TABLE I

N,N-DIBENZYL-N'-ARALKYL-N'-SUBSTITUTED ETHYLENEDIAMINES $RN(CH_2R')CH_2CH_2N(CH_2C_6H_5)_2$

R^a	R	B.p.,		Yield,	$n^{25}D$	Nitrogen, %		
		°C.	Mm.	%		Formula	Calcd.	Found
C_5H_4N	C_6H_5	200–204	0.05	95	1.6082	$C_{28}H_{29}N_3$	10.33	10.47
C_5H_4N	$C_6H_5(OCH_3)(4)^b$	234–236	.10	76	1.6059	$C_{29}H_{31}N_3O$	9.60	9.55
C_5H_4N	$C_6H_4Cl(4)^c$	212–213	.08	78	1.6118	$C_{28}H_{28}ClN_3$	9.51	9.45
$C_4H_3N_2$	$C_6H_4(OCH_3)(4)$	210–212	.01	27	1.6021	$C_{28}H_{30}N_4O$	12.77	12.79
$C_{10}H_8N$	$C_6H_5Cl(4)$	164–165.5^d		83		$C_{33}H_{32}ClN_3\cdot 2HCl$	7.26	7.15
C_3H_2NS	C_6H_5	216–219	0.05	68	1.6100	$C_{26}H_{27}N_3S$	10.16	9.93

[a] C_5H_4N, $C_4H_3N_2$, $C_{10}H_8N$, C_3H_2NS are 2-pyridyl, 2-pyrimidyl, 2-lepidyl and 2-thiazolyl, respectively. [b] The picrate melted at 119.5–120° after two recrystallizations from methanol. Calcd. for $C_{29}H_{31}N_3O\cdot 2C_6H_3N_3O_7$: N, 12.61. Found: N, 12.20. [c] The picrate, recrystallized twice from methanol, melted at 149–150°. *Anal.* Calcd. for $C_{28}H_{28}ClN_3\cdot 2C_6H_3N_3O_7$: N, 14.01. Found: N, 13.80. [d] Melting point of dihydrochloride after three recrystallizations from isopropyl alcohol.

ability to retard the growth of sarcoma 180 in mice.[5b]

Experimental[7]

Intermediates.—2-Dibenzylaminoethyl chloride hydrochloride, prepared in 85% yield by the procedure of Gump and Nikawitz,[3] melted at 187–189° after one recrystallization from isopropyl alcohol. Although this is below the reported melting point (194–195°), the product gave a satisfactory analysis (Calcd. for $C_{16}H_{19}Cl_2N$: Cl, 23.94. Found: Cl, 24.00) and was used successfully in the condensation reactions. The 2-(benzyl, *p*-methoxybenzyl and *p*-chlorobenzyl) - aminopyridines,[8] 2 - (*p* - methoxybenzyl)-aminopyrimidine,[8] 2-(*p*-chlorobenzyl)-aminolepidine[9] and 2-benzylaminothiazole[10] were described in other publications.

Benzohydryl Ether of 2-Dibenzylaminoethanol.—A mixture of 24.7 g. (0.1 mole) of the benzohydryl ether of ethylenechlorohydrin[11] and 39.4 g. (0.2 mole) of dibenzylamine was heated at a bath temperature of 150–155° for 36 hours. Ether was added to the cooled melt and the dibenzylamine hydrochloride was removed by filtration and washed well with ether. To the filtrate was added ethereal hydrogen chloride to maximum precipitation. The crude salt was separated by filtration and washed with ether. After air-drying, it weighed 31.2 g. (71%) and melted at 185–187°. After two recrystallizations from acetone, the melting point remained constant at 186–187°.

Anal. Calcd. for $C_{29}H_{29}NO\cdot HCl$: N, 3.16; Cl, 7.99. Found: N, 3.10; Cl, 7.78.

N,N-Dibenzyl-N'-aralkyl-N'-(2-pyridyl, 2-Pyrimidyl, 2-Lepidyl and 2-Thiazolyl)-ethylenediamines.—A mixture of 0.05 mole of the secondary amine, 17.8 g. (0.06 mole) of 2-dibenzylaminoethyl chloride hydrochloride, 3.1 g. (0.12 mole) of 90% lithium amide and 100 ml. of benzene (previously dried over calcium hydride) was refluxed for 24 hours. The reaction mixture was filtered while still hot and the insoluble material washed well with benzene. After removing the solvent from the filtrate, the oil which remained was distilled *in vacuo*.

In the condensation with 2-(*p*-methoxybenzyl)-aminopyrimidine by this method, about one-half of the reactants were recovered and a non-distillable substance obtained. Modifying the procedure by adding the 2-dibenzylaminoethyl chloride hydrochloride to a mixture of lithium amide, the 2-pyrimidylamine and benzene, which had been refluxed for 24 hours, and refluxing for an additional 24 hours, gave the desired product in low yield.

N,N-Dibenzyl-N'-(*p*-chlorobenzyl)-N'-(2-lepidyl)-ethylenediamine was isolated and purified as its water-insoluble hydrochloride. The remaining products failed to form crystalline salts other than picrates, which were prepared from two of the bases. Results are summarized in Table I.

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(7) Melting points are corrected; boiling points are not.

(8) I. A. Kaye and I. C. Kogon, *Rec. trav. chim.*, in press.

(9) I. A. Kaye, THIS JOURNAL, **71**, 2322 (1949).

(10) I. A. Kaye and C. L. Parris, *ibid.*, in press.

(11) I. A. Kaye, *ibid.*, **73**, 5468 (1951).

A Convenient Method for Fluorinating Certain Chlorocarbons with Antimony Trifluoride

BY H. DEAN MALLORY

A number of methods are available for fluorinating chlorocarbons through the use of anhydrous hydrogen fluoride or elementary fluorine at some stage in the process; however, the amount of equipment necessary to handle these compounds is sometimes prohibitive in the small laboratory. The process described in this note requires no special apparatus, and when applicable is capable of yielding high purity fluorocarbons. It was developed specifically for the preparation of methylfluoroform[1] from methylchloroform although it is well adapted to the preparation of difluorodichloromethane from carbon tetrachloride, or difluorochloromethane from chloroform. Large scale production of the latter two compounds has been reported[2] by Booth and Bixby using the same starting materials as used here although the procedures differ. This process is applicable if the final product is: (a) gaseous at room temperature or slightly above and (b) the most highly fluorinated compound obtainable with antimony trifluoride. The final product will contain on the order of 95% of the highest fluoride. An exception is noted with ethylidene fluoride; it is easily formed from CH_3CHCl_2 but is then quickly decomposed to tar by the fluorinating mixture and the yields approach zero after three seconds contact. This process will give 25% yields[3] of CH_3CHF_2 if the reaction gases are collected after the first stage but no CH_3CHClF was ever isolated. Whalley[4] has obtained 40% yields of the monofluoride with a HF–$SnCl_4$ process.

Experimental Details

The apparatus is shown in Fig. 1 and consists of a flask with a separatory funnel for adding antimony pentachloride, a water jacketed glass column reactor, sodium hydroxide scrubber, drying tube and a Dry Ice–acetone trap. The initial reaction between chlorocarbon and SbF_3 catalyzed by a few drops of $SbCl_5$, occurs in the flask containing the calculated amount of reactants. The gas products from this stage consist of materials boiling near room temperature but which are incompletely reacted; the amount of ultimate product present may be 30% or less. Flow of gas from the flask to the column reactor is controlled by adding $SbCl_5$

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(1) Reported in the author's Ph.D. thesis, The State University of Iowa, Iowa City, Iowa, February, 1950.

(2) A. S. Booth and E. May Bixby, *Ind. Eng. Chem.*, **24**, 637 (1932).

(3) About that reported for a similar process by Albert L. Henne and Mary W. Renoll, THIS JOURNAL, **58**, 889 (1936).

(4) Wm. B. Whalley (to Imperial Chemical Industries, Ltd.), U. S. Patent 2,452,975, Nov. 2, 1948.

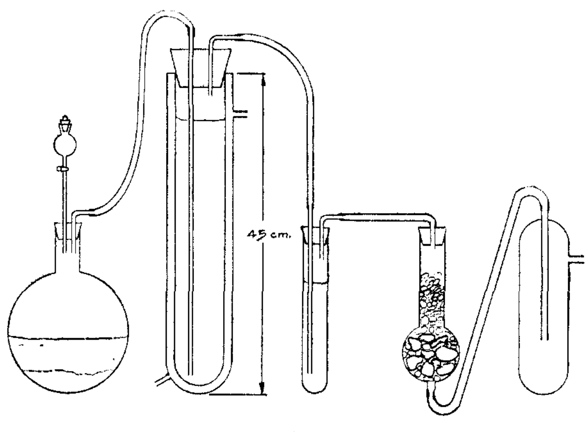

Fig. 1.—Fluorinating system.

dropwise from the separatory funnel until reaction begins, then cooling the flask in ice water as needed. Gas products enter the column and pass up through the fluorinating mixture composed of SbF_3 and $SbCl_5$ in the ratio of about 60 g. to 200 ml., respectively. A large excess of $SbCl_5$ is necessary to keep the mixture fluid and may be recovered after the reaction. Transit time for a gas bubble is from 2 to 4 seconds depending on the temperature and consequent fluidity of the mixture. A freshly prepared fluorinating mixture requires a column temperature between 25 and 35° for efficient reaction; at these temperatures much solid material is present which may clog the gas inlet. After a few ml. of product have been condensed in the cold trap, the operating temperature may be raised to 45°, where no solids are present, without impairing efficiency. If the reaction is begun at the higher temperature, especially with CH_3CCl_3, much of it is decomposed. Progress of the reaction may be easily followed by bleeding off a small amount of the gas and measuring its density with a gas density balance.[5]

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(5) J. D. Edwards, Technological Paper No. 89, U. S. Bureau of Standards.

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Synthesis of Nitriles in Ethylene Glycol[1]

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Low-boiling nitriles cannot be made from alkyl halides and sodium cyanine in aqueous alcohol because of the difficulty of isolating the products from the solvent. However, other solvents which dissolve appreciable amounts of sodium cyanide can be used. Thus, ethylene glycol has been used in the preparation of 5-hexenonitrile from 5-bromo-1-pentene,[2] and its monoalkyl ethers, as well as tetrahydrofurfuryl alcohol, have been used in the preparation of succinonitrile and adiponitrile.[3]

There are relatively few examples in the literature of the formation of secondary cyanides by displacement reactions, and none at all of tertiary cyanides. Low yields in these reactions are commonly attributed to olefin formation,[4] but there have been no quantitative studies to bear this out.

Several of the solvents tried were found to be quite unsatisfactory. *n*-Butyl bromide was largely unchanged after a 40-hour reflux with sodium cyanide in *n*-butyl cellosolve or nitrobenzene. *t*-Butyl chloride in *t*-butyl alcohol gave a high yield of isobutylene. *t*-Butyl bromide in hydrogen cyanide gave a little olefin along with unidentifiable material, although the sodium cyanide dissolved in the hydrogen cyanide to the extent of 0.54 g. per 100 cc. *t*-Butyl bromide in cold saturated aqueous sodium cyanide gave only a black tar.

Ethylene glycol proved to be a much more suitable solvent, even though it is not miscible with the alkyl halides. Table I shows the results of experiments with several primary, secondary and tertiary halides. In all runs there is some loss in the form of undistillable black residues. Other than this, the main side-reaction is the formation of glycol monoalkyl ethers (solvolysis); olefins are a relatively minor product.

The reactions with the primary halides were particularly gratifying. Valeronitrile, for instance, was prepared in 90% yield after one hour of reflux, and was readily separated from the reaction mixture by distillation. The best yield reported in aqueous alcohol after 25–30 hours of reflux and a careful, 10-hour distillation is 80%.[5] Butyronitrile has been made in aqueous alcohol, but not isolated.[6]

TABLE I

REACTION OF ALKYL HALIDES WITH SODIUM CYANIDE

Alkyl halide	Initial temp., °C.	Reaction time, hr.	Yield, % Nitrile	Ether	Olefin
n-BuBr	101	1	90		
n-PrBr	72	1	92		
i-PrBr	60	24	39		
i-PrBr[a]	60	15	39	16	7
s-BuBr[a]	92	4	28	Low	
s-BuCl	68	22	No reaction		
t-BuBr[a]	73	3[b]	Low	44	
t-BuCl	50	6	Low	41	
t-BuCl[a]	46	6	10[c]	27	18

[a] Sulfuric acid added. [b] Reaction seemed to be complete in one hour. [c] Impurities may reduce this to about 5%.

TABLE II

IDENTIFICATION OF PRODUCTS

Compound	Property	Observed	Reported	Reference
n-BuCN	B.p.	138–142°	140.75°	*a*
n-PrCN	B.p.	116–119°	117.28°	*a*
i-PrCN	B.p.	103–104°	103.7°	*a*
	$n^{20}D$	1.3728	1.37348	*a*
s-BuCN	B.p.	124–126°	125.4°	*a*
	$n^{30}D$	1.3857	1.38562	*a*
t-BuCN	B.p.	100–107°	103.5°[b]	*b*
	$n^{20}D$	1.3809	1.3792	*b*
i-PrOR[c]	B.p.	142.5–143°	144°	*d*
t-BuOR[c]	B.p.	153–154°	153°	*e*

[a] J. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Company, Inc., New York, N. Y., 1950, pp. 531–541. [b] Boiling point at 738 mm., F. C. Whitmore, C. I. Noll and V. C. Meunier, THIS JOURNAL, **61**, 683 (1939). [c] R = $—CH_2CH_2OH$. [d] L. H. Cretcher and W. H. Pittenger, THIS JOURNAL, **46**, 1503 (1924). [e] T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, **28**, 1186 (1936).

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(1) From the M.S. thesis of Peter V. Susi, September, 1951.

(2) F. B. LaForge, N. Green and W. A. Gersdorff, THIS JOURNAL, **70**, 3707 (1948).

(3) A. O. Rogers, U. S. Patent 2,415,261, Feb. 4. 1947.

(4) D. T. Mowry, *Chem. Revs.*, **42**, 189 (1948).

(5) R. Adams and C. S. Marvel, THIS JOURNAL, **42**, 310 (1920).

(6) K. W. Rosenmund, K. Luxat and W. Tiedemann, *Ber.*, **56**, 1950 (1923).