temperature for 1 hr, the reaction mixture was poured onto ice and extracted with ether. The ether extracts were washed with 5% sodium hydroxide solution and with water and were dried over magnesium sulfate. Evaporation gave 4.9 g (70%) of a white solid (VIII), mp 150–151°. The $H^1$ nmr spectrum (acetone-$d_6$) showed a multiplet at $\tau$ 1.6–2.5, NH absorption at 1.5, and $COCH_3$ at 7.88. $F^{19}$ nmr spectrum showed a singlet at +69.4 ppm (external $FCCl_3$) in acetone-$d_6$. The ultraviolet showed $\lambda_{max}$ 340 m$\mu$ (sh, $\epsilon$ 114), 257 m$\mu$ ($\epsilon$ 7970).

*Anal.* Calcd for $C_{11}H_8N_2O_3F_6$: C, 40.01; H, 2.44; N, 8.49; F, 34.53. Found: C, 40.89; H, 2.69; N, 8.71; F, 34.71.

***m*-Nitro-$\alpha$,$\alpha$-bis(trifluoromethyl)benzylamine.**—A 1.0-g sample of N-acetate VIII was refluxed for 4 hr with 20 ml of 50% aqueous sulfuric acid. After being stirred at room temperature for 4 days, the mixture was poured onto ice and extracted with ether. The extract was washed with water and dried over magnesium sulfate; the ether was evaporated; and infrared analysis of the residue indicated that the hydrolysis was incomplete. This residue was combined with 2.0 g of additional N-acetate and 60 ml of 50% sulfuric acid and the mixture was refluxed for 24 hr and worked up as before. The infrared spectrum of the residue (1.93 g) showed little or no starting material present. Short-path distillation gave 0.8 g of amine IX, bp 128–131° (10 mm). $H^1$ nmr spectrum showed a multiplet (area 4) at $\tau$ 1.3–2.5 for aromatic –H and a singlet at 7.66 for $NH_2$. The infrared spectrum showed the characteristic $NO_2$ bands and no amide –CO. The mass spectrum showed the parent and expected fragmentation.

*Anal.* Calcd for $C_9H_6N_2O_2F_6$: C, 37.56; H, 2.10; N, 9.72; F, 39.56. Found: C, 37.54; H, 2.36; N, 9.72; F, 39.80.

***m*-Bromo-$\alpha$,$\alpha$-bis(trifluoromethyl)benzylamine (X) and Bis-(trifluoromethyl)benzylamine Hydrobromide (XI).**—A mixture of 24 g of $\alpha$,$\alpha$-bis(trifluoromethyl)benzylamine VI (0.1 mol) and 0.3 g of iron powder was heated at 100° with stirring while 16 g of liquid bromine (0.1 mol) was added in one portion. The reaction mixture was heated at 120° for 1.5 hr and at 100° for 17 hr. Crystals appeared on the thermometer. Filtration and washing with ether gave 4.6 g of a slightly orange solid which was purified by recrystallization from absolute ethanol–ether, mp 170–171°. The ultraviolet spectrum showed aromatic absorption at 266 m$\mu$ ($\epsilon$ 308), 260 (385), 253 (294), 250 (194). The infrared spectrum showed broad absorption suggestive of an amine hydrobromide. $F^{19}$ nmr spectrum was a singlet at +72.2 ppm from $FCCl_3$. $H^1$ nmr showed a multiplet at $\tau$ 2.3 (5 H aromatic) and a singlet at $\tau$ 3.1 (3 H). The solid was, therefore, the hydrobromide XI of the starting amine.

*Anal.* Calcd for $C_9H_8BrF_6N$: C, 33.35; H, 2.50; F, 35.18; Br, 24.66. Found: C, 33.61; H, 2.82; F, 35.20; Br, 24.17.

The filtrate was taken up in ether, washed with 6 *N* HCl, 10% sodium bisulfite solution, brine, and water, and dried over magnesium sulfate. Infrared and gas chromatographic analyses showed mainly starting material; so the residue was recycled with 1.0 g of iron powder and 13 g of bromine. After the mixture was heated for 1 hr at 120° and 17 hr at 80° (no more crystals appeared), the above work-up was repeated. Distillation (spinning band) afforded 7.4 g (23% yield) of *m*-bromo-$\alpha$,$\alpha$-bis(trifluoromethyl)benzylamine (X), bp 56° (1 mm). The mass spectrum showed the parent ions and expected fragmentation. The ultraviolet spectrum was that of a disubstituted benzene with bands at 275 m$\mu$ ($\epsilon$ 380), 268 (480) and 262 (362). The $F^{19}$ nmr spectrum showed a singlet at +74.70 ppm (calibrated in $FCCl_3$). The $H^1$ nmr spectrum showed a complex multiplet at $\tau$ 2.3 (total area 4, but *o*-H at $\tau$ 2.05 distinct) and an $-NH_2$ absorption at 7.98.

*Anal.* Calcd for $C_9H_6BrF_6N$: C, 33.56; H, 1.88; Br, 24.81; F, 35.38; N, 4.35. Found: C, 34.12; H, 2.17; Br, 24.63; F, 35.84; N, 4.12.

**3,5-Dimethyl-4-hydroxy-$\alpha$,$\alpha$-bis(trifluoromethyl)benzylamine by the Quinomethan Route.**—An 8.1-g (0.03 mol) sample of $\alpha$,$\alpha$-bis(trifluoromethyl)-2,6-dimethylquinomethan[5] was dissolved in 50 ml of anhydrous ether (orange color) and treated with ammonia gas for 1 hr at 25° and 0.5 hr at 35° (until color faded to light yellow). Excess ammonia and solvent were evaporated and the colorless solid residue was recrystallized from petroleum ether (40–60°) to give white cubes of 3,5-dimethyl-4-hydroxy-$\alpha$,$\alpha$-bis(trifluoromethyl)benzylamine (8.0 g, 93%), mp 62–63° (74–75° when the melt was allowed to solidify and then remelted).

*Anal.* Calcd for $C_{11}H_{11}F_6NO$: C, 46.00; H, 3.86; F, 39.69; N, 4.88. Found: C, 46.15; H, 3.95; F, 39.27; N, 4.72.

See Table I for spectral details.

**Registry No.**—IIa, 15580-91-3; IIb, 15580-92-4; cyclohexene trisubstituted enamine adduct, 15580-93-5; III, 15580-94-6; cyclopentene tetrasubstituted enamine adduct, 15580-95-7; cyclopentene trisubstituted enamine adduct, 15580-96-8; 2-(hexafluoroisopropylamino)cyclopentanone, 15580-97-9; 4-[1-amino-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]benzoic acid, 15580-98-0; VII, 15580-99-1; VIII, 15581-00-7; IX, 15581-01-8; X, 15581-02-9; XI, 15581-03-0; cyclohexene tetrasubstituted enamine adduct, 15581-06-3.

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# N,N-Difluoroalkylamines by Direct Fluorination of Alkylamines[1]

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Alkylamines were successfully fluorinated in bicarbonate-buffered aqueous solution to give N,N-difluoroalkylamines. In this way were synthesized N,N-difluorocyclohexylamine, N,N,N′,N′-tetrafluorohexamethylenediamine, N,N-difluoro-*n*-butylamine, N,N-difluorocyclopentylamine, and N,N-difluoro-*t*-butylamine. Attempts to convert N,N-dichloroalkylamines into N,N-difluoroalkylamines by metathetical reactions failed. An unusual method of oxidizing primary amines to nitriles was found. Chlorination of alkylamines to N,N-dichloramines followed by cesium fluoride dehydrochlorination gives the corresponding nitrile in high yield.

In 1961 Grakauskas[3] reported the elegant aqueous fluorination of urea to give N,N-difluorourea. Subsequently additional examples of aqueous fluorination were reported[3,4] which gave amide-type N,N-difluoro compounds. In our laboratories in 1959–1961 our goal was to synthesize N,N-difluoroalkylamines by direct fluorination of alkylamines. We succeeded by a procedure similar to that of Grakauskas but included an essential bicarbonate buffer. In this paper we report our successful and unsuccessful attempts to synthesize N,N-difluoroalkylamines.

The first N,N-difluoroalkylamine was synthesized by Frazer[5] who allowed both methyl and ethyl iodides to react with tetrafluorohydrazine in a light-initiated

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[1] Abstracts, the Fourth International Symposium on Fluorine Chemistry, Estes Park, Colo., July 24–28, 1967, p 72.

[2] Department of Chemistry, San Diego State College, San Diego, Calif. 92115.

[3] V. Grakauskas, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 23M; also British Patent 960,126 (June 1964); *Chem. Abstr.*, **61**, 5523*b* (1964).

[4] R. E. Banks, R. N. Haszeldine, and J. P. Lalu, *Chem. Ind.* (London), 1803 (1964); *J. Chem. Soc. Sect. C*, 1514 (1966).

[5] J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

gas phase reaction to give N,N-difluoromethyl- and difluoroethylamines.

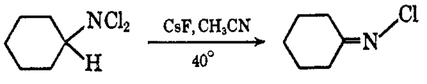
Petry and Freeman[6] synthesized difluoramines by reaction of tetrafluorohydrazine with azo compounds or with hexaphenylethane. Alkylation of carbonium ions with difluoramine ($HNF_2$) was reported by Graham and Freeman[7] to give N,N-difluoramines. Synthesis of bis(difluoramino) compounds by addition of tetrafluorohydrazine to unsaturated aliphatic and aromatic compounds has been reported by several authors.[8-14] Of the methods reported only the thermal addition of tetrafluorohydrazine to alkenes is really a useful method for preparing large quantities of difluoramino compounds. However, two difluoramino groups are introduced rather than just one. Further, the thermal addition reaction is *extremely hazardous;* tetrafluorohydrazine must be handled with great skill and caution. The method of synthesis which we report here is a direct fluorination of amines in which only one difluoramino group need be introduced and then only at the position of the original amino group. The reaction has the further advantage that it may be carried out safely on a convenient synthetic scale.

## Results and Discussion

Our initial attempts to synthesize N,N-difluoroalkylamines were by metathetical reactions on N,N-dichloroalkylamines. Standard fluorinating agents were used such as cesium fluoride, potassium fluoride, silver(I) fluoride, antimony(III) fluoride, and sulfur tetrafluoride. In no case was an N,N-difluoroalkylamine obtained. However, some interesting results were obtained.

Reaction of silver(I) fluoride with N,N-dichloro-*t*-butylamine in refluxing acetonitrile gave isobutylene in greater than 80% yield. Reaction of sulfur tetrafluoride with N,N-dichloro-*t*-butylamine gave an hydrolytically unstable product which appeared to be *t*-butyliminosulfur difluoride on the basis of comparison of its infrared spectrum with infrared spectra of authentic iminosulfur difluorides. Cesium fluoride in refluxing acetonitrile very cleanly dehydrohalogenated amines with $\alpha$ hydrogens in over 90% yields.

$$CH_3CH_2CH_2CH_2NCl_2 \xrightarrow[40^\circ]{CsF,\ CH_3CN} CH_3CH_2CH_2C{\equiv}N$$

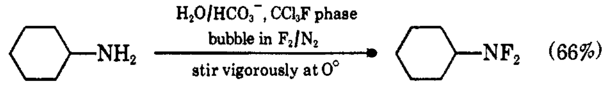


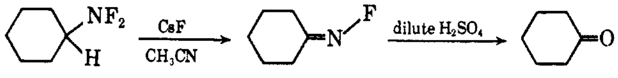
This finding provides a very unique and clean way of oxidizing amines under very mild conditions. The initial hypochlorite chlorination of amines to N,N-dichloramines is extremely mild and essentially a quantitative reaction when the procedure of Jackson, Smart, and Wright is followed.[15] The dehydrohalogenation occurs under such mild conditions that other functional groups in the molecule will be unaffected.

The discouraging results obtained in the attempted metathetical reactions prompted a change in the course of the investigation. The synthesis of N,N-dichloroamines for initial work was by aqueous chlorination in bicarbonate solution.[15] Although not expected

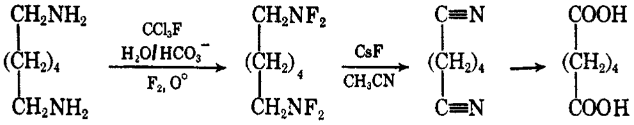
$$RNH_2 \xrightarrow[0^\circ]{HCO_3^-/H_2O,\ Cl_2} RNCl_2$$

to succeed, it was decided to fluorinate cyclohexylamine under the conditions used for forming N,N-dichloramines. In the first attempt about a 1% yield of a mixture of N,N-difluorocyclohexylamine and cyclohexanone was obtained from Dry Ice traps. The conditions of the reaction were modified to include an equal volume of inert trichlorofluoromethane as a second phase to extract product as fast as formed. Under these conditions N,N-difluorocyclohexylamine was obtained in 66% yield. The structure was proved by dehydrofluorination to N-fluorocyclohexylimine and then hydrolysis to cyclohexanone. The infrared and nmr spectral properties of N,N-difluorocyclohexylamine are given in Table I and are consistent with the structure assigned. Comparisons with the spectral properties of other N,N-difluoroalkylamines are made in Table I.





Aqueous fluorination of diamines can also be carried out. From hexamethylenediamine was obtained N,N,N′,N′-tetrafluorohexamethylenediamine in 25% yield. The infrared spectra and nmr spectra of the bisdifluoramine were consistent with the structure assigned. Chemical proof of structure was obtained by a stepwise conversion into adipic acid.



$$CH_2NH_2(CH_2)_4CH_2NH_2 \xrightarrow[F_2,\ 0^\circ]{CCl_3F,\ H_2O/HCO_3^-} CH_2NF_2(CH_2)_4CH_2NF_2 \xrightarrow[CH_3CN]{CsF} N{\equiv}C(CH_2)_4C{\equiv}N \longrightarrow HOOC(CH_2)_4COOH$$

Using bicarbonate-buffered aqueous fluorination, cyclopentylamine, *n*-butylamine, and *t*-butylamine were converted into their corresponding N,N-difluoramines. The crude N,N-difluorocyclopentylamine contained mainly nitrocyclopentane and cyclopentanone as side-reaction products. The primary side-reaction products with N,N-difluoro-*n*-butylamine were butyronitrile and butyraldehyde. Side-reaction products predominated in the fluorination of *t*-butylamine and the yield of the corresponding difluoramine was low. Pertinent absorptions in the infrared and nmr spectra of the preceding difluoramines are summarized in Table I.

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[6] R. C. Petry and J. P. Freeman, *J. Amer. Chem. Soc.*, **83**, 3912 (1961).

[7] W. H. Graham and J. P. Freeman, *ibid.*, **89**, 716 (1967).

[8] A. L. Logathetis and G. N. Sausen, *J. Org. Chem.*, **31**, 3689 (1966).

[9] T. E. Stevens, *ibid.*, **32**, 670 (1967).

[10] F. A. Johnson, C. Haney, and T. E. Stevens, *ibid.*, **32**, 466 (1967).

[11] T. S. Cantrell, *ibid.*, **32**, 911 (1967).

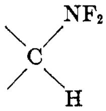
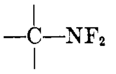
[12] T. E. Stevens and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 182 (1967).

[13] R. C. Petry, C. O. Parker, F. A. Johnson, and T. E. Stevens, *J. Org. Chem.*, **32**, 1534 (1967).

[14] R. C. Petry, C. O. Parker, F. A. Johnson, T. E. Stevens, and J. P. Freeman, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, *O201.*

[15] L. L. Jackson, G. N. R. Smart, and G. F. Wright, *J. Amer. Chem. Soc.*, **69**, 1539 (1947).

TABLE I
NMR AND INFRARED SPECTRAL DATA ON N,N-DIFLUOROALKYLAMINES

| | Nmr spectra | | | Ir spectra, |
|---|---|---|---|---|
| Difluoramine, $RNF_2$ | Group | F[a] | H[b] | absorptions, 10–12-μ region[c] |
| Cyclohexyl |  | Doublet, −2318 cps<br>($J_{HF}$ = 25 cps) | Triplet, 202 cps<br>($J_{HF}$ = 25 cps) | 10.1 (w), 10.4 (s), 10.7 (w), 10.9 (w), 11.45 (w), 11.89 (vs), 12.12 (m) |
| Bishexamethylene | $-CH_2NF_2$ | Triplet, −3122 cps<br>($J_{HF}$ = 30 cps) | Triplet, 207 cps<br>($J_{HF}$ = 30 cps) | 10.4 (w), 10.6 (w), 11.20 (s), 12 00 (vs), broad shoulders at 12.20, 12.50 |
| *n*-Butyl | $-CH_2NF_2$ | Broad poorly resolved triplet, −3080 cps | Triplet, 198 cps<br>($J_{HF}$ = 28 cps) | 10.2 (w), 10.85 (s), 11.45 (m), 11.85 (s), 12.50 (w) |
| *t*-Butyl |  $-C-NF_2$ | Singlet, −1530 cps | | 9.6 (s), 10.5 (vs), 11.2 (vs) |
| Cyclopentyl | | | | 9.85 (m), 10.67 (m), 11.45 (s) |

[a] F spectra at 56.4 Mc/sec relative to $CCl_3F$. [b] H spectra at 60.0 Mc/sec reported as positive values downfield from tetramethylsilane. [c] Wavelengths in μ. The N–F characteristic absorptions are in the 10–12-μ region.

The aqueous fluorination of amines was best achieved at a constant buffered pH near 7.5. No difluoramines were formed below pH 5.5 or above 9. Aromatic amines are insoluble in bicarbonate solution. At pH values low enough to bring aromatic amines into solution only azo-coupling products were obtained. The most probable fluorinating specie is hypofluorous acid formed initially from reaction of fluorine and water ($F_2 + H_2O = [HOF] + HF$). No evidence is available to rule out hydrated molecular fluorine as an intermediate ($F_2 \cdot (H_2O)_x$). The presence of an equilibrium amount of free amine is probably important. A detailed study of the reaction of fluorine with water and with carefully buffered aqueous solutions seems highly desirable and will be carried out in the future.

## Experimental Section

All melting points are corrected. Spectra were obtained with a Perkin-Elmer Model 21 and a Varian HR-56.4/60.0. Fluorine nmr spectra were recorded at 56.4 Mc/sec and are reported in cycles per second (cps) relative to the F absorption of trichlorofluoromethane. Proton nmr spectra were recorded at 60.0 Mc/sec and are reported in cycles per second (cps) relative to tetramethylsilane.

**N,N-Difluorocyclohexylamine.**—To an ice-cooled 2-l. flask equipped with a thermometer, Dry Ice condenser, high speed stirrer, and a gas sparger was added 1200 ml of water, 200 g (2.38 mol) of sodium bicarbonate, 70.0 g (0.707 mol) of cyclohexylamine, and 200 ml of trichlorofluoromethane. The mixture was stirred with great vigor to achieve intimate mixing (very important) until an internal temperature of less than 2° was observed. A fluorine–nitrogen stream (100 cc of $F_2$/min, 200 cc of $N_2$/min) was bubbled through the mixture for 5.5 hr. Nitrogen (200 cc/min) was bubbled through for 0.5 hr and 200 ml of $CH_2Cl_2$ was then added. The organic phase was separated and reduced in volume to 100 ml by distillation. The $CH_2Cl_2$ was washed successively with two 20-ml portions of cold concentrated $H_2SO_4$, three 100-ml portions of water, 100 ml of 5% $HCO_3^-$ solution, and finally with 100 ml of water. After drying over $MgSO_4$, the $CH_2Cl_2$ solution was distilled under reduced pressure through a 25-cm Vigreaux column. N,N-difluorocyclohexylamine was collected over the boiling point range 69–81° (80–90 mm), $n^{25}D$ 1.4058.

*Anal.* Calcd for $C_6H_{11}NF_2$: C, 53.32; H, 8.20; N, 10.36. Found: C, 52.12; H, 8.26; N, 11.14.

The original aqueous phase was made basic with sodium hydroxide and extracted continuously with diethyl ether. From the ether extract was recovered 52 g of unreacted cyclohexylamine. The yield of N,N-difluorocyclohexylamine was 66% based on cyclohexylamine and 23% based on fluorine.

The sulfuric acid washes were neutralized with sodium hydroxide and extracted continuously with $CH_2Cl_2$. From the $CH_2Cl_2$ extract was obtained 1.0 g of cyclohexanone.

The structure of N,N-difluorocyclohexylamine was proved by treating 2.0 g with 10.0 g of cesium fluoride in 25 ml of dry $CH_3CN$ at 40° for 48 hr. Solids were separated and the solution distilled. About 1.5 g of the product N-fluorocyclohexylimine was obtained by distillation under reduced pressure, bp ~60° (80 mm). The fluorine nmr spectrum at 56.4 Mc/sec had a single absorption at −935 cps from $CCl_3F$.

*Anal.* Calcd for $C_6H_{10}NF$: F, 12.7. Found: F, 12.3.

The sample of N-fluorocyclohexylimine was heated under reflux with 10 ml of 2 *M* $H_2SO_4$. Cyclohexanone was steam distilled and identified by its infrared spectrum and formation of a 2,4-dinitrophenylhydrazone, mp 160–161°.

**N,N,N′,N′-Tetrafluorohexamethylenediamine.**—A slurry prepared from 23.2 g (0.200 mol) of hexamethylene diamine, 66 g (0.80 mol) of sodium bicarbonate, 600 ml of water, and 200 ml of trichlorofluoromethane was fluorinated in a manner similar to that just described. Following a similar work-up 6.0 g (23% based on recovered starting material) of N,N,N′,N′-tetrafluorohexamethylenediamine was obtained, bp 70–75° (0.1 mm).

*Anal.* Calcd for $C_6H_{12}N_2F_4$: C, 38.29; H, 6.43; N, 14.89; F, 40.39. Found: C, 37.04; H, 6.58; N, 15.46; F, 39.6.

The structure of N,N,N′,N′-tetrafluorohexamethylenediamine was proved by a series of steps to convert it into dimethyl adipate. Purified 1,6-bis(difluoroamino)hexane (2.0 g) was heated in $CH_3CN$ with 20 g of CsF under gentle reflux. Solid was filtered and solvent stripped off under reduced pressure to give a dark brown oil whose spectrum contained all the bands corresponding to adiponitrile plus extra bands from impurities. The impure adiponitrile was hydrolyzed with a solution containing 10 ml of 85% $H_3PO$, 4 ml of concentrated $H_2SO_4$ and 1 ml of water. After work-up 1.0 g of crude adipic acid, mp 149.3–150.8° (lit.[16] mp 153°) was obtained whose infrared spectrum was identical with that of authentic material. The adipic acid was converted by diazomethane into dimethyl adipate which had an identical gas chromatographic retention time and identical infrared spectrum with those of authentic dimethyl adipate.

**Other N,N-Difluoroalkylamines.**—The method for synthesis of N,N-difluorocyclohexylamine was used to synthesize the *n*-butyl, *t*-butyl, and cyclopentyl analogs. Structure of N,N-difluoro-*n*-butylamine was proved by dehydrofluorination to butyronitrile. Structure of N,N-difluorocyclopentylamine was proved by dehydrofluorination followed by hydrolysis to cyclopentanone. The structure of N,N-difluoro-*t*-butylamine was inferred from spectral data.

**N,N-Dichlorocyclohexylamine.**—The title compound was prepared by the method of Jackson, Smart, and Wright[15] with consistent yields of over 90%. The product was characterized by an intense absorption in its infrared spectrum at 14.45 μ.

**N-Chlorocyclohexylimine.**—A mixture of 10.0 g (0.0599 mol) of N,N-dichlorocyclohexylamine, 20.0 g (0.132 mol) of cesium fluoride and 100 ml of acetonitrile was stirred and heated at 45° for 48 hr. The reaction mixture was cooled to room temperature and filtered. The filtrate was subjected to sufficiently reduced pressure to distil off $CH_3CN$ and the pressure was then reduced to 1 mm. N-Chlorocyclohexylimine distilled at 60° and amounted to 7.1 g (90%). On one occasion, rapid and violent decomposition occurred during distillation. Rudner[17] has previously reported that decomposition of N-chlorocyclohexylimine occurs at 90°.

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(16) Handbook of Chemistry and Physics, 45th ed, The Chemical Rubber Co., Cleveland, Ohio, p C-358.

(17) B. Rudner, U. S. Patent 2,894,028 (1956).

Extreme caution must be exercised in distilling N-chlorocyclohexylimine.

The infrared spectrum of a film of N-chlorocyclohexylimine has absorption bands ($\mu$) and relative intensities (absorbancies) as follows: 3.44 (vs), 5.78 (w), 6.20 (m), 6.91 (vs), 7.00 (s), 7.45 (m), 7.65 (m), 8.03 (m), 8.30 (m), 8.89 (m), 9.13 (w), 9.25 (w), 9.86 (w), 10.19 (s), 10.95 (w), 11.10 (w), 11.69 (m), 11.90 (w), 13.10 (m), and ~14.9 $\mu$ (s) cut-off of spectrum. Shoulders are not reported.

**Oxidation of *n*-Butylamine to Butyronitrile.**—The procedure of Jackson, Smart, and Wright[15] was used to synthesize N,N-dichlorobutylamine in greater than 90% yield. The dichloroamine was dehydrochlorinated and worked up in a manner similar to the procedure described for N-chlorocyclohexylimine. Butyronitrile was obtained in greater than 90% yield and identified by its infrared spectrum and by its identical gas chromatographic retention time with that of authentic butyronitrile.

**Registry No.**—N,N-Difluorocyclohexylamine, 14182-78-6; N-fluorocyclohexylimine, 15645-66-6; N,N,N′,N′-tetrafluorohexamethylenediamine, 15645-67-7; N,N-difluoro-*n*-butylamine, 10524-16-0; N,N-difluoro-*t*-butylamine, 646-55-9; N,N-difluorocyclopentylamine, 14182-80-0; N-chlorocyclohexylimine, 6681-70-5.

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# The Trichloromethylation Reaction. III. Reaction with Benzoic Anhydride and Participation by the Solvent 1,2-Dimethoxyethane[1]

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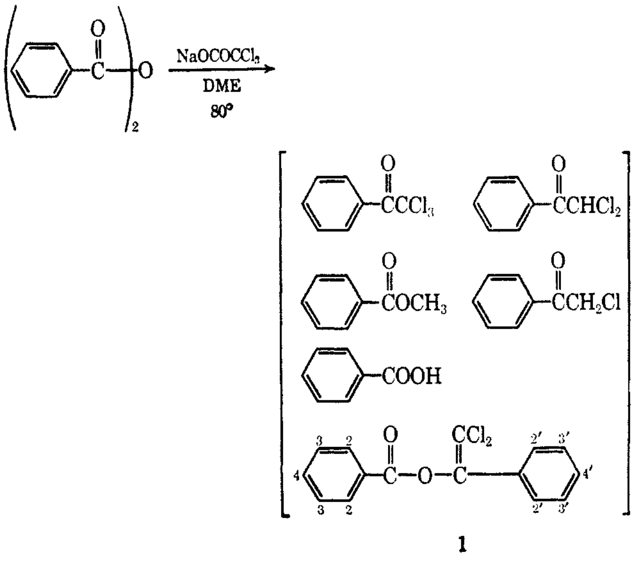
Reaction of sodium trichloroacetate with benzoic anhydride in dimethoxyethane (DME) solution yields $C_6H_5COOC(=CCl_2)C_6H_5$ (**1**, 79%), benzoic acid, some methyl benzoate, and minor amounts of $\alpha,\alpha,\alpha$-trichloro-, $\alpha,\alpha$-dichloro-, and $\alpha$-chloroacetophenone. A similar reaction with $p,p'$-dichlorobenzoic anhydride gives the corresponding $p,p'$-dichloro analog (**2**) of **1**, methyl *p*-chlorobenzoate, and the *p*-chloro analogs of the other minor components. The reaction of sodium trichloroacetate with $\alpha,\alpha,\alpha$-trichloroacetophenone and $p,p'$-dichlorobenzoic anhydride in DME produces $p\text{-}ClC_6H_4COOC(=CCl_2)C_6H_5$ (**3**). The proposed mechanism for the formation of **1**, **2**, and **3** involves the abstraction of chlorine from $\alpha,\alpha,\alpha$-trichloroacetophenone, initially produced by a normal trichloromethylation reaction, followed by a condensation of the enolate anion with the parent anhydride. The methyl benzoate originates from the DME solvent. Reaction of sodium trichloroacetate, $\alpha,\alpha,\alpha$-trichloroacetophenone, and DME also gives methyl benzoate. Reaction of DME with various bases produces formaldehyde and ethylene. These results are accounted for by a mechanism involving the abstraction of a proton from the methyl group of DME and a resulting decomposition of the DME. The methoxide ion produced in the decomposition then attacks the trichloroacetophenone to give methyl benzoate.

Sodium trichloroacetate has been shown to be a useful reagent for the trichloromethylation of anhydrides.[2,3] The success of this reaction is greatly dependent upon the nature of the anhydride and the reactivity of the resulting product. High yields (70–90%) of trichloromethylation products are obtained in several instances, but in others the yields are moderate to very low. One factor which definitely affects the yield is the ease by which the primary trichloromethylation product reacts with sodium trichloroacetate to provide additional reaction products. In the case of succinic anhydride, the initially formed 5,5,5-trichlorolevulinic acid reacts further with the trichloromethyl anion to give dichloroprotoanemonin, apparently by $\alpha$-proton abstraction followed by cyclization and elimination of hydrogen chloride.[4] The reaction of sodium trichloroacetate with benzoic anhydride, which was previously reported to give a 13% yield of $\alpha,\alpha,\alpha$-trichloroacetophenone,[2] has now been found to be another case in which further reactions of the product occur. In this paper a detailed account of this reaction will be presented along with studies which have provided reasonable mechanisms to account for most of the observed products. An unusual participation by the solvent, dimethoxyethane, is included.

The reaction of sodium trichloroacetate with benzoic anhydride in dimethoxyethane (DME) solution results in a complex mixture of products (Scheme I). After removal of the benzoic acid, the residue was separated by distillation into three fractions. The low boiling fraction was fairly pure methyl benzoate. The second fraction was a mixture of $\alpha,\alpha,\alpha$-trichloro-, $\alpha,\alpha$-dichloro-, and $\alpha$-chloroacetophenone in 1.4, 2.8, and 1.0% yield, respectively, as determined by vpc analysis. The

SCHEME I



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[1] Taken in part from the M. S. Thesis of R. E. Thomas, West Virginia University, Morgantown, W. Va., 1967, and the M. S. Thesis of D. E. Battin, Kanawha Valley Graduate Center of West Virginia University, Morgantown, W. Va., 1965. Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, and at the 42nd Annual Meeting of the West Virginia Academy of Science, Morgantown, West Virginia, April, 1967.

[2] A. Winston, J. P. M. Bederka, W. G. Isner, P. C. Juliano, and J. C. Sharp, *J. Org. Chem.*, **30**, 2784 (1965).

[3] A. Winston, J. C. Sharp, K. E. Atkins, and D. E. Battin, *ibid.*, **32**, 2166 (1967).

[4] A. Winston and J. C. Sharp, *J. Amer. Chem. Soc.*, **88**, 4196 (1966).