

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Fluorination of Methoxydichlorophosphine¹BY DONALD RAY MARTIN AND PHILIP J. PIZZOLATO²

The application of the Swarts reaction to the fluorination of inorganic halides is well known. Only in recent years have there been any attempts to evaluate the effect upon the fluorination reaction of the substitution of organic radicals for halogen atoms. Booth, *et al.*, have fluorinated some alkyl chlorosilanes³ and Emeléus and Heal⁴ have studied the effect of fluorination upon the properties of the organic derivatives of the halides of sulfur, selenium and tellurium. Alkoxy derivatives of phosphorus(V) sulfochloride have been synthesized by Booth, Martin and Kendall.⁵ It was decided to study the fluorination of an alkoxy halide of phosphorus(III) in order to extend the knowledge obtained in the studies mentioned above, and to compare the results with those obtained in the fluorination of phosphorus(III) halides.

Experimental

Preparation and Purification of Methoxydichlorophosphine.—Methoxydichlorophosphine was prepared by a modification of the procedure used by Kowalewski.⁶ One mole of anhydrous methanol was added dropwise to one mole of phosphorus(III) chloride with vigorous stirring at a reaction temperature well below 0°. The methanol was added at a rate of 35 ml. per hour. The reactor was a three-necked flask fitted with a stirrer, drying tube containing barium oxide, and a dropping funnel. Upon the completion of the addition of the methanol, the reaction products were allowed to rise slowly to room temperature to facilitate in the evolution of the dissolved hydrogen chloride. The remaining mixture of reaction products was fractionally distilled twice at atmospheric pressure. The second fractionation was conducted in a fractionating column packed with glass helices (1/8 in. i. d.). The purified methoxydichlorophosphine was obtained in a yield of about 60%.

Fluorination of Methoxydichlorophosphine.—The method and apparatus used for the stepwise fluorination by means of the Swarts reaction was the same as previously described,⁵ except that no catalyst was required. The temperature of the fluorination was maintained below 10° and, for the best yields of the chlorofluoride and the difluoride, the pressure within the generator was maintained below 50 mm. Apparently little or none of the chlorofluoride is produced when the pressure within the generator exceeds 80 mm. Below 25 mm. there appears to be no appreciable increase in the yield with diminution in pressure; this fact may be due to the increased tendency for the dichloride to volatilize along with the products of the fluorination. Typical experiments gave the yields shown.

Pressure, mm.	CH ₃ OPClF	Yields, %	CH ₃ OPF ₂
25-50	8		41
80-160	0		28

The products of fluorination were fractionally distilled in a modified Dufton column as previously described by Martin and Faust,⁷ except that in the electronic circuit for operating the controls of the column a Radio Corporation of America vacuum tube (OA4G) was employed instead of the General Electric thyratron tube (G57).

Methoxychlorofluorophosphine and methoxydifluorophosphine were purified by redistillation in the above-mentioned column under the conditions shown

	CH ₃ OPClF	CH ₃ OPF ₂
Pressure within the column, mm.	85	740
Temperature of head of column, °C.	-13.0	-16.5

Analyses.—The samples were collected and weighed in sealed glass ampoules of approximately 1 ml. capacity. These samples were hydrolyzed in 125 ml. of a solution containing sodium hydroxide in slight excess over the quantity required for complete hydrolysis. The concentration of caustic was maintained as low as possible as a precaution against obtaining silica in the solution, which would interfere with the analysis for phosphorus. The chlorofluoride and difluoride were hydrolyzed instantaneously, whereas the dichloride sample required as long as twenty minutes.

Chlorine was determined by the Volhard procedure, the necessary precautions being exercised to prevent the phosphite from reducing the silver(I) ion.⁸ Phosphorus was determined gravimetrically as magnesium pyrophosphate after oxidation of the phosphite to phosphate by means of bromine and nitric acid, followed by a double precipitation as magnesium ammonium phosphate. Carbon and hydrogen were determined by means of the standard methods of microanalysis.⁹ Some difficulty was experienced in the determination of carbon in methoxydifluorophosphine. However, separate analyses for the methoxy group checked very well with each other and with the theoretical value. The methoxy analysis was conducted on 2.5-3.0 g. samples. These were hydrolyzed and the methanol fractionally distilled into a tared receiver.^{8,10} From the weight and density (*d*₂₀²⁰) of the distillate the percentage of methoxy group was calculated.¹¹ Qualitative tests established the presence of fluorine in the chlorofluoride and the difluoride. A summary of the analyses is contained in Table I.

Determination of the Physical Constants (see Table I).

—Methoxydichlorophosphine and its chlorofluoride and difluoride derivatives are all colorless gases which condense to colorless liquids. Upon freezing, the dichloride and difluoride are transformed to white solids, but the chlorofluoride forms a transparent glass. The freezing points were obtained by the procedure described by Booth and Martin.¹²

The vapor pressures were determined by the static method of Booth, Elsey and Burchfield,¹³ and the neces-

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society on April 17, 1950, at Detroit, Michigan.

(2) The Solvay Process Company, Hopewell, Virginia.

(3) H. S. Booth and P. H. Carnell, *THIS JOURNAL*, **68**, 2650-2652 (1946), *et seq.*

(4) H. J. Emeléus and H. G. Heal, *J. Chem. Soc.*, 1126-1131 (1946).

(5) H. S. Booth, D. R. Martin and F. E. Kendall, *THIS JOURNAL*, **70**, 2523-2525 (1948).

(6) W. A. Kowalewski, *J. Russ. Phys.-Chem. Soc.*, **29**, 217-222 (1897).

(7) D. R. Martin and J. P. Faust, *J. Phys. Coll. Chem.*, **53**, 1255-1262 (1949).

(8) H. S. Booth and A. R. Bozarth, *THIS JOURNAL*, **61**, 2927-2931 (1939).

(9) Clark Microanalytical Laboratory, Urbana, Illinois.

(10) O. v. Lupin, *Z. anal. Chem.*, **97**, 210-220 (1934).

(11) W. Dittmar and C. A. Fawsitt, *Trans. Roy. Soc. Edinburgh*, **33**, 509-534 (1887).

(12) H. S. Booth and D. R. Martin, *THIS JOURNAL*, **64**, 2198-2205 (1942).

(13) H. S. Booth, H. M. Elsey and P. E. Burchfield, *ibid.*, **57**, 2064-2065 (1935).

sary temperature corrections have been applied. The values for the boiling points, heats of vaporization and Trouton's constants were calculated from the equations representing the straight lines obtained when the vapor pressure data were plotted as $\log p$ vs. $1/T$. The vapor densities were determined by the Regnault procedure.

Aside from the hydrolytic reactions requisite to analyses, no chemical properties of these compounds were studied. It was observed, however, that the materials, when dry, did not attack glass. The dichloride slowly attacked mercury upon standing, and all of the compounds exerted some solvent action upon Lubriscal stopcock grease.

TABLE I

	CH ₃ -OPCl ₂	CH ₃ -OPClF	CH ₃ OPF ₂
Boiling point, °C.	93.0	38.9	-15.5
Heat of vaporization, g. cal./mole	8295	7077	5722
Trouton's constant	22.7	22.7	22.2
Vapor pressure constants ^a { A	7.8300	7.8362	7.7335
B	1812.6	1546.5	1250.5
Liquid density, d ₄ ⁰	1.406	1.318
Freezing point, ±0.4°	-91.0	Glass ^b	-117.3
Molecular weight { Calculated	132.93	116.47	100.01
Found	115.2	100.6
Carbon, % { Calculated	9.03	10.31	12.01
Found	9.03	10.14	11.04
Hydrogen, % { Calculated	2.27	2.60	3.02
Found	2.33	2.73	2.98
Phosphorus, % { Calculated	23.31	26.60	30.98
Found	23.20	26.82	31.3
Chlorine, % { Calculated	53.35	30.44
Found	53.24	30.24
Methoxy, % { Calculated	31.05
Found	30.9

^a Constants in the equation: $\log p_{(\text{mm.})} = A - B/T$.

^b Glass forms at some temperature below -79°.

Discussion

The boiling point of the methoxydichlorophosphine prepared in this investigation was observed to be 93.0°, as compared with a value of 94° reported many years ago by Kowalewski.⁵ Although the replacement of a chlorine atom in phosphorus(III) chloride by a methoxy radical lowers the molecular weight very slightly, the boiling point of the methoxy derivative is slightly higher. Other related properties such as the heat of vaporization and Trouton constant are changed correspondingly and indicate a trend toward the values for methanol, as shown below:

Compound	B. p., °K.	Heat of vapn., cal./mole	Trouton's constant
PCl ₃	349.2	7060	20.2
CH ₃ OPCl ₂	366.2	8295	22.7
CH ₃ OH	337.8	8420	24.9

Stepwise replacement of the chlorine atoms by fluorine atoms in phosphorus(III) chloride results in the lowering of the boiling points of the resulting compounds by the increments shown below. The methoxy derivatives exhibit the same trend, but with more nearly constant increments.

	B ₂ p., °C.	Increment		B ₂ p., °C.	Increment
PCl ₃	76.0		CH ₃ OPCl ₂	93.0	
PCl ₂ F	13.9	62.1	CH ₃ OPClF	38.9	54.1
PClF ₂	-47.3	61.2	CH ₃ OPF ₂	-15.5	54.4
PF ₃	-101.2	53.9			

Although Emeléus and Heal⁴ observed that the displacement of halogen atoms by fluorine reduced the thermal stability of alkyl and phenyl derivatives of sulfur, selenium and tellurium halides, no evidence was obtained in this investigation in support of this trend. Earlier work with phosphorus(V) ethoxysulfodichloride and the chlorofluoride and difluoride derivatives thereof indicated that thermal stability increased with fluorine content.⁵

Emeléus and Heal⁴ also observed that thermal stability increased with the number of alkyl or aryl radicals introduced into a compound in place of halogen atoms. Dimethoxychlorophosphine was not prepared in this investigation, but earlier work on the derivatives of the reaction of ethylene chlorohydrin with boron trichloride gave evidence that thermal stability increases with the number of alkoxy groups which replace halogen atoms. Thus, (ClC₂H₄O)₂B is more stable than (ClC₂H₄O)₂-BCl which is more stable than ClC₂H₄OBCl₂.¹⁴

It was observed that the substitution of a methoxy radical for a chlorine atom in phosphorus(III) chloride produced a more reactive molecule. Methoxydichlorophosphine is more easily fluorinated than phosphorus(III) chloride at comparable temperatures. This is demonstrated by the fact that phosphorus(III) chloride requires a catalyst, while methoxydichlorophosphine does not. Similarly, it is observed that a lower temperature is required to fluorinate phosphorus(V) ethoxysulfodichloride than is required to fluorinate phosphorus(V) sulfochloride.¹⁵

The ease of hydrolysis is greater with methoxydifluorophosphine than with methoxydichlorophosphine, as discussed above. This behavior is the opposite of that demonstrated by the halides of the non-metals which contain no organic radicals, but is analogous to the behavior of the phosphorus(V) ethoxysulfodihalides toward hydrolysis, since it was observed that phosphorus(V) ethoxysulfodifluoride is more easily hydrolyzed than phosphorus(V) ethoxysulfodichloride.⁵

Summary

1. Methoxydichlorophosphine has been synthesized by the reaction of methanol with phosphorus(III) chloride (yield about 60%).

2. Methoxydichlorophosphine has been fluorinated by means of the Swarts reaction to give methoxychlorofluorophosphine and methoxydifluorophosphine.

3. The above compounds have been purified and characterized by determination of their molecular weights, percentage compositions, freezing points, vapor pressures, heats of vaporization, boiling points, Trouton's constants and liquid densities.

4. The physical and chemical properties of

(14) D. R. Martin and Leona S. Mako, unpublished laboratory notes.

(15) H. S. Booth and M. Catherine Cassidy, *THIS JOURNAL*, **62**, 2369-2372 (1940).

these compounds have been compared with those of phosphorus(III) chloride, methanol, the chloro-

fluorophosphines, and other similar compounds.

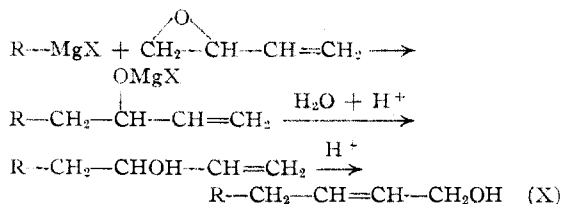
RECEIVED APRIL 7, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation and Properties of Some Thienyl Butenols^{1a}

BY GEORGE T. GMITTER^{1b} AND F. LEE BENTON

When α -thienylmagnesium bromide was allowed to react with butadiene monoxide there was obtained a butenol (I) which was tentatively assumed to be 4-(α -thienyl)-buten-2-ol-1. This assumption was based on the preparation by Semeniuk and Jenkins² of a series of butenols (to which was assigned the general structure of R—CH₂—CH=CH—CH₂OH (X)) by the reaction of various Grignard reagents with butadiene monoxide. They favored the reaction course



as an explanation of the formation of (X) rather than the expected R—CH₂—CHOH—CH=CH₂. They did not exclude however, the possibility of "1,4-addition" of the Grignard reagent to butadiene oxide. Evidence for assigning the general structure (X) to this series of compounds rested solely on the identification, by physical constants of the product obtained from the reaction of methylmagnesium bromide with butadiene monoxide as penten-2-ol-1. The possibility that isomeric products³ might result from the reaction of Grignard reagents with butadiene monoxide made it desirable to confirm the tentative structure assigned to (I). Confirmation was obtained in the following manner.

1-(α -Thienyl)-buten-3-ol-2 (II) and 1-(α -thienyl)-buten-3-ol-1 (III)⁴ were prepared by the reaction of α -thienylsodium with butadiene monoxide

(1a) Abstracted in part from the dissertation presented to the Graduate School of the University of Notre Dame by George T. Gmitter.

(1b) General Tire Research Fellow 1946-1949. Present address: Velsicol Corporation, Chicago, Illinois.

(2) Semeniuk and Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 118 (1948).

(3) Since the completion of our investigation, Gaylord and Becker (*J. Org. Chem.*, **15**, 305 (1950)) have reported the formation of 1-(1-naphthyl)-buten-3-ol-2 when butadiene oxide reacted with 1-naphthylmagnesium bromide. Jenkins and Semeniuk,² on the other hand, report having obtained only 1-(1-naphthyl)-buten-2-ol-4 from the same reaction.

(4) Isobutylene oxide and styrene oxide have been reported by Henry (*Compt. rend.*, **145**, 21 (1907)) and Tiffeneau and Fourneau (*ibid.*, **146**, 697 (1908)) to react as isobutyraldehyde and phenylacetaldehyde, respectively, with Grignard reagents. (III) was synthesized to exclude the possibility that butadiene monoxide had reacted with α -thienylmagnesium bromide in a similar fashion.

and allylmagnesium bromide with 2-thiophene aldehyde respectively. Attempts to synthesize (II) by an alternate route, the reaction of α -thienylmethylmagnesium chloride with acrolein and the Barbier modification⁵ of this method yielded, as the only isolable product,⁶ *sym*-di-(α -thienyl)-ethane.

A comparison of the physical constants of (I) with those of II and III indicated (I) is not identical with either compound, a fact which was further confirmed by the difference in melting points of the corresponding 3,5-dinitrobenzoates. Although the three butenols (I), (II) and (III) underwent cleavage on ozonization⁷ indicating the presence of an olefinic linkage⁸ in their structures, formaldehyde (isolated as a 2,4-dinitrophenylhydrazone) was obtained as an ozonization product only in the case of (II) and (III) but not in the case of (I) a fact indicating that the olefinic linkage in (I) is not terminally located. Failure to obtain acetaldehyde as an ozonization product of (I) was considered to exclude the possibility that (I) possessed the structure Th—CH(OH)—CH=CH—CH₃ which could conceivably result if butadiene monoxide rearranged to crotonaldehyde which then underwent a normal reaction with the Grignard reagent.

Dehydration of (I), (II) and (III) yielded an unsaturated intermediate (IV) which, without further purification⁹ was converted in each case to the same maleic anhydride addition compound (V) according to the Diels-Alder method.¹⁰

If the possibility of migration of a thiophene ring from its original position on the butene chain during dehydration is excluded, then the dehydration product (IV) must be 1-(α -thienyl)-butadiene-1,3, the maleic anhydride addition compound (V), 3-(α -thienyl)- Δ^4 -tetrahydrophthalic anhydride, the carbon skeleton of (I), Th—C—C—C—C—

and the original butenols must differ only in the

(5) Barbier, *Compt. rend.*, **128**, 110 (1899).

(6) Delaby (*Compt. rend.*, **194**, 1248 (1932)) reported that the reaction of benzylmagnesium bromide with acrolein gave only a 6% yield of benzylvinylcarbinol.

(7) Thiophene under identical conditions was not oxidized.

(8) Attempts to establish the presence of an olefinic linkage in compounds (I), (II) and (III) by catalytic hydrogenation were unsuccessful. The compounds failed to add hydrogen.

(9) The tendency for α -thienyl butadienes to polymerize was so pronounced that attempts to purify these compounds by distillation *in vacuo* and at temperatures as low as 40-50° led to their extensive polymerization.

(10) Diels, Alder and Pries, *Ber.*, **62**, 2081 (1929).