neutral oxalate by adding a solution of 1 g. anhydrous oxalic acid in 10 cc. absolute alcohol. Yield 1.65 g. (93%). It was recrystallized from 80% alcohol and had a m.p. 201–202°.

Anal. Calcd. for $C_{10}H_{24}O_8N_2$: C, 40.0; H, 8.0; N, 9.3. Found: C, 39.9; H, 8.1; N, 9.3.

DL-*Threoninol.* Three and one half g. of raw *N*-benzylthreonine was debenzylated as above and converted into the neutral oxalate. Yield 2.55 g. (94%). After recrystallization from 80% alcohol, it had m.p. 211.5° (dec.).

Anal. Calcd. for $C_{10}H_{24}O_8N_2$: C, 40.0; H, 8.0; N, 9.3. Found: C, 40.0; H, 7.6; N, 9.3.

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C=N Stretching Frequency in Infrared Spectra of Aromatic Azomethines

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In conjunction with a study of the stereochemistry of aromatic Schiff-bases, 17 compounds of this type have been synthesized by standard techniques[1] and their infrared spectra determined. Each compound was found to exhibit an absorption band of medium intensity in the double-bond stretching region at 1613–1631 cm.$^{-1}$, as shown in Table I. This band, which occurs in the spectra just to the high frequency side of the normal aromatic band near 1600 cm.$^{-1}$, appears to be of considerable diagnostic value.

TABLE I

C=N STRETCHING FREQUENCIES IN AROMATIC SCHIFF BASES. (Measurements made on Beckman IR-3 spectrophotometer, NaCl optics.)

Compound	Frequency (cm^{-1})[a]
N-benzylidineaniline*	1631
N-(2-hydroxy)benzylidineaniline*	1622
N-(4-hydroxy)benzylidineaniline	1629[b]
N-(4-methoxy)benzylidineaniline*	1630
N-(2-nitro)benzylidineaniline	1621[b]
N-(4-acetylamino)benzylidineaniline	1629[b]
N-(4-dimethylamino)benzylidineaniline*	1626
N-benzylidine-2-aminophenol	1629
N-benzylidine-2-anisidine	1631[c]
N-(4-methoxy)benzylidine-2-anisidine	1627[c]
N-benzylidine-4-anisidine*	1629
N-(4-methoxy)benzylidine-4-anisidine	1626[b]
N-benzylidine-4-toluidine	1628[c]
N-benzylidine-*N*′-dimethyl-4-phenylenediamine*	1627
N-(2-hydroxy)benzylidine-2-aminophenol	1624[b]
N-(4-dimethylamino)benzylidine-2-aminophenol	1613
N,*N*′-dibenzylidine-4-phenylenediamine	1628

[a] in CCl_4 solution; [b] in $CHCl_3$ solution; [c] as KBr pellets; * indicates the compounds reduced using $NaBH_4$.

The absorption frequency characteristic of the stretching mode of the C=N group in compounds of this type has not been known with any degree of certainty.[2] Therefore, in order to ascertain whether the absorption band in this region was attributable to the C=N group, it was necessary to compare the infrared spectra of the Schiff-bases with those of similar compounds that do not contain this grouping. Consequently, six of the azomethines listed in Table I were reduced to the corresponding substituted *N*-benzylanilines by means of sodium borohydride, using a modification of the procedure of Chaikin and Brown.[3] Since this band is absent in the infrared spectra of these amines, this indicates that the absorption bands shown by *N*-benzylidine aniline and its ring-substituted derivatives are indeed due to the stretching mode of the C=N group.

It is also worth noting that the sodium borohydride reduction of aromatic azomethines usually proceeds very smoothly and results in fair yields (60–80% of theoretical). Consequently this reaction may find application in the synthesis of secondary amines of this type.

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(1) Cf. G. Smets and A. Delvaux, *Bull. soc. chim. Belg.*, **56**, 106 (1947).

(2) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y. (1954), pp. 226–229.

(3) S. W. Chaikin and W. G. Brown, *J. Am. Chem. Soc.* **71**, 122 (1949).

Chloroalkyl and Chloroaryl Chloromethylphosphonates

RICHARD L. MCCONNELL, MARVIN A. MCCALL, AND H. W. COOVER, JR.

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In 1950, Kabachnik and Medved reported the preparation of chloromethylphosphonic dichloride by the reaction of paraformaldehyde with phosphorus trichloride.[1] We have prepared and characterized several chlorinated esters from this acid chloride.

In order to prevent alkyl halide formation when an alcohol reacts with a phosphonic chloride, it is generally necessary to use a tertiary amine to absorb the liberated hydrogen chloride. We found, however, that 2-chloroethanol and 2,2,2-trichloroethanol could be successfully treated with chloromethylphosphonic dichloride at reflux tempera-

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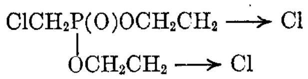
(1) M. I. Kabachnik and T. Ya. Medved, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim Nauk*, 635 (1950); [*Chem. Abstr.*, **45**, 8444 (1951)].

tures without using a tertiary amine. No alkylene halide was formed.

$$ClCH_2P(O)Cl_2 + 2HOCH_2CH_2Cl \longrightarrow ClCH_2P(O)(OCH_2CH_2Cl)_2 + 2HCl$$

The fact that no dealkylation was observed in this reaction can probably be explained by the inductive effect of the chlorine atoms present in the alcohol portion of the molecule. These chlorine

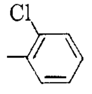
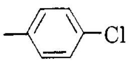
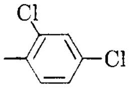


$$\begin{array}{l} ClCH_2P(O)OCH_2CH_2 \longrightarrow Cl \\ \quad\quad\;\; | \\ \quad\quad\;\; OCH_2CH_2 \longrightarrow Cl \end{array}$$

atoms would tend to withdraw electrons from the oxygen atom and thus decrease its electronegative nature. This effect would decrease the possibility of an electrophilic attack by the hydrogen chloride on the oxygen atom with resulting dealkylation of the phosphonate.

TABLE I

CHLOROMETHYLPHOSPHONATES, $ClCH_2P(O)(OR)_2$

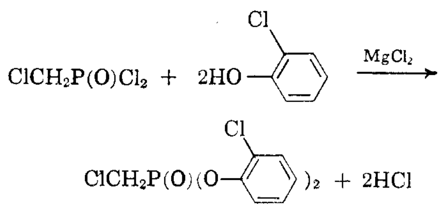
	Boiling Point					Analyses					
						Carbon		Hydrogen		Phosphorus	
R	Temp., °C.	Pressure, mm.	M.P., °C.	n_D^{20}	Yield, %	Calcd.	Found	Calcd.	Found	Calcd.	Found
$—CH_2CH_2Cl$	161–165	3.2	..	1.4869	65.5	23.50	23.63	3.95	4.11	12.13	12.40
$—CH_2CCl_3$	177–181	4.5	49–51	1.5102[a]	59	15.27	15.78	1.54	1.65	7.88	8.33
	214–216	3.0	..	1.5752	87.5	44.41	44.72	2.87	3.03	8.81	9.05
	214–216	2.5	48–51	1.5741[a]	96	44.41	44.10	2.87	3.03	8.81	8.71
	244–245	3.8	..	1.5898	72	37.13	37.06	1.92	2.07	7.37	7.50

[a] Determined on distillates, which did not crystallize for several days.

Our observation is in complete agreement with that of Gerrard and associates, who reported that 2,2,2-trichloroethanol and 2,2,2-trichloro-1,1-dimethylethanol react with phosphorus trichloride in the absence of a tertiary amine without dealkylation.[2]

Unlike most alcohols, 2,2,2-trichloroethanol did not react with chloromethylphosphonic dichloride at 25°C. This reaction proceeded readily, however, at slightly higher temperatures when catalyzed by anhydrous magnesium chloride.

We also prepared some chloromethylphosphonates from chlorinated phenols. Although a catalyst was not required for preparing these aromatic esters, use of a small amount of anhydrous magnesium chloride was beneficial. This catalyst was used by Caprio and Shuman to prepare phosphates from chlorinated phenols.[3]



The chloromethylphosphonates are insoluble in water but soluble in the common organic solvents. The chloromethylphosphonates derived from 2,2,2-trichloroethanol and *p*-chlorophenol are white, crystalline solids. The other chloromethylphosphonates are clear, colorless oils.

The physical properties, yields, and analyses of products are given in Table I.

EXPERIMENTAL

Chloromethylphosphonic Dichloride.[1] A mixture of paraformaldehyde (200 g., 6.67 moles) and phosphorus trichloride (1320 g., 9.6 moles) was heated at 250° in a stainless steel autoclave for 5 hr. The crude reaction product was a light brown liquid. This material was distilled at atmospheric pressure until the head temperature reached 90°. Then the remainder was distilled under reduced pressure through a short Claisen column, and 470 g. of product was collected at 63–65° (3 mm.), n_D^{20} 1.4972. This fraction was redistilled to yield 393 g. (35%) of chloromethylphosphonic dichloride, b.p. 59° (2 mm.), n_D^{20} 1.4981 (n_D^{20} reported[1] 1.4983).

Bis(2,2,2-trichloroethyl) chloromethylphosphonate. A mixture of chloromethylphosphonic dichloride (16.8 g., 0.1 mole), 2,2,2-trichloroethanol (30.0 g., 0.2 mole), and anhydrous magnesium chloride (0.1 g.) was refluxed gently until hydrogen chloride was no longer evolved (8–10 hr.). The dark, oily reaction mixture was then distilled at reduced pressure through a short Claisen column.

Bis(2-chloroethyl) chloromethylphosphonate. 2-Chloroethanol (16.1 g., 0.2 mole) was added dropwise to chloromethylphosphonic dichloride (16.8 g., 0.1 mole) while the reaction mixture was stirred. Hydrogen chloride was evolved rapidly. After the initial exothermic reaction had subsided, the reaction mixture was refluxed gently for 6 hr. The product was isolated by distillation of the mixture at reduced pressure through a short Claisen column.

Bis(chloroaryl) chloromethylphosphonates. A mixture of chloromethylphosphonic dichloride (16.8 g., 0.1 mole) and

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(2) W. Gerrard, W. J. Green, and R. J. Phillips, *J. Chem. Soc.*, 1148 (1954).

(3) A. F. Caprio and R. L. Shuman (to Celanese Corp. of America), U. S. Patent 2,561,493 (1951).

the appropriate chlorinated phenol (0.2 mole) was refluxed for 8 hr. The reaction mixture was then cooled to 25° and slowly reheated to reflux under reduced pressure (10–15 mm.) for 4 hr. to remove the last traces of hydrogen chloride and thus complete the reaction. The product was purified by distillation at reduced pressure through a short Claisen column.

Addition of about 0.1 g. of anhydrous magnesium chloride catalyzed the reaction of the chlorinated phenols and facilitated the removal of the hydrogen chloride.

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Organometallic Reactions of ω-Fluoroalkyl Halides. III.[1] ω-Fluoroalkyllithium Compounds

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In earlier reports[2,3] in this series have been described the preparation and reactions of ω-fluoroalkylmagnesium halides.[4] The present communication deals with a very brief examination of the corresponding ω-fluoroalkyllithium compounds. From a comparison of the yields obtained with the two metals, it seems reasonable to conclude that, with the one possible exception noted below, lithium is probably less effective than magnesium in syntheses involving organometallic derivatives of ω-fluoroalkyl halides.

The ω-fluoroalkyllithium compounds were prepared by standard procedures[5,6] and in the equipment previously described.[2] Petroleum ether[7] and ethyl ether[5,6] were examined as solvents; the latter appeared to be more satisfactory. Successful reactions included the following:

$$\mathrm{F(CH_2)_6Br} \xrightarrow[\mathrm{C_6H_5CN}]{\mathrm{Li}} \mathrm{F(CH_2)_6COC_6H_5} \quad (47\%)$$

$$\mathrm{F(CH_2)_9Cl} \xrightarrow[\mathrm{C_6H_5CN}]{\mathrm{Li}} \mathrm{F(CH_2)_9COC_6H_5} \quad (43\%)$$

$$\mathrm{F(CH_2)_{10}Cl} \xrightarrow[\mathrm{(CH_2)_2O}]{\mathrm{Li}} \mathrm{F(CH_2)_{12}OH} \quad (24\%)$$

There was no evidence of disubstitution products formed by replacement of both the fluorine and the halogen atoms; nor was there any sign of preferential replacement of fluorine, such as occurred when ω-fluoroalkyl bromides and iodides were treated with magnesium.[2] Nevertheless, it was apparent that considerable disruption of the ω-fluoroalkyl halides had occurred, since unreacted starting materials were seldom recovered.

The observation that preferential replacement of fluorine did not occur suggests the possible advantage of using lithium in place of magnesium in those instances in which the higher ω-fluoroalkyl bromides are more readily available than the corresponding ω-fluoroalkyl chlorides.

Under the same conditions, the lower ω-fluoroalkyl halides failed to give any of the expected products. Members examined included 3-fluoropropyl bromide, 4-fluorobutyl chloride, 4-fluorobutyl bromide, 5-fluoroamyl chloride, and 5-fluoroamyl bromide.

EXPERIMENTAL[8]

6-Fluorohexyl phenyl ketone. In the main reaction vessel,[2] cooled to −10° in a dry ice–acetone bath,[6] were placed lithium[9] (1.4 g., 0.20 g. atom) and anhydrous ethyl ether (25 ml.). Approximately 10 ml. of a solution of 6-fluorohexyl bromide (13.0 g., 0.071 mole) in ethyl ether (50 ml.) were added with stirring. There was evidence of a reaction almost immediately. The remainder of the fluorobromide solution was added dropwise over 1 hr. at a temperature of −10° or less. When the addition was complete, the mixture was stirred for 3 hr., while warming to 15°. The resultant organolithium solution was filtered under nitrogen pressure into the dropping funnel of the subsidiary vessel,[2] and was added (over 15 min.) at room temperature with stirring to a solution of benzonitrile (7.4 g., 0.072 mole) in ethyl ether (50 ml.). A vigorous reaction took place, and the color changed to orange. The mixture was gently refluxed for 1 hr. after the addition, and then allowed to stand overnight in an atmosphere of nitrogen. The mixture was cooled and hydrolyzed by the gradual addition of excess 10% sulfuric acid. The ether was removed on a water bath, and the residue was heated for a further 30 min. to ensure hydrolysis of the ketimine salt. The mixture was cooled and extracted with ether. The extracts were washed successively with water, 10% sodium carbonate, and water, and dried over magnesium sulfate. After removal of the ether, the residue on fractionation yielded 6-fluorohexyl phenyl ketone (6.9 g., 47%), b.p. 171–172° (13 mm.), 103° (0.15 mm.), m.p. 27–28° (corr.).

Anal. Calcd. for $C_{13}H_{17}FO$: C, 74.99; H, 8.17. Found: C, 75.02; H, 8.18.

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(1) Issued as DRB Report No. SW-34.

(2) F. L. M. Pattison and W. C. Howell, Part I, *J. Org. Chem.*, **21**, 879 (1956).

(3) W. C. Howell, W. J. Cott, and F. L. M. Pattison, Part II, *J. Org. Chem.*, **22**, 255 (1957).

(4) To avoid ambiguity, fluorine is not generally referred to as halogen in this communication.

(5) H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933).

(6) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

(7) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(8) The microanalyses were performed by Mr. J. F. Alicino, Metuchen, N. J. and by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(9) The lithium was obtained from the Lithium Corp. of America, Inc., Minneapolis, 2, Minn., in the form of 5 mm. ribbon, covered with a protective coating of vaseline. It was found that the average weight of a 10 cm. length of ribbon was 0.19 g. When the apparatus had been assembled, the appropriate length of ribbon was measured off and wiped as free as possible from vaseline. This length was then cut with scissors into small pieces (*ca.* 2–3 mm.) and transferred rapidly to the reaction vessel. All subsequent operations were conducted in an atmosphere of nitrogen. The lithium particles were washed with dry petroleum ether to remove the last traces of vaseline, and the washings were removed by filtration through the filter disc. The flask and lithium particles were then washed thoroughly with several portions of anhydrous ethyl ether, and the washings removed. The metal was then considered ready for reaction.