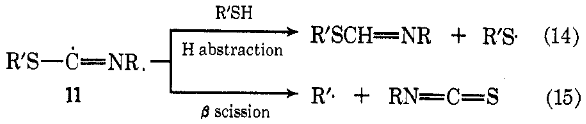
and the hydrogen abstraction from thiol determine the whole course of reaction (eq 12–15). Thus three radi-

$$R'SH + In\cdot \longrightarrow R'S\cdot + InH \qquad (12)$$

$$R'S\cdot + RNC \longrightarrow \underset{\textbf{11}}{R'S{-}\dot{C}{=}NR} \qquad (13)$$



$$\underset{\textbf{11}}{R'S{-}\dot{C}{=}NR} \begin{cases} \xrightarrow[\text{H abstraction}]{R'SH} R'SCH{=}NR + R'S\cdot & (14) \\ \xrightarrow[\beta\text{ scission}]{} R'\cdot + RN{=}C{=}S & (15) \end{cases}$$

cal reactions of isocyanide are all summarized by the scheme involving the corresponding imidoyl radicals, **8**, **10**, and **11**, whose reactivities are decisive of determining the reaction courses.

Experimental Section

Materials.—All isocyanides were prepared from the corresponding formamides according to Ugi's procedure[4] and stored under nitrogen. Diethylphosphine[5] and diphenylphosphine[6] were prepared according to the respective literatures and were stored under nitrogen. Benzene as solvent was used after the purification in the usual method. Azobisisobutyronitrile (AIBN) was a commercial reagent and used without further purification.

Representative Procedure for the Reaction of Isocyanide with Phosphine.—A mixture of benzyl isocyanide (30 mmol), diethylphosphine (40 mmol), AIBN (1.5 mmol), and benzene (10 ml) was heated at 70° for 18 hr under nitrogen atmosphere. Then, the reaction mixture was subjected to the fractional distillation under nitrogen. A product, toluene, was analyzed by glpc and nmr. An analytical sample of diethylcyanophosphine (1) was prepared by further purification of the distillation fraction [bp 71–72° (22 mm)] using preparative glpc. The structure of 1 was established by nmr, ir, and mass spectra, and elemental analysis: ir (neat) $\nu_{C\equiv N}$ 2210 cm^{-1} (weak); mass spectrum parent mass 115 (mol wt, 115).

Anal. Calcd for $C_5H_{10}NP$: C, 52.16; H, 8.77; N, 12.17; P, 26.90. Found: C, 52.01; H, 9.03; N, 12.06; P, 26.71.

This compound is vulnerable to air.

The other reactions were carried out by the same procedure. The spectra data and elementary analyses of the reaction products are shown below.

***N*-Cyclohexylformimidoyldiethylphosphine $(C_2H_5)_2PCH{=}N$-*c*-C_6H_{11}** was analyzed as follows: bp 110–112° (6 mm); ir (neat) $\nu_{C=N}$ 1605 cm^{-1} (strong); nmr ($CDCl_3$) δ 8.35 (doublet, J_{PH} = 33 cps, 1 H, >PCH=N–).

Anal. Calcd for $C_{11}H_{22}NP$: C, 66.30; H, 11.13; N, 7.03; P, 15.54; mol wt, 199. Found: C, 65.94; H, 11.14; N, 7.07; P, 14.69; mol wt (cryoscopy in benzene), 202.

N*-*n*-Hexylformimidoyldiethylphosphine (3d) $(C_2H_5)_2PCH{=}N{-}C_6H_{13}$-*n was analyzed as follows: bp 105° (8 mm); ir (neat) $\nu_{C=N}$ 1614 cm^{-1} (strong); nmr ($CDCl_3$) δ 8.35 ppm (doublet, J_{PH} = 36 cps, 1 H, >PCH=N–), 3.50 (triplet, 2 H, $-CH{=}NCH_2CH_2-$).

Anal. Calcd for $C_{11}H_{24}NP$: C, 65.62; H, 12.04; N, 6.96. Found: C, 65.11; H, 12.46; N, 6.98.

Diphenylcyanophosphine $(C_6H_5)_2PCN$ was analyzed as follows: 113.5° (0.13 mm); ir (neat) $\nu_{C\equiv N}$ 2180 cm^{-1} (weak).

Anal. Calcd for $C_{13}H_{10}NP$: C, 73.92; H, 4.78; N, 6.63; P, 14.67. Found: C, 73.83; H, 5.43; N, 6.38; P, 14.56.

Registry No.—**1**, 26306-14-9; **3c**, 19911-05-8; **3d**, 26306-16-1; diphenylcyanophosphine, 4791-48-4; *tert*-butyl isocyanide, 7188-38-7; benzyl isocyanide, 10340-91-7; cyclohexyl isocyanide, 931-53-3; *n*-hexyl isocyanide, 15586-23-9; diethylphosphine, 627-49-6; diphenylphosphine, 829-85-6.

[4] I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

[5] K. Issleib and A. Tzschach, *ibid.*, **92**, 704 (1959).

[6] D. Witenberg and H. Gilman, *J. Org. Chem.*, **23**, 1063 (1958).

On the Stereochemistry of $^5J_{HF}$

Leon M. Stock and Michael R. Wasielewski[1a]

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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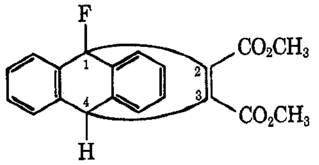
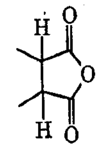
Long-range proton fluorine spin–spin coupling over five bonds is a well-known phenomenon.[1] The magnitude of the coupling constant depends importantly on the distance between the nuclei[1c] and on the spacial arrangement[1g] of the nuclei in the molecule under examination. Although the available data are not wholly consistent, the evidence suggests a direct,[2] or a very specific indirect,[1g] coupling mechanism is important.[1] We have examined this question by an investigation of the nmr spectra of three rigid bicyclic molecules (**1**–**3**) in which the hydrogen and fluorine nuclei have the geometry (a trans coplanar relationship between F and C_2 and between H and C_3) that is thought to be ideal for a completely indirect[2] coupling mechanism but in which the hydrogen and fluorine nuclei are separated by approximately 5 Å.



1



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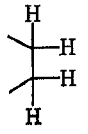


3

The signal for the bridgehead hydrogen atom of **1** was a broadened doublet. Double resonance experiments with irradiation in the aryl hydrogen atom region narrowed the signal from $\Delta\nu_{1/2}$ = 2.6 Hz to 2.1 Hz and enabled the confident definition of $^5J_{HF}$ as 0.88 ± 0.05 Hz (Figure 1).

Similar experiments with compounds **2** and **3** do not yield definitive values for $^5J_{HF}$ but do establish the value of this coupling constant as certainly less than 0.5 Hz. For **2**, the resonance of the bridgehead hydrogen atom was a somewhat broadened doublet $^3J_{HH} = 1.7 \pm 0.1$ Hz. Double resonance experiments with irradiation in the region of H_2 and H_3 confirmed the assignment of the doublet and decreased $\Delta\nu_{1/2}$ to 1.8 Hz. For **3**, the resonance of the bridgehead hydrogen atom was a broadened triplet, $^3J_{HH} = 1.9 \pm 0.1$ Hz. Double resonance work with H_2 and H_3 confirmed the origin of the triplet and decreased $\Delta\nu_{1/2}$ to 2.2 Hz. Irradiation in the aryl hydrogen atom region narrowed the signal for H_4 by about 0.5 Hz for **2** and **3**. These results and the closely related behavior of **1** in similar experiments suggest that $^5J_{HF}$ is less than 0.5 Hz for **2** and **3**, but probably greater than 0.3 Hz.

The nmr spectrum of 1-fluorobicyclo[2.2.2]octane has

[1a] NOTE ADDED IN PROOF.—National Science Foundation Undergraduate Research Participant.

[1] (a) D. R. Davis, R. P. Lutz, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 246 (1961); (b) M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962); (c) A. D. Cross and P. W. Landis, *ibid.*, **86**, 4005 (1964); (d) J. Burdon, *Tetrahedron*, **21**, 1101 (1965); (e) P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Amer. Chem. Soc.*, **88**, 2459 (1966); (f) A. B. Foster, R. Hems, L. D. Hall, and J. F. Manville, *Chem. Commun.*, 158 (1968); (g) C. W. Jefford, D. T. Hill, L. Ghosez, S. Toppet, and K. C. Ramey, *J. Amer. Chem. Soc.*, **91**, 1532 (1969).

[2] The terminology of M. Barfield and M. Karplus, *ibid.*, **91**, 1 (1969), has been adopted.

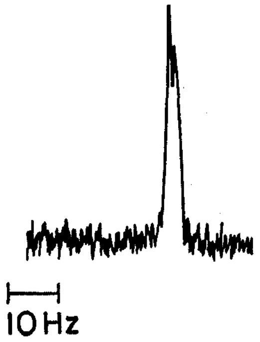


Figure 1.—The nmr signal of H_4 of **1** with the aryl hydrogen atoms decoupled.

been reported by Morita.[3] His finding that $^5J_{HF}$ was undetectably small was confirmed in this study.

The geometry presumably necessary for the maximum indirect coupling between the hydrogen and fluorine nuclei is attained in compounds **1–3**. The finding that $^5J_{HF}$ is very small indicates that a direct interaction, or an indirect interaction between F and C_4 as proposed by Jefford and his associates,[1g] is responsible for the large coupling constants observed in other compounds.

Experimental Section

Compounds **1–3** were available from previous work.[4] The spectra were obtained with conventional equipment in solvents dictated, in part by the limited solubility of **1–3**. Selective heteronuclear decoupling experiments were also carried out for **2** and **3**, but the results were not conclusive. The chemical shifts are summarized in Table I.

TABLE I
CHEMICAL SHIFTS FOR COMPOUNDS 1–3

Nucleus–compd	Chemical shift, ppm[a] **1**[b]	**2**[c]	**3**[d]
H_4	−5.63	−4.57	−4.17
H_2,H_3[e]		−2.82	−1.82
ArH[e]	−7.32	−7.20	−7.25
F[e,f]	+31.3	+29.8	+23.0

[a] Relative to internal TMS. [b] In $CDCl_3$. [c] In $(CD_3)_2SO$. [d] In CCl_4. [e] Multiplet structure. [f] In ppm from internal hexafluorobenzene. Hexafluorobenzene is +121.88 ppm from CCl_3F.

Registry No.—**1**, 26306-23-0; **2**, 26306-24-1; **3**, 26306-25-2.

[3] K. Morita, Proceedings of the Sixth Nmr Symposium, Kyoto, Japan, 1967; K. Morita, private communication, 1969.

[4] G. L. Anderson, Dissertation, The University of Chicago Library, 1969; G. L. Anderson and L. M. Stock, *J. Amer. Chem. Soc.*, **91**, 6804 (1969).

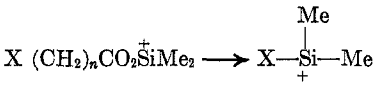
Functional Group Interactions in the Mass Spectra of Trimethylsilyl Derivatives of Halo Acids and Halo Alcohols

EDWARD WHITE, V, AND JAMES A. MCCLOSKEY*

Institute for Lipid Research and Department of Biochemistry, Baylor College of Medicine, Houston, Texas 77025

Received June 12, 1970

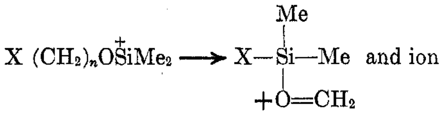
As one aspect of general studies dealing with migration of the trimethylsilyl (TMS) group upon electron impact,[1] several reports have been made in which part or all of a group containing a heteroatom migrates to the charge center generated by loss of a TMS methyl radical (eq 1 and 2).[1a,b] Most previously observed migrations of this type involve participation of unshared electrons of O, N, or S, the exception being formation of the dimethylphenylsiliconium ion from M − 15 (CH_3) of the TMS derivatives of benzyl alcohol and related compounds.[1a] Interesting analogies have been reported by Weber in systems containing carbon-bound TMS groups, which produce rearranged ions of types a (X = Ph,[2] Cl[3]) and c.[4]



$$X\,(CH_2)_nCO_2\overset{+}{Si}Me_2 \longrightarrow X-\underset{+}{\overset{\overset{\displaystyle Me}{|}}{Si}}-Me \qquad (1)$$

a

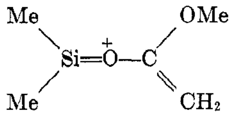
(e.g., X = TMSO, MeO, PhO)



$$X\,(CH_2)_nO\overset{+}{Si}Me_2 \longrightarrow X-\underset{\underset{\displaystyle +O{=}CH_2}{|}}{\overset{\overset{\displaystyle Me}{|}}{Si}}-Me \text{ and ion a} \qquad (2)$$

b

(e.g., X = TMSO, TMSS,
MeO, PhO, PhNH,
PhS, Me_2N, $C_6H_{11}O$)



c

We have therefore examined the mass spectra of TMS derivatives of halo acids (**1–5**) and halo alcohols (**6–10**) to determine whether remote functional group interactions between TMS and halogen can be promoted by the latter's unshared electrons. Of the possible series,

$X(CH_2)_nCO_2TMS$		(both series)	$X(CH_2)_nOTMS$	
1	$n = 1$	a X = F	**6**	$n = 2$
2	$n = 2$	b X = Cl	**7**	$n = 3$
3	$n = 5$	c X = Br	**8**	$n = 6$
4	$n = 9$	d X = I	**9**	$n = 10$
5	$n = 10$		**10**	$n = 11$

25 of 40 compounds indicated were examined, including the TMS-d_9 derivatives[1e] of the **3**, **5**, **8**, and **10** bromides, with full high resolution mass spectra recorded of **3b**, **4a**, **5a**, **b**, and **c**, and **10a**, **c**, and **d**.

The rearranged ion of type a was observed in the mass spectra of both the ester and ether series, as shown

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* To whom correspondence should be addressed.

[1] For examples of rearrangements involving the trimethylsilyl group in a variety of molecules see the following and references therein: (a) J. Diekman, J. B. Thompson, and C. Djerassi, *J. Org. Chem.*, **32**, 3904 (1967); (b) *ibid.*, **33**, 2271 (1968); (c) *ibid.*, **34**, 3147 (1969); (d) W. Richter, M. Vecchi, W. Vetter, and W. Walther, *Helv. Chim. Acta*, **50**, 364 (1967); (e) J. A. McCloskey, R. N. Stillwell, and A. M. Lawson, *Anal. Chem.*, **40**, 233 (1968); (f) P. Capella and C. M. Zorzut, *ibid.*, **40**, 1458 (1968); (g) W. J. Richter and A. L. Burlingame, *Chem. Commun.*, 1158 (1968); (h) J. A. McCloskey, A. M. Lawson, K. Tsuboyama, P. M. Krueger, and R. N. Stillwell, *J. Amer. Chem. Soc.*, **90**, 4182 (1968); (i) G. H. Draffan, R. N. Stillwell, and J. A. McCloskey, *Org. Mass Spectrom.*, **1**, 593 (1968); (j) D. C. DeJongh, T. Radford, J. D. Hribar, S. Hanessian, M. Bieber, G. Dawson, and C. C. Sweeley, *J. Amer. Chem. Soc.*, **91**, 1728 (1969); (k) J. A. Gustafsson, R. Ryhage, J. Sjövall, and R. M. Moriarty, *ibid.*, **91**, 1234 (1969); (l) M. Zinbo and W. R. Sherman, *ibid.*, **92**, 2105 (1970).

[2] W. P. Weber, R. A. Felix, and A. K. Willard, *Tetrahedron Lett.*, 907 (1970).

[3] W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, **91**, 6544 (1969).

[4] W. P. Weber, R. A. Felix, and A. K. Willard, *ibid.*, **92**, 1420 (1970).