frared and mass spectra as well as chromatographic analyses.

Further work in our laboratory has shown that β-methoxysynephrine can be synthesized by dissolving (−)-synephrine in 2 *N* anhydrous HCl in methanol. This procedure, like the one using thionyl chloride, gives the racemic compound. A third method of synthesis resulted in the formation of optically active (−)-β-methoxysynephrine. (−)-Synephrine absorbed on a Dowex 50W (H^+) ion exchange resin in methanol was rapidly converted to (−)-β-methoxysynephrine.

Preliminary experiments indicate that (−)-octopamine is similarly converted to (−)-β-methoxyoctopamine. This method of synthesizing ethers of optically active phenolic amines on ion exchange resins may have application for syntheses of other classes of compounds. Furthermore, the possibility that (−)-methoxysynephrine from the tangerine extract could be an artifact formed on the ion exchange column during isolation cannot be overlooked. The ease with which this reaction occurs must be recognized as a possible source of artifacts in the isolation of compounds from biological materials.

Experimental Section

Racemic β-Methoxysynephrine Hydrochloride.—(−)-Synephrine (1 g) was added slowly to an excess of thionyl chloride (15 g) under nitrogen. Reaction was complete after a few minutes, and the chloro compound which precipitated was filtered and washed first with benzene and then with ether (yield 0.95 g). The chloro compound was refluxed in 10 ml of methanol in a water bath at 60° for 1 hr. The mixture was evaporated to a small volume on a flash evaporator at 30°. Acetone was added and crystals formed on cooling. After two recrystallizations from absolute ethanol and ether, the yield of the hydrochloride was 0.59 g, mp 175–176°.

Anal. Calcd for $C_{10}H_{15}NO_2 \cdot HCl$: C, 55.29; H, 7.37; N, 6.45; OCH_3, 14.29. Found: C, 54.63; H, 7.16; N, 6.72; OCH_3, 14.36.

The mass spectra of the hydrochloride showed major peaks at *m/e* 44, 77, 107, 121, 137, and 181. The compound did not react with potassium periodate which degrades synephrine to *p*-hydrozybenzaldehyde. β-methoxy-synephrine was converted to synephrine after standing overnight in 6 *N* aqueous HCl.

The free base was made by passing the hydrochloride salt in methanol through a Dowex 50 (NH_4^+) resin column and eluting with 2 *N* NH_4OH in methanol. When the eluate was taken to dryness, the free base was found to be very hygroscopic. The hydrochloride and oxalate salts were much more satisfactory for analysis than the free base.

Descending chromatography on No. 1 Whatman paper using tertiary amyl alcohol–methyl amine–water 80:10:10 (v/v) separated a prepared mixture of β-methoxysynephrine (R_f 0.80), synephrine, (R_f 0.53), and octopamine (R_f 0.33). The compounds were detected with diazotized *p*-nitroaniline. β-Methoxysynephrine gave a bluish-pink color that was slow to form, synephrine and octopamine gave pink spots, and *p*-methoxy compounds did not react. Ion exchange chromatography by methods previously described[5] also separated β-methoxysynephrine (eluted in 44 min), synephrine (42 min), and octopamine (39 min).

Racemic β-methoxysynephrine was also prepared as follows. (−)-Synephrine (1 g) was dissolved in 25 ml of 2 *N* anhydrous HCl in methanol and left overnight at 25°. Analysis by ion exchange chromatography showed 99% conversion of synephrine to β-methoxysynephrine.[5] The mixture was neutralized with ammonia and diluted with water to 100 ml. The remaining synephrine was degraded by treating the mixture overnight with potassium periodate (1 g). The mixture was then passed through a Dowex 50 (NH_4^+) resin column and washed with methanol. The ether was eluted with 2 *N* NH_4OH in methanol and taken to dryness in a flash evaporator at 30°. The residue was dissolved in methanol, neutralized with 2 *N* methanolic HCl, clarified with Darco 60 charcoal and then filtered. Absolute ethanol was added and the solvent evaporated. When ethyl ether was added to the concentrated solution, colorless crystals formed. After two crystallizations, the yield was 0.60 g of the hydrochloride salt. The infrared and mass spectra, and chromatographic analysis indicated that this compound was the same as that synthesized with thionyl chloride.

(−)-β-Methoxysynephrine.—(−)-Synephrine (1 g) dissolved in 100 ml of methanol was neutralized with 2 *N* anhydrous HCl in methanol. A Dowex 50 H^+ column 30 mm × 55 mm was prepared by passing methanol through the column to remove water. The synephrine methanol mixture was then passed through the column followed by a methanol wash. Synephrine remained on the column for about 2 hr. The column was then eluted with 2 *N* NH_4OH in methanol. The resin was stirred to help dissipate the heat. The eluate was taken to dryness on a flash evaporator at 30°. Analysis of the eluate indicated 99% conversion to the methyl ether.

The hydrochloride salt was formed and the remaining synephrine removed by the procedure reported above. After recrystallization twice from absolute ethanol and ethyl ether, the yield was 0.62 g of the hydrochloride salt. The infrared spectra and chromatographic analysis indicated the compound was similar to that synthesized from the thionyl chloride and HCl–methanol procedures. However, the compound prepared on the resin column had an optical rotation $[\alpha]^{25}D$ −11.2. It is not certain that this constitutes complete retention of optical activity since the rotation of the optically pure methyl ether is not known.

Registry No.—Racemic β-methoxysynephrine hydrochloride, 15096-17-0; (−)-β-methoxysynephrine, 15096-18-1.

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Reactions of Some Fluorine-Containing Vinyllithium Compounds with Triethylchlorosilane

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We have reported[1] the preparation of trifluoroisopropenyllithium and trifluoropropynyllithium and have studied their reactions with carbonyl compounds and triethylchlorosilane

In an accompanying paper,[2] we described the preparation of a series of fluorine-containing vinyllithium reagents and studied their reactions with carbonyl compounds. Several of these lithium reagents (CF_2=CFLi, CF_2=CClLi, and CFCl=CClLi) were obtained *via* proton-exchange reactions using butyllithium rather than by the more conventional halogen-exchange procedure; *e.g.*

$$CF_2{=}CClH + C_4H_9Li \xrightarrow[-78°]{\text{ether}} CF_2{=}CClLi + C_4H_{10}$$

$$CF_2{=}CClLi \xrightarrow{(CF_3)_2C{=}O} CF_2{=}CClC(OH)(CF_3)_2$$

56%

(1) F. G. Drakesmith, O. J. Stewart, and P. Tarrant, *J. Org. Chem.*, **33**, 280 (1968).

(2) F. G. Drakesmith, R. D. Richardson, O. J. Stewart, and P. Tarrant, *ibid.*, **33**, 286 (1968).

TABLE I

REACTIONS OF FLUORINE-CONTAINING VINYLLITHIUM COMPOUNDS WITH TRIETHYLCHLOROSILANE

Lithium reagent	Products	Yield, %	Bp, °C (mm)	Refractive index	Formula	Anal. Calcd, % C	Calcd, % H	Calcd, % F	Found, % C	Found, % H	Found, % F
CF_2=CFLi	$(CH_3CH_2)_3SiCF$=CF_2 (1)	79	141–143[a]	$n^{24}D$ 1.4052	$C_8H_{15}SiF_3$	48.98	7.65	29.06	49.89	7.48	29.19
CF_2=CClLi	$(CH_3CH_2)_3SiCCl$=CF_2 (2)	10	170	$n^{25}D$ 1.4300	$C_8H_{15}SiClF_2$	45.15	7.05	17.88	44.99	7.10	17.60
	$(CH_3CH_2)_3SiF$ (3)	18									
CF_2=CHLi	Unstable silane		109[b]	$n^{25}D$ 1.3891[b]	$C_6H_{15}SiF$	53.73	11.19	14.18	53.58	10.98	14.42
CH_2=CFLi	$(CH_3CH_2)_3SiC$≡CH (4)	30	138[c]	$n^{23}D$ 1.4325[c]	$C_8H_{16}Si$	68.52	11.42		68.80	11.61	
CFCl=CClLi	$(CH_3CH_2)_3SiCCl$=CClF (5)	55	50 (1.0)	$n^{24}D$ 1.4635[d]	$C_8H_{15}SiCl_2F$	41.92[d]	6.55[d]		41.92[d]	6.50[d]	
				$n^{24}D$ 1.4662[e]		41.92[e]	6.55[e]		41.72[e]	6.57[e]	

[a] D. Seyferth and T. Wada (*Inorg. Chem.*, **1**, 78 (1962)) report bp 35° (9.6 mm), $n^{25}D$ 1.4003. [b] M. G. Voronkov and Yu. I. Skorik (*Izv. Akad. Nauk SSSR., Ser. Khim.*, 1215 (1964); *Chem. Abstr.*, **61**, 12027 (1964)) report bp 110°, $n^{20}D$ 1.3902. [c] L. L. Shchukovskaya and A. D. Petrov (*Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, 1011 (1958); *Chem. Abstr.*, **53**, 1119 (1959)) report bp 138–138.5°, $n^{20}D$ 1.4302. [d] Isomer A. [e] Isomer B.

Attempts to prepare 2,2-difluorovinyl- and 1-fluorovinyllithium by this route were unsuccessful, but these reagents were obtained by treatment of 2,2-difluorovinyl bromide and 1-fluorovinyl bromide, respectively, with butyllithium; *e.g.*

$$CF_2{=}CHBr + C_4H_9Li \xrightarrow[-78°]{\text{ether}} CF_2{=}CHLi + C_4H_9Br$$

We now wish to report the reaction of the above lithium compounds with triethylcholorsilane. The products obtained are shown in Table I.

Treatment of triethylchlorosilane with trifluorovinyllithium gave triethyltrifluorovinylsilane in good yield (79%) (see eq 1). This silane had previously been

$$CF_2{=}CFH + C_4H_9Li \xrightarrow[-100°]{\text{ether}}$$
$$CF_2{=}CFLi \xrightarrow[-78°]{Et_3SiCl} Et_3SiCF{=}CF_2\ (79\%) + LiCl \quad (1)$$
$$+$$
$$C_4H_{10}$$

prepared in lower yield (42%) by treatment of triethylchlorosilane with trifluorovinylmagnesium bromide in tetrahydrofuran. The first trifluorovinylsilane was prepared by Knunyants,[3] who obtained tetrakis(trifluorovinyl)silane as the product of the reaction between trifluorovinylmagnesium iodide and silicon tetrachloride. Seyferth[4] prepared trifluorovinyllithium by reaction of phenyllithium with phenyltrisperfluorovinyltin. He then reacted this lithium reagent with trimethylbromosilane and isolated trifluorovinyltrimethylsilane in low yield (45%). On treatment of trifluorovinyllithium, prepared *via* halogen exchange in trifluorovinylbromide, with trimethylchlorosilane we obtained a better yield of trifluorovinyltrimethylsilane (65%).[5]

Reaction of 1-chloro-2,2-difluorovinyllithium with triethylchlorosilane gave the expected product, triethyl(1-chloro-2,2-difluorovinyl)silane in low yield (10%) along with a larger amount of triethylfluorosilane (18%) (eq 2). The most likely route to triethylfluorosilane involves decomposition of the expected product with the formation of chlorofluoroacetylene as shown in eq 3. However, no acetylenic product was

$$CF_2{=}CClLi + (CH_3CH_2)_3SiCl \longrightarrow$$
$$(CH_3CH_2)_3SiCCl{=}CF_2\ (10\%) + LiCl \quad (2)$$
$$+$$
$$(CH_3CH_2)_3SiF\ (18\%)$$

$$(CH_3CH_2)_3Si{-}CCl{=}C(F)F \longrightarrow (CH_3CH_2)_3SiF + CCl{\equiv}CF \quad (3)$$

isolated from the reaction. Triethylfluorosilane has also been obtained in these laboratories from reaction of trifluoroisopropenyllithium with triethylchlorosilane and a similar decomposition has been proposed[1] (eq 4).

$$CF_3C(Li){=}CH_2 + (CH_3CH_2)_3SiCl \xrightarrow[-78°]{\text{allow to stand in ether at}} CF_2{=}C{=}CH_2 + LiF$$
$$\left[(CH_3CH_2)_3Si{-}C(CH_2){-}CF_2F\right] + LiCl \quad (4)$$
$$\downarrow$$
$$(CH_3CH_2)_3SiF + CH_2{=}C{=}CF_2$$

In this instance, the other product expected from the decomposition (difluoroallene) was isolated but, as can be seen above, this could also have originated from decomposition of trifluoroisopropenyllithium. The reaction of triethylchlorosilane with lithium fluoride did not afford triethylfluorosilane thus eliminating this possible route to the product. The instability of silicon compounds containing a β-halogenated alkyl group is well-known.[6]

Triethyl(2,2-difluorovinyl)silane was not obtained from reaction of 2,2-difluorovinyllithium with triethylchlorosilane. A reaction product decomposed during distillation, but no triethylfluorosilane was isolated.

(3) R. N. Sterlin, I. L. Knunyants, L. N. Pinkina, and R. D. Yatsenko, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, 1492 (1959); *Chem. Abstr.*, **54**, 1270 (1960).

(4) D. Seyferth, D. W. Welch, and G. Raab, *J. Am. Chem. Soc.*, **84**, 4266 (1962).

(5) P. Tarrant and W. H. Oliver, *J. Org. Chem.*, **31**, 1143 (1966).

(6) C. Eaborn, "Organosilicon Compounds," Butterworth and Co., Ltd., London, 1960, p 133.

Reaction of 1-fluorovinyllithium with triethylchlorosilane gave triethylethynylsilane (30%) and not the expected triethyl(1-fluorovinyl)silane. The most likely route to this product involves initial formation of the expected product (eq 5). One of the terminal vinylic

$$(CH_3CH_2)_3SiCl + CH_2{=}CFLi \longrightarrow (CH_3CH_2)_3SiCF{=}CH_2 + LiCl \quad (5)$$

expected product

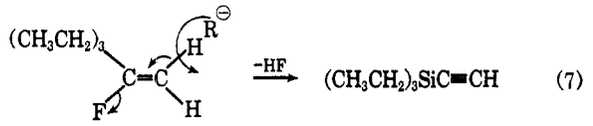
protons in this product is then exchanged as in eq 6

$$(CH_3CH_2)_3SiCF{=}CH_2 + \begin{matrix} C_4H_9Li \\ \text{or} \\ CH_2{=}CFLi \end{matrix} \longrightarrow (CH_3CH_2)_3SiCF{=}CHLi + \begin{matrix} C_4H_{10} \\ \text{or} \\ CH_2{=}CF_2 \end{matrix} \quad (6)$$

$$(CH_3CH_2)_3SiCF{=}CHLi \xrightarrow{-LiF} (CH_3CH_2)_3Si{-}C{\equiv}CH$$

triethylethynylsilane

and subsequent elimination of lithium fluoride then gives triethylethynylsilane. This second step (eq 7) may more accurately be described as a concerted process resulting in the elimination of hydrogen fluoride in the presence of excess base.



(7)

A 1:1 mixture of *cis*- and *trans*-1,2-dichloro-1-fluoroethylene was treated with butyllithium and the resulting 1,2-dichloro-2-fluoro-vinyllithium was allowed to react with triethylchlorosilane. The normal substitution product, triethyl(1,2-dichloro-2-fluorovinyl)silane, was isolated in good yield (55%). No triethylfluorosilane was obtained. The product consisted of two geometric isomers in a ratio of 4:1. A similar isomer distribution was obtained on reaction of 1,2-dichloro-2-fluorovinyllithium with carbonyl compounds.[2]

Experimental Section[7]

The fluorine-containing vinyllithium reagents were prepared in ether as described previously.[2] Triethylchlorosilane (0.05 mole) was slowly added in ether (30 ml) to a cooled (−78°) solution of the lithium reagent in the same solvent (150 ml). The reaction mixture was stirred while it was warmed gradually (over 3 hr) to room temperature. Lithium chloride was normally precipitated between 0° and room temperature. The latter was removed by filtration and the solvent by distillation. The products were further purified by distillation followed by preparative-scale glpc. Physical properties and analyses of the compounds isolated are given in Table I.

Registry No.—Triethylchlorosilane, 994-30-9; **1**, 680-76-2; **2**, 15038-82-1; **3**, 358-43-0; **4**, 1777-03-3; **5**, 14897-57-5.

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(7) Analyses were carried out by Galbraith Laboratories Inc., Knoxville, Tenn.

The Preparation of Some Phenoxaphosphine Derivatives by the Friedel–Crafts and Diazo Reactions[1]

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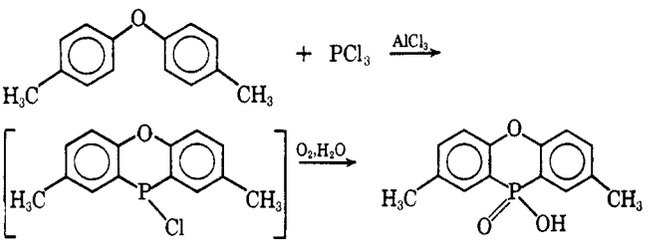
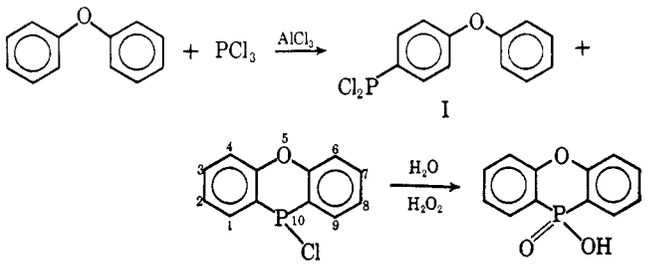
Although 10-chlorophenoxarsine[3] is easily prepared by refluxing phenyl ether with arsenic trichloride and a small quantity of aluminum chloride, the analogous reaction with phosphorus trichloride has been reported to yield only *p*-phenoxyphenyldichlorophosphine[4] (I). It seemed likely to us that some 10-chlorophenoxaphosphine (II) was also produced in this reaction and had been overlooked. Thus, phosphorus trichloride is known[5] to attack the *ortho* positions of *p*-tolyl ether and to give a good yield of a phenoxaphosphine derivative (III). In the present paper we are presenting



III

evidence that 10-chlorophenoxaphosphine (II) is indeed formed in the reaction of phosphorus trichloride with phenyl ether. Thus, phenoxaphosphinic acid (IV)



II IV

has been obtained in 2% yield from phenyl ether and phosphorus trichloride. A large amount of aluminum chloride (178 g/mole of phenyl ether) was employed in this reaction; under these conditions, the *p*-phenoxyphenyldichlorophosphine apparently undergoes further reaction to give undistillable products, while the 10-chlorophenoxaphosphine is relatively unaffected. When intermediate amounts of aluminum chloride were used, a mixture of products (probably *p*-phenoxyphenyldichlorophosphine and 10-chlorophenoxaphosphine) was obtained on distillation of the reaction mixture.

(1) Abstracted from the Ph.D. thesis of Jack B. Levy, North Carolina State University, 1967.

(2) University Chemical Laboratory, Cambridge University, Cambridge, England.

(3) W. L. Lewis, C. D. Lowry, and F. H. Bergeim, *J. Am. Chem. Soc.*, **43**, 891 (1921).

(4) W. C. Davies and C. J. O. R. Morris, *J. Chem. Soc.*, 2880 (1932).

(5) L. D. Freedman, G. O. Doak, and J. R. Edmisten, *J. Org. Chem.*, **26**, 284 (1961).