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.

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

The Addition of Hydrogen Fluoride to Halo-olefins

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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.[3,6]

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

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(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).

TABLE OF PHYSICAL CONSTANTS

Compounds	F. p., °C.	B. p., °C.	t, °C.	n^t_D	d^t_4	MR	A.R.F	Fluorine, % Found	Fluorine, % Calcd.	Chlorine, % Found	Chlorine, % Calcd.
$(CH_3)_2CHCHFCl$	− 69.3	82.5	20	1.3891	1.0362	25.2	0.8	17.1	17.2	32.1	32.1
$C_2H_5CFClCH_3$	−110.0	67.7	20	1.3782	0.9982	25.55	1.11	17.0	17.2	32.3	32.1
$CH_2ClCFClCH_3$	− 91.7	88.6	20	1.4099	1.2624	25.71	1.03				
CH_3CFCl_2	−103.5	32.0	10	1.3600	1.250	21.20	1.14				

The second compound, prepared with J. B. Hinkamp,[7] was tranformed to the known $C_2H_5CF_2CH_3$ to demonstrate the location of its halogen atoms. The third compound, prepared with F. W. Haeckl, improves the data in reference no. 1. The fourth compound improves the data of THIS JOURNAL, 58, 889 (1936).

contrast, it should be recalled that the combination of HF with $CH_2ClCCl=CH_2$ is considerably less vigorous and yields mostly the straight addition product $CH_2ClCClFCH_3$[1] with very little further substitution to $CH_2ClCF_2CH_3$ unless long heating is resorted to. Experiments with alpha-chlorostyrene were inconclusive but in this case the chlorine atom is somewhat activated by the phenyl group and cannot be regarded as strictly vinylic.

Asymmetrical dihalo-olefins of the $RR'C=CX_2$ type combined smoothly with hydrogen fluoride, preferably at about 65°, and without much substitution. After three hours at 65° with four moles of hydrogen fluoride $CH_2=CCl_2$ gave traces of CH_3CF_2Cl, 50% of CH_3CFCl_2, 10% of recovered material, 5% of CH_3CCl_3 and some 15% of tar. The addition of hydrogen fluoride to $CH_3CH=CCl_2$ and to $CH_3CH=CClF$ has been described before.[2] After sixteen hours at 65°, $CH_3CH_2CH=CCl_2$ gave 15% of $C_3H_7CF_2Cl$, 28% of $C_3H_7CFCl_2$, and 23% of unreacted olefin; higher temperatures favored further substitution.[7] After one hour of heating at 100° with two moles of hydrogen fluoride, $(CH_3)_2C=CCl_2$ (b. p. 109, $n^{20}D$ 1.4580) gave about 35% of a product (b. p. 105–109, $n^{20}D$ 1.4558) which was held to be mostly $(CH_3)_2CHCCl_2F$, 10% of recovered material and the rest tar; at 120° tar formation became preponderant.

The addition of hydrogen fluoride to **symmetrical dihalo-olefins $RCX=CXR'$** gave contradictory results. No addition was observed to $CHCl=CHCl$, despite the variety of conditions tried. In contrast, addition took place smoothly at 120° in the case of $CH_3CCl=CHCl$. Both the *cis* and the *trans* forms gave the same addition product, $CH_3CClFCH_2Cl$, and it was observed that the *trans*-olefin gave consistently a slightly higher yield of substitution product, CH_3CF_2CHCl. To illustrate, after four hours at 95° with six moles of HF, the *trans* and *cis* olefins gave, respectively, 10 and 7% of $CH_3CF_2CH_2Cl$, 5 and 8% of $CH_3CFClCH_2Cl$, 62 and 60% of recovered olefin and 15 and 18% of residue. Similarly, the *trans* and *cis* forms of $CH_3CF=CHCl$ reacted very easily with HF to yield CH_3CF_2CHCl; here again the *trans*-olefin reacted somewhat more readily.[8]

Trichloroethylene, $CHCl=CCl_2$, and its homolog $CH_3CCl=CCl_2$ did not combine with hydrogen fluoride even at 160°, and the original olefins were recovered unchanged.

Perchloro-olefins and hydrogen fluoride did not add. Perchloroethylene was recovered intact. In the case of $CCl_2=CClCCl_3$, no addition took place, but substitution in the CCl_3 group became more important as the temperature of reaction rose.[9]

Summary

The addition of hydrogen fluoride to the following types of halo-olefins is described: $RHC=CHX$, $RR'C=CHX$, $RCX=CR'R''$, $RR'C=CX_2$, $RCX=CXR'$, $RCX=CX_2$, and $CX_2=CX_2$.

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(7) Hinkamp, unpublished Ph.D. Dissertation, The Ohio State University, 1943.

(8) Henne and Mahan, unpublished.

(9) Henne, Whaley and Stevenson, THIS JOURNAL, 63, 3478 (1941).