The ethereal extract was washed with water before drying over Na_2SO_4. The solvent was concentrated under vacuum and the residue was distilled, yielding 3.4 g (100%) of **10**: bp 38–39° (0.2 mm) [lit.[15] bp 51–52° (1.0 mm)]; ir (CCl_4) 3500–3200 (OH) and 1710 cm^{-1} (C=O); nmr ($CDCl_3$) τ −2.36 (s, 1, CO_2H) and 9.16 (s, 6, 2 CH_3).

Preparation of 2,2-Dichloro-1-acetoxy-1-(*o*-chlorophenyl)propane (5).—A stirred solution of **3b** (2.0 g, 0.0084 mol) in glacial acetic acid (100 ml) and concentrated sulfuric acid (5 ml) was heated at 45° for 3 hr. The solution was poured into ice water (800 ml) and extracted with ether. The combined extracts were washed with 10% $NaHCO_3$ and water before drying over Na_2SO_4. Removal of the solvent left a residue which recrystallized from methanol to afford 1.5 g (64%) of **5** as colorless crystals: mp 86–87°; ir (KBr) 1745 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.43 (m, 4, ArH), 3.24 (s, 1, CH), 7.83 (s, 3, CH_3), and 7.85 (s, 3, CH_3); mass spectrum *m/e* 280 (M^+), 245 ($M^+ - 35$), 183 ($M^+ - 97 - Cl_2CCH_3$), and 141 ($M^+ - 139$).

Anal. Calcd for $C_{11}H_{11}Cl_3O_2$: C, 46.92; H, 3.94. Found: C, 47.12; H, 4.19.

Preparation of 2,2-Dichloro-1-tosyloxy-1-(*o*-chlorophenyl)propane (6).—A solution of **3b** (1.2 g, 0.005 mol) and *p*-toluenesulfonyl chloride (1.6 g, 0.008 mol) in pyridine (50 ml) was stirred for 5 days at room temperature. The solution was poured into ice-cold 10% HCl (500 ml) and the product was extracted into ether. The ethereal solution was washed with water and 5% KOH before drying over Na_2SO_4. Removal of the solvent afforded **6** as an oil which crystallized from hexane–petroleum ether (bp 30–60°) as colorless crystals (1.0 g, 68%): mp 88–89°; nmr ($CDCl_3$) τ 2.55 (m, 8, ArH), 3.75 (s, 1, CH), 7.64 (s, 3, CH_3), and 7.83 (s, 3, CH_3); mass spectrum *m/e* 392 (M^+), 295 ($M^+ -$ 97- Cl_2CCH_3), 186 ($M^+ - 106$), 155 ($M^+ - 237$), 115 ($M^+ - 277$), and 91 ($M^+ - 301$).

Registry No.—**3b**, 35996-56-6; **3c**, 37610-56-3; **4**, 37610-57-4; **5**, 37610-58-5; **6**, 37610-59-6; DDD, 72-54-8; DDT, 50-29-3; *o*-chloropropiophenone, 6323-18-8; α,α-dichloro-*o*-chloropropiophenone, 35996-45-3.

Addition of Simple Siloxanes to β-Methallyl Chloride[1]

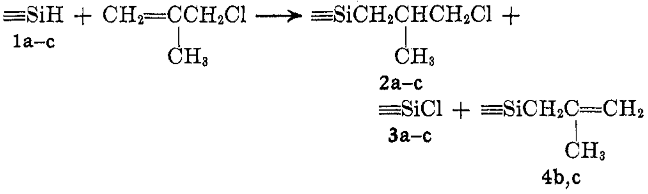
THERESA A. BARRY,[2,3a] FRANKLIN A. DAVIS,*[3a]
AND PETER J. CHIESA[3b]

*Department of Chemistry, Drexel University,
Philadelphia, Pennsylvania 19104, and
National Foam System, Inc., West Chester, Pennsylvania 19380*

Received June 26, 1972

The importance of silicone surfactants prompted this investigation of the catalyzed addition of small siloxane units to β-methallyl chloride. The resulting adducts may serve as intermediates for surfactant synthesis.

Three types of products were observed from the reaction of siloxanes **1a–c** with β-methallyl chloride:



$$\underset{\textbf{1a-c}}{\equiv SiH} + CH_2{=}\underset{CH_3}{\underset{|}{C}}CH_2Cl \longrightarrow \underset{\textbf{2a-c}}{\equiv SiCH_2\underset{CH_3}{\underset{|}{C}H}CH_2Cl} + \underset{\textbf{3a-c}}{\equiv SiCl} + \underset{\textbf{4b,c}}{\equiv SiCH_2\underset{CH_3}{\underset{|}{C}}{=}CH_2}$$

a, $Me_3SiOSiMe_2H$
b, $(Me_3SiO)_2SiMeH$
c, $(Me_3SiO)_3SiH$

adducts (**2a–c**), rearrangement products (**3a–c**), and methallylsiloxanes (**4b,c**).

β-Methallyl chloride, a siloxane, and catalyst were heated at reflux for an appropriate time. Products were identified and yields were determined by comparison with authentic samples using gas chromatography. These results are summarized in Table I.

TABLE I

SILOXANE ADDITION TO β-METHALLYL CHLORIDE

Siloxane	Catalyst	Reaction time, hr	Products (yield, %)
1a	H_2PtCl_6	2	**2a** (97)
1b	H_2PtCl_6	1	**2b** (34), **3b** (18), **4b** (9)
1b	Pt/C	72	**2b** (30), **3b** (18), **4b** (10)
1c	H_2PtCl_6	1.5	**2c** (14), **3c** (42), **4c** (23)
1a	Pd/C	Immediate	**3a** (96)
1b	Pd/C	100	**3b** (74)
1b[a]	$PdCl_2$	Immediate	**3b** (100)
1b	Ru/C	4	**3b** (60)
1c	Pd/C	48	**3c** (24)
1b	None	48	No conversion

[a] Reaction in the absence of β-methallyl chloride.

Structural proof of the adducts, **2a–c**, was based on their ir, nmr, mass spectra, and elemental analysis. The mass spectra of **2a–c** failed to show molecular ions, but did show predominant fragments at *m/e* 73 (Me_3Si^+) and $M - CH_2CH(CH_3)CH_2Cl$. The nmr spectra of **2a–c** are in full accord with the proposed structures and are summarized in Table II.

The structures of the chlorosilanes, **3a–c**, were based upon elemental analysis, mass spectra, nmr, and infrared spectra. The mass spectra of **3a–c** also failed to show molecular ions, but did have fragments at $M - CH_3$ and $M - Cl$. A predominant fragment corresponding to Me_3Si was observed for all the chlorosilanes. The nmr spectra of **3a–c** were similar to those of the corresponding siloxanes **1a–c**, and the infrared spectra of **3a–c** showed the absence of Si–H stretching at 2200 cm^{-1}.[4] Rapid hydrolysis of **3a–c** to the corresponding silanols with evolution of hydrogen chloride further supports the presence of the SiCl bond.

Methallylsiloxanes (**4b,c**) could not be purified by distillation, but were satisfactorily separated by preparative gas chromatography. Elemental analysis, ir, nmr, and mass spectra of these compounds were fully in accord with the proposed structure. Their ir spectra indicated an allylic structure[5] with absorption at 1635 and 1250 cm^{-1}. The nmr spectra are similar to those reported by Egorochkin, *et al.*, for analogous compounds.[6] The mass spectra of **4c** indicated a molecular ion at *m/e* 350 and predominant fragments at NCH_3 and $M - C_4H_7$ and for Me_3Si.

Two additional synthetic routes to siloxanes **2a–c** were explored. First, the reaction of **5**[7] with pyridine, followed by the addition of trimethylsilanol, gave a 20% yield of **2b**. The second route involved the cohydrolysis of **5** with trimethylchlorosilane in water to give a 32% yield of **2b**. The most convenient

---

(1) Reported in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

(2) National Science Foundation Undergraduate Research Participant, 1971.

(3) (a) Chemistry Department, Drexel University; (b) Research Department, National Foam System, Inc.

(4) R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, Chapter 5.

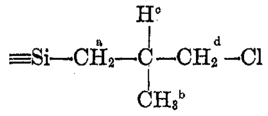
(5) R. J. H. Voorhoeve, "Organohalosilanes: Precursors to Silicones," Elsevier, Amsterdam, 1967, p 372.

(6) A. N. Egorochkin, M. L. Khidekel, G. A. Razuvaev, G. G. Petukhov, and V. F. Mironov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1521 (1964).

(7) J. W. Ryan, G. K. Menzie, and J. L. Speier, *J. Amer. Chem. Soc.*, **82**, 3601 (1960).

TABLE II

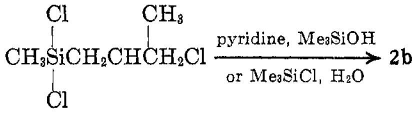
CHEMICAL SHIFTS FOR THE PROTONS IN ADDUCTS **2a–c**



$\equiv Si-\overset{a}{C}H_2-\underset{CH_3^{b}}{\overset{H^{c}}{C}}-CH_2^{d}-Cl$

Siloxane[a]	CH_3Si	$OSi(CH_3)O$	H_a	H_b	H_c	H_d
2a	10.1 (s, 15)		9.6 (q, 2)	9.1 (d, 3)	8.2 (m, 1)	6.8 (q, 2)
2b	10.1 (s, 18)	10.00 (s, 2.5)	9.5 (q, 2)	9.0 (d, 3)	8.1 (m, 1)	6.7 (q, 2)
2c	10.1 (s, 27)		9.6 (q, 2)	9.1 (d, 3)	8.3 (m, 1)	6.7 (q, 2)

[a] Chemical shifts are τ values. Samples were run neat, referenced against benzene as an internal standard.



$CH_3\underset{Cl}{\overset{Cl}{Si}}CH_2\overset{CH_3}{CH}CH_2Cl \xrightarrow[\text{or } Me_3SiCl,\ H_2O]{\text{pyridine, } Me_3SiOH} \mathbf{2b}$

5

method for the preparation of **2b** proved to be the platinum-catalyzed addition of **1b** to β-methallyl chloride to give a greater than 30% yield of **2b** (Table I).

The course of the reactions studied appears to be influenced by both the choice of siloxane and catalyst. Platinum, as chloroplatinic acid or platinum on charcoal, forms adducts **2a–c**, chlorosiloxanes **3b,c**, and methallylsiloxanes **4b,c**. Palladium and ruthenium, on the other hand, generate only chlorosiloxanes (**3a–c**). The formation of alkyl silanes and chlorosilanes from silanes, allyl chlorides, and chloroplatinic acid has been observed by others,[7,8] but to our knowledge this is the first report of the preparation of methallylsiloxanes under these conditions.

These results suggest that two mechanisms are at work, one pathway leading to addition and the other to chlorosiloxanes. The form of catalyst (homogeneous *vs.* heterogeneous) had little effect on reaction products; chloroplatinic acid gave essentially identical results with platinum on charcoal.

It is clear that any mechanism proposed must consider a metal center in its intermediate states. Chalk and Harrod have proposed a mechanism for homogeneous silane additions with chloroplatinic acid.[9] They suggested that platinum(IV) is reduced by the olefin to platinum(II). Platinum(II) complexes with the silane to reform a platinum(IV) structure which decomposes to the alkylsilane. This is then displacement by another olefin. Palladium, however, does not catalyze addition and is rapidly reduced to the metal.

To account for the formation of chlorosilanes from silanes, allyl chloride, and chloroplatinic acid, Ryan and Speier proposed the formation of an intermediate complex of the silane, metal, and olefin.[10] This complex or intermediate could generate either the alkyl silane or chlorosilane. Both these mechanistic schemes, however, fail to explain why platinum catalysts generate chlorosiloxanes in varying proportions along with other products, whereas palladium forms chlorosiloxanes exclusively.

Studies of platinum and palladium organic complexes reveal important structural differences.[11] When treated with mesityl oxide, for example, platinum(II) chloride tends to form localized π-olefin complexes, whereas the corresponding palladium compounds are π-allylic. Allyl and methallyl chloride palladium complexes are also known to be π-allylic.[12–14] In addition, the isomerization of olefins (which accompanies catalytic hydrosilations) occurs readily with palladium, but to a lesser extent with platinum. Both metals are generally acknowledged to accomplish this through π-allyl complex formation.[15] Localized platinum–olefin complexation is consistent with requirements for the accepted hydrosilation mechanism,[9] and leads to addition products. A delocalized π-allylic interaction characteristic of palladium and in some cases platinum apparently fails to generate the adduct. If chlorosiloxanes are produced from a metal–allylic intermediate (or transition state) which accomplishes the necessary isomerization to isobutylene, the experimental results are accounted for. Interaction of palladium with the C–Cl bond may form a transient π-allylic complex and a Pd–Cl bond which reacts with the siloxane to give **3a–c**.

In support of this interpretation, palladium chloride vigorously converted **1b** to **3b** quantitatively. Furthermore, to test the validity of a palladium complex of β-methallyl chloride as an intermediate, bis[isobutenylpalladium(II) chloride][16] was treated with **1b** to give an instantaneous, quantitative conversion to **3b**.

Effects of the siloxanes in these reactions are less obvious. Chalk and Harrod related the strength of the Si–H bond in silanes (determined from Si–H in the infrared) to that of its silicon–metal derivative. They concluded that the stronger the $\equiv$Si–H bond, the more stable the complex derived from it would be. In siloxanes **1a–c**, the increasing electron-withdrawing effect of Me_3SiO substituents increase the strength of the silicone–hydrogen bond in the order **1c** > **1b** > **1a**. Presumably, stability of the intermediate complexes should be in the same order. Accompanying this change, however, is steric shielding of the reactive site. Together these two factors affect the reactivity of the siloxane. In the case of a platinum catalyst, these effects may destabilize the π-olefin complex resulting in a π-allylic complex, and hence the formation of the chlorosiloxanes.

One final point concerns the formation of methallylsiloxanes **4b,c**. These compounds were apparently not formed from the adducts, since heating **2c** with chloroplatinic acid or triethylamine for extended periods of time failed to give **4c**. Compounds **4b,c** may, therefore,

---

[8] J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1967).

[9] A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 16 (1965).

[10] J. W. Ryan and J. L. Speier, *ibid.*, **86**, 859 (1964).

[11] G. W. Parshall and G. Wilkinson, *Inorg. Chem.*, **1**, 896 (1962).

[12] W. E. Oberhansli and L. F. Dahl, *J. Organometal. Chem.*, **3**, 43 (1965).

[13] A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965).

[14] R. Mason and D. R. Russell, *Chem. Commun.*, **1**, 26 (1966).

[15] F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969).

[16] R. Huttel, J. Kratyer, and M. Bechter, *Chem. Ber.*, **94**, 766 (1961).

be formed from the olefin, siloxane, platinum intermediate.

Experimental Section

Siloxanes **1a–c** were obtained from Marshallton Chemical Co. and were analyzed for purity by glc. β-Methallyl chloride was purified according to literature procedures. Infrared spectra were taken on a Perkin-Elmer Model 457 spectrometer. Proton nmr spectra were measured on a Varian A-60A instrument and mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6 mass spectrometer. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. Gas chromatographic analyses were performed on a Perkin-Elmer 900 gas chromatograph and Perkin-Elmer F-21 preparative gas chromatograph using a 3% OV-17 on 80/100 mesh Chromosorb W (regular) and a 10% OV-1 on 60/80 mesh Chromosorb W (regular) columns, respectively.

General Reaction Procedure.—Catalyst and β-methallyl chloride were heated at reflux for 10 min prior to addition of the siloxane unless otherwise noted. After the reaction mixture was refluxed for an appropriate time period (Table I) the reaction was cooled, and a known weight of standard was added and analyzed by gas chromatography by comparison of peak areas with standard solution of the reaction products. Peak heights gave essentially the same results. Authentic samples of the reaction products were obtained by distillation of the reaction mixture or by preparative gas chromatography. Analyses were performed at least twice and the results were averaged.

Starting Materials. Pentamethyldisiloxane (1a)[17] had bp 85° (750 mm); ir (thin film) 2105 (SiH), 1250 ($SiCH_3$), 1035–1065 (SiOSi), 895–960 (SiH); nmr (neat, benzene standard) τ 10.12 (t, 17, CH_3Si), 5.43 (m, 1, SiH).

1,1,1,3,5,5,5-Heptamethyltrisiloxane (1b) had bp 142° (750 mm); ir (thin film) 2155 (SiH), 1260 ($SiCH_3$), 1050–1080 (SiOSi), 915 (SiH); nmr (neat, benzene standard) τ 9.87 (s, 19, CH_3Si), 5.20 (m, 1, SiH).

Tris(trimethylsiloxy)silane (1c) had bp 185° (750 mm); ir (thin film) 2210 (SiH), 1250–1260 ($SiCH_3$), 1040–1100 (SiOSi), 910 (SiH); nmr (neat, benzene standard) τ 10.00 (s, 27, CH_3Si), 5.83 (s, 1, SiH).

Reactions Catalyzed by Chloroplatinic Acid.—Olefin and approximately a 10^{-4} molar ratio of catalyst/reactants of a 10% chloroplatinic acid solution in isopropyl alcohol were heated to reflux under nitrogen. Siloxane was added and heated until the solution darkened (usually accompanied by an exotherm). The reaction mixture was distilled or analyzed by gas chromatography.

Pentamethyldisiloxane (1a), 7.4 g (0.05 mol), β-methallyl chloride, 4.5 g (0.05 mol), and chloroplatinic acid, 0.028 g (0.0000054 mol), were allowed to react to yield **1-(chloro-2-methylpropyl)pentamethyldisiloxane (2a)**: bp 97° (25 mm); ir (thin film) 1460, 1440, 1410, 1380 (aliphatic CH), 1250–1270 ($SiCH_3$), 1030–1090 cm^{-1} (SiOSi); mass spectrum *m/e* (rel intensity) 56 (65) C_4H_8, 73 (59) Me_3Si, 147 (89) M − $CH_2CHMeCH_2Cl$, 167 (100).

Anal. Calcd for $C_9H_{23}Si_2OCl$: C, 45.23; H, 9.67. Found: C, 45.08; H, 9.52.

1,1,1,3,5,5,5-Heptamethyltrisiloxane (1b), 22.2 g (0.1 mol), methallyl chloride, 9 g (0.1 mol), and chloroplatinic acid, 0.056 g (0.00011 mol), were allowed to react to from three major products.

3-(3-Chloro-2-methylpropyl)heptamethyltrisiloxane (2b) had bp 115° (14 mm); ir (thin film) 1460, 1443, 1410, 1380, (aliphatic CH), 1250–1270 ($SiCH_2$), 1030–1100 (SiOSi); mass spectrum *m/e* (rel intensity) 56 (63) isobutylene, 73 (100) Me_3Si, 221 (64) M − C_4H_8Cl.

Anal. Calcd for $C_{11}H_{29}Si_3O_2Cl$: C, 42.20; H, 9.33; Cl, 11.32. Found: C, 42.11; H, 9.42; Cl, 11.21.

3-Chloroheptamethyltrisiloxane (3b) had 57° (12 mm); ir 1250–1270 ($SiCH_3$), 1050–1070 (SiOSi), 560 (SiCl); nmr (neat, benzene standard) τ 10.03 (s, 18, $SiCH_3$), 9.82 (s, 3, CH_3Si–); mass spectrum *m/e* (rel intensity) 73 (75) Me_3Si, 221 (6) M − Cl, 241 (100) M − Me.

Anal. Calcd for $C_7H_{21}Si_3O_2Cl$: C, 32.72; H, 8.24. Found C, 32.86; H, 8.13.

3-(2-Methyl-1-propenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (4b) had bp (approximate) 92° (14 mm). Analytical samples were obtained by gas chromatography: ir (thin film) 3070 (C═C), 1935 (allylic C═C),[5] 1260 ($SiCH_2$),[5] 1050–1070 (SiOSi), 840 ($SiMe_3$), and 750 cm^{-1} (SiMe); nmr ($CDCl_3$, $CHCl_3$ internal standard) τ 9.97 (d, 21, SiMe), 8.57 (s, 2, $SiCH_2$), 8.3 (d, 3, CCH_3, $J = 0.5$ Hz), and 5.48 (m, 2, ═CH_2).

Anal. Calcd for $C_{11}H_{28}Si_3O_2$: C, 47.76; H, 10.20. Found: C, 47.76; H, 10.30.

Tris(trimethylsiloxyl)silane (1c), 14.8 g (0.05 mol), methallyl chloride, 4.5 g (0.05 mol), and chloroplatinic acid, 0.028 g (0.0000054 mol), were allowed to react to give three products.

3-Chloro-2-methylpropyltris(trimethylsiloxyl)silane (2c) had bp 90° (8 mm); ir (thin film) 1440, 1410, 1380 (aliphatic CH), 1255–1230 ($SiCH_3$), 1030–1060 (SiOSi); mass spectrum *m/e* (rel intensity) 56 (27) C_4H_8, 73 (65) Me_3Si, 207 (100), 268.5 (meta), 295 (5.5) M − C_4H_8Cl, 371 (3.5) M − Me.

Tris(trimethylsiloxy)chlorosilane (3c) had bp 78° (12 mm); ir (thin film) 1250–1270 ($SiCH_3$), 1050–1110 (SiOSi), 590 cm^{-1} (SiCl); nmr (neat, benzene standard) τ 9.67 (s, Me_3Si); mass spectrum *m/e* (rel intensity) 73 (64) Me_3Si, 207 (100), 295 (5) M − Cl, 315 (25) M − Me.

Anal. Calcd for $C_9H_{27}Si_4O_3Cl$: C, 32.65; H, 8.33. Found C, 32.88; H, 8.10.

(2-Methyl-1-propenyl)tris(trimethylsiloxy)silane (4c) had bp 77° (7.3 mm); ir (thin film) 3080 (olefinic CH), 1630 (allylic C═C), 1445, 1405–1420, 1378, 1330, 1320 (CH bending), 1255–1270 ($SiCH_3$), 1040–1079 cm^{-1} (SiOSi); nmr ($CDCl_3$, $CHCl_3$ internal standard) τ 9.93 (s, 27, $SiCH_3$), 8.35 (s, 2, $SiCH_2$), 8.40 (t, 3, CH_3, $J = 1.0$ Hz), 5.43 (m, 2, C═CH_2); mass spectrum *m/e* (rel intensity) 73 (100) Me_3Si, 295 (9) M − C_4H_7, 335 (5) M − Me, 350 (1.5) M^+.

Anal. Calcd for $C_{13}H_{34}Si_4O_3$: C, 44.52; H, 9.77. Found: C, 44.44; H, 9.56.

Platinum on Charcoal.—β-Methallyl chloride, 4.5 g (0.05 mol), and 0.098 g (0.000005 mol) of 1% platinum on charcoal were heated at reflux for 5 min and 11.1 g (0.05 mol) of **1b** was heated at reflux until there was no further evidence (by glc) of product formation. Compounds **2b**, **3b**, and **4b** were obtained (*vide supra*).

Reactions Catalyzed by Palladium on Charcoal.—β-Methallyl chloride (0.05 mol) and 10% palladium on charcoal, 1.06 g (0.001 mol), were heated at reflux for 10 min, at which time siloxanes **1a–c** (0.05 mol) were added. The reaction mixture was refluxed until there was no further evidence of product formation by glc. Siloxane **1a** gave **1-chloropentamethyldisiloxane (3a)**: bp 87° (760 mm); ir (thin film) 1265 ($SiCH_3$), 1040–1090 cm^{-1} (SiOSi); nmr (neat, benzene standard) τ 10.03 (s, 9, $OSiCH_3$), 9.75 (s, 6, $OSiMe_2Cl$); mass spectrum *m/e* (rel intensity) 73 (100) Me_3Si, 147 (29) M − Cl, 167 (47) M − Me.

Anal. Calcd for $C_5H_{15}Si_2OCl$: C, 32.85; H, 8.27. Found: C, 33.12; H, 8.38.

Siloxanes **1b,c** under these conditions gave **3b,c** (Table I).

Ruthenium on Charcoal.—Compounds **1b** and β-methallyl chloride (0.05 mol of each) were refluxed with 2.02 g (0.001 mol) of 5% Ru/C for 4 hr. There was a 67% yield of **3b**, verified by glc and nmr.

No Catalyst.—Compound **1b** and methallyl chloride (0.05 mol of each) were heated at reflux without catalyst; no products were noted after 48 hr. Continued heating for 100 hr yielded adduct **2b** (24%).

Dehydrohalogenation of Adduct.—A sample of pure **2b** (38.6 g, 0.1 mol) was heated with chloroplatinic acid, 0.056 g (0.000011 mol), for 120 hr. No products were found by glc analysis. Treatment of **2c** with excess triethylamine or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) caused some polymerization, with no evidence of **4c** having been generated.

Reaction with Palladium(II) Chloride.—Palladium(II) chloride (0.18 g, 10^{-3} mol) was added in portions to a solution of **1b** (0.22 g, 10^{-3} mol) in *n*-pentane. Hydrogen chloride was evolved, and there was a quantitative conversion to the chlorosiloxane **3b**.

Reaction of Bis[isobutenylpalladium(II) chloride] with 1b.—Compound **1b**, 0.113 g (0.00051 mol), was dissolved in 10 ml of dry benzene in a 50-ml single-necked flask equipped with magnetic stir bar and reflux condenser. Bis[isobutenylpalladium(II) chloride][16] 0.10 g (0.00025 mol), in 1 ml of benzene was added with stirring to the above reaction mixture. Immediate reduction of the complex to palladium metal and evolution of heat was noted. Gas chromatography of the reaction mixture indicated that a quantitative yield of **3b** was obtained.

Cohydrolysis of Trimethylchlorosilane and $MeCl_2SiCH_2CHMeCH_2Cl$ (5).—Compound **5** (0.24 mol, 50 g) and an excess

---

(17) R. Okawara and M. Sakiyama, *Bull. Chem. Soc. Jap.*, **29**, 547 (1956).

of Me_3SiCl (0.55 mol, 59.5 g) were premixed and added dropwise to 300 ml of vigorously stirring ice water in a 500-ml erlenmeyer flask. When complete, the solution was transferred to a separatory funnel, and the organic layer was separated, dried over Na_2SO_4, and distilled to give **2b** in 32% yield.

Reaction of Trimethylsilanol and $MeCl_2SiCH_2CHMeCH_2Cl$ (5).—Compound **5** (0.5 mol, 57 g) in 100 ml of dry THF was charged into a 250-ml flask equipped with stirrer, thermometer, and dropping funnel, and cooled to −5°. Pyridine (1 mol, 79 g) was added dropwise, keeping temperature below 0°; trimethylsilanol (1 mol, 90 g) was added dropwise to this solution, again keeping the temperature below 0°. When addition was complete, the mixture was brought to room temperature and water was stirred into the reaction mixture; the organic layer was washed three times with water and dried over Na_2SO_4. Distillation gave 32 g (20%) of **2b**. Triethylamine was substituted for pyridine and glyme for THF with no change in product yield.

Registry No.—**1a**, 1438-82-0; **1b**, 1873-88-7; **1c**, 1873-89-8; **2a**, 37611-45-3; **2b**, 37611-46-4; **2c**, 37611-47-5; **3a**, 2943-62-6; **3b**, 22407-46-1; **3c**, 17905-99-6; **4b**, 37611-51-1; **4c**, 37611-52-2; β-methallyl chloride, 563-47-3.

Acknowledgment.—We would like to thank Dr. A. Berry, University of Pennsylvania, for helpful discussions.

Synthesis, Reactivity, and Spectral Properties of 2,7-Difluoro-9-chloromethylenexanthene. Isoelectronicity with Heptafulvene Derivatives

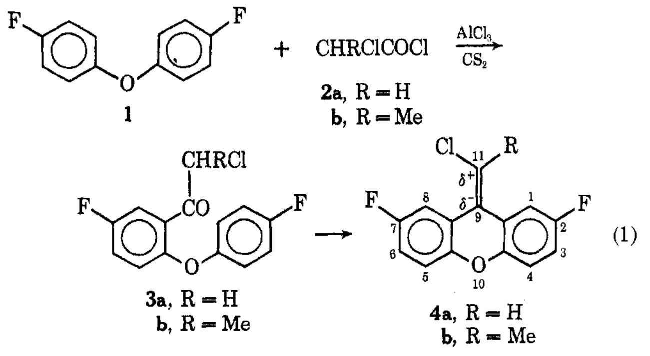
ITSHAK GRANOTH* AND ASHER KALIR

Israel Institute for Biological Research, Tel-Aviv University Medical School, Ness-Ziona, Israel

Received July 21, 1972

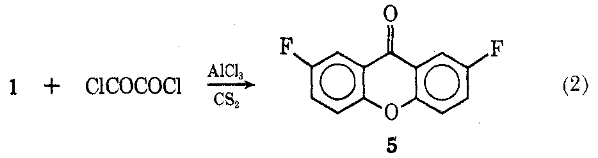
The application of the Friedel–Crafts reaction for the preparation of phenoxaphosphines[1] and phenothiaphosphines[2] from aromatic ethers and sulfides, respectively, has now been extended to the xanthene system.

Synthesis, Structure, and Spectra.—2,7-Difluoro-9-chloromethylenexanthene (**4a**) was the only product isolated (in a good yield) from the reaction of **1** with **2a** (eq 1). 2-Chloroacetyl-4,4′-difluorodiphenyl ether (**3a**) was assumed as an intermediate since **2a** has been known to chloroacetylate aromatics.[3]



The structure of **4a** was elucidated from its spectral properties. The ir showed no carbonyl absorption and the nmr exhibited one vinylic proton and a characteristic low-field resonance at δ 8.22. The latter was a multiplet of 1 H, ortho to the fluorine (J_{HF} = 9 Hz), and further coupled with meta aromatic protons only. It was shown to be H-8 by the absence of this strong deshielding effect in other derivatives, such as **7a** and **b**, but not in **4b**. This deshielding must result from the long-range electrical effect of the chlorine atom.[4] A similar deshielding effect has been observed recently, though not confirmed, in α-chloro- and α-bromo-9-anisilidenefluorene.[5] These observations indicated the structure of **4a**, further confirmed by the analysis and the mass spectrum, which disclosed the presence of one chlorine atom and verified the molecular weight. The mass spectrum of **4a** exhibited a very intense peak corresponding to $(M - ClO)^+$. Its direct formation from the molecular ion was shown by an appropriate metastable transition. The elimination of $ClO\cdot$ as one entity from chlorinated aromatic ethers is known for some time.[6] However, until now the chlorine was directly attached to the aromatic ring.

The characteristic uv band of **4a** in EtOH appeared at 338 nm and was not shifted in cyclohexane. This, and the absence of the 338-nm band in the xanthene itself, suggested that the latter band is due to the $\pi \rightarrow \pi^*$ transition connected with the extended conjugation in 9-methylenexanthene derivatives as compared with xanthene. The methylenexanthene skeleton of **4a** was established by its oxidation with potassium permanganate to 2,7-difluoroxanthen-9-one (**5**). This compound was identical with a sample prepared as in eq 2.[7] Decarbonylation of oxalyl chloride during Friedel–Crafts reactions with aluminum chloride is well known.[8] Thus, two one-step syntheses of 2,7-difluoroxanthene derivatives were achieved.



The reaction described by eq 1 was markedly influenced by the substituent R. When R = H, the intermediate **3a** was very reactive, not allowing its isolation under the reaction conditions. When R = Me, **3b** was not cyclized by aluminum chloride in boiling carbon disulfide, thus enabling its isolation and characterization by nmr. (See Experimental Section.) Crude **3b** gave eventually **4b** upon heating on a water bath with little methanol and a trace of hydrochloric acid. However, no **4** (R = C_6H_5) was isolated from the reaction of **1** and **2** (R = C_6H_5), which yielded unidentified oil.[9] The introduction of an α-methyl group in **4a**,

---

[1] J. B. Levy, G. W. Whitehead, and I. Granoth, *Israel J. Chem.*, **10**, 27 (1972), and references cited therein.

[2] I. Granoth, A. Kalir, Z. Pelah, and E. D. Bergmann, *Tetrahedron*, **25**, 3919 (1969).

[3] F. Tutin, *J. Chem. Soc.*, **97**, 2495 (1910).

[4] R. F. Zürcher in "Nuclear Magnetic Resonance in Chemistry," B. Pesce, Ed., Academic Press, New York, N. Y., 1965, p 45.

[5] Z. Rappoport and A. Gal, *J. Org. Chem.*, **37**, 1174 (1972).

[6] I. Granoth and J. B. Levy, *J. Chem. Soc. B*, 2391 (1971).

[7] J. W. Cusic and R. A. Robinson, U. S. Patent 2,776,299 (1957); *Chem. Abstr.*, **51**, 8146 (1957).

[8] P. E. Sokol, *Org. Syn.*, **44**, 69 (1964).

[9] A study of the scope and mechanisms of the reactions outlined by eq 1 and 3 is now in progress, including reactions of other aromatics with various α-substituted acid halides.