hours at 100°, $CH_3CH{=}CHCl$ gave traces of $CH_3CH_2CHF_2$, 5% of unchanged olefin, 10% CH_3CH_2CHFCl, 20% CH_3CHFCH_2Cl, 20% $CH_3CHClCH_2Cl$, and the remainder of the material was tar. After two hours at 65°, $C_2H_5CH{=}CHCl$ gave traces of $C_3H_7CHF_2$, 25% of recovered olefin, 10% of C_3H_7CHFCl, 5% of $C_4H_8Cl_2$ and tar; higher temperatures increased the amount of tar.

The two isomeric C_3H_6FCl were distinguished as follows. The lower boiling isomer (b. p. 46–49°, d^{20}_4 1.030, n^{20}_D 1.3685) did not react with zinc and proved identical with the compound obtained from $CH_3CH_2CHCl_2$ and mercuric fluoride[5]; its formula is therefore CH_3CH_2CHClF. The higher boiling isomer (b. p. 68.5°, d^{20}_4 1.086, n^{20}_D 1.3824) must therefore be CH_3CHFCH_2Cl.

The butane derivative (b. p. 73–76, d^{20}_4 0.968, n^{20}_D 1.3890) was interpreted as predominantly $CH_3CH_2CH_2$-$CHFCl$ because it boiled only slightly higher than 31° above its propane homolog. Such a boiling point difference is known to exist between homologs.[5,6]

In contrast, $(CH_3)_2C{=}CHCl$, **a monochloro-olefin of the RR′C=CHCl type,** was found to react very readily with hydrogen fluoride at 0° and also at −23°, and a 65% yield of $(CH_3)_2$-$CHCHClF$ was easily obtained. Tar formation was negligible at the lower temperatures, but increased rapidly in importance at higher temperatures. The same chlorofluorobutane was obtained almost as readily from methallyl chloride. This was due to the fact that hydrogen fluoride isomerized methallyl chloride rapidly to isocrotyl chloride. The physical properties are listed in the table.

Originally the assumption was made that the chlorofluoride was $(CH_3)_2CFCH_2Cl$ but the error of interpretation became apparent when it was observed that the compound did not react with zinc, an indication that the halogen atoms are not located on adjacent carbon atoms. The correct formula was settled definitely by synthesis. Isobutyraldehyde was transformed to $(CH_3)_2CHCHCl_2$, in which one of the chlorine atoms was exchanged for fluorine by means of mercuric fluoride.[5] Mixed freezing curves demonstrated the identity of the three preparations.

Monohalo-olefins of the RCX=CR′R″ type reacted extremely readily with hydrogen fluoride to give mixtures of difluorides RCF_2R' and dichlorides $RCCl_2R'$ in preference to the straight addition product $RCClFR'$. Experiments on $CH_3CCl{=}CH_2$, $CH_3CH_2CCl{=}CH_2$, $CH_3CH{=}CClCH_3$ and $CH_3CH_2CCl{=}CHCH_3$ gave results in agreement with Miss Renoll's reports.[3] In

---

[1] Henne and Haeckl, THIS JOURNAL, **63**, 2692 (1941).

[2] Henne and Whaley, *ibid.*, **64**, 1157 (1942).

[3] Mary Renoll, *ibid.*, **64**, 1115 (1942).

[4] The experiments described by Miss Renoll[3] were published while the present paper was being written; they are specifically limited to one class of compounds. As we agree with Miss Renoll's results we have removed from our paper the description of the class reported by her.

[5] Henne, THIS JOURNAL, **60**, 1569 (1938).

[6] Henne, Renoll and Leicester, *ibid.*, **61**, 938 (1939).