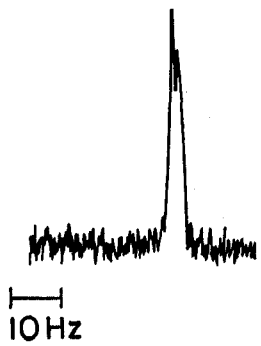

Figure 1.—The nmr signal of H_4 of **1** with the aryl hydrogen atoms decoupled.

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

	Chemical shift, ppm[a]		
Nucleus–compd	**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

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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

$$X(CH_2)_nCO_2\overset{+}{S}iMe_2 \longrightarrow X-\overset{+}{S}i(Me)-Me \quad (1)$$

a

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

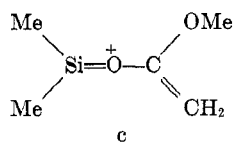
$$X(CH_2)_n\overset{+}{O}SiMe_2 \longrightarrow X-Si(Me)-Me \text{ and ion a} \quad (2)$$

$$+O{=}CH_2$$

b

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

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]



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,

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

* 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).

by the per cent of total ion current (% Σ_{40}) values[5] listed in Table I. In addition, ion a (*m/e* 137, 139) is

TABLE I
% Σ_{40} VALUES FOR ION a ($XSiMe_2^+$) IN THE MASS SPECTRA OF TMS DERIVATIVES OF HALO ACIDS (1–5) AND HALO ALCOHOLS (6–10)

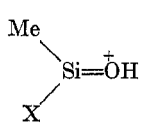
Compd	F (a)	Cl (b)	Br (c)	I (d)
1				0.1
2			19	
3		14	9.6	3.8
4	6.0		2.8	1.2
5	4.9	3.0	2.3	1.0
6			42	33
7			26	
8		7.6	6.9	5.0
9		2.3	1.9	1.2
10	2.6	1.8	1.7	1.1

abundant (30% Σ_{40}) in the spectrum of trimethylsilyl 3-bromobutyrate. Ion b was found in spectra of the alcohol series (Table II), in analogy to its formation in other

TABLE II
% Σ_{40} VALUES FOR ION b ($XSi(OCH_3)Me_2^+$) IN THE MASS SPECTRA OF TMS DERIVATIVES OF HALO ALCOHOLS (6–10)

Compd	F (a)	Cl (b)	Br (c)	I (d)
6			0.0	0.0
7			16	
8		8.5	6.6	4.6
9		4.0	2.9	1.7
10	5.0	3.5	2.7	1.9

systems (eq 2).[1b,e] In addition, an ion corresponding to d, the analog of well-known e[6] was present in low abundance in the spectra of most compounds. Identi-

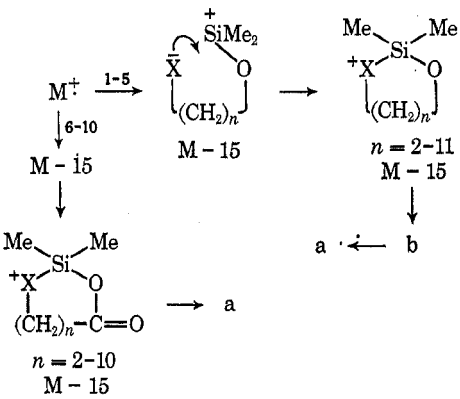


d, X = halogen
e, X = Me, *m/e* 75

ties and compositions of ions a, b, and d in the present study were supported by measurement of exact mass and appropriate mass shifts[1e] in the spectra of the deuterium labeled derivatives. Further, **10c**-1,1-d_2 was prepared and examined, which showed complete retention of the label in ion b (*m/e* 139, 141) in accordance with the proposed structure.

No metastable peaks were observed in any mass spectra to indicate the mechanistic precursors of a or b. Compounds **3c** and **5d** were examined on the high resolution instrument using the metastable focusing technique,[7] which showed a to be derived from M − 15. In the halo ether compound **10d**, the same method established the fragmentation sequence M → M − 15 → b → a. For shorter chain members of the ether series the direct formation of a from M − 15 cannot be excluded, particularly in the case of **6c** and **d**, for which formation of b is prevented by the unfavorable requirement of expulsion of methylene. For the same reason, formation of ion a from **1d** is unfavorable and therefore not observed. Otherwise, Tables I and II show that the abundances of ions a and b decrease smoothly with chain length and rise with increased electronegativity of the halogen atom.

Based on the above data, we envision a mechanism for the formation of ions a and b similar to that proposed by Djerassi for the analogous ions from phenoxy- and trimethylsilyloxypolymethylene TMS ethers[1b] and esters.[1c]



The apparent lack of preference for a fixed ring size in the cyclic intermediate is characteristic of a general class of fragmentation reactions, which as in the present case (e.g., **5**, **10**), may involve closure of large rings.[8] We attribute the increased abundance of a and b with increased electronegativity of X to decreased stability of the cyclic form of M − 15, in which tetrahedral[9] halogen is required to bear a positive charge.

Ions of type a and b appear to occur generally in the mass spectra of halogenated TMS derivatives, and recognition of their existence is necessary to avoid misinterpretation of the spectra. For instance, ion a (*m/e* 93, 95) is prominent (10% Σ_{40}) in the mass spectrum of the TMS derivative of 6-chloropurine,[10] for which its occurrence would *a priori* seem unlikely.

Experimental Section

Mass Spectra.—Mass spectra were recorded on either an LKB-9000 gas chromatograph–mass spectrometer or CEC 21-110B high resolution instrument equipped with a gas chromatographic inlet system.[11] Spectra were recorded at 70 eV ionizing energy with ion source and separator temperatures of 250–270°. All samples were introduced directly from their reaction mixtures through the gas chromatographic inlet systems (1% SE-30 at 30–160° isothermal for low resolution spectra and 1% SE-30 with temperature programming for high resolution spectra). All gas chromatographic peaks for which spectra were recorded were symmetrical and well separated from other peaks. Care was taken to obtain low resolution spectra which were unbiased, as indicated by the total ion current chromatogram. All mass spectra were free of ions above the molecular ion (except the ion–molecule reaction product M + H) and of ions characteristic of starting materials, homologs, and expected by-products. Complete mass spectra of all compounds studied have been submitted to the Archives of Mass Spectral Data, F. W. McLafferty, Ed., Wiley-Interscience, New York, N. Y.

Trimethylsilyl Derivatives.—TMS derivatives were generally prepared at concentrations of about 10 $\mu g/\mu l$ by heating about 1

(5) % Σ_{40} values for ions a and b represent the sum of all isotopic species.
(6) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 471.
(7) K. R. Jennings, *J. Chem. Phys.*, 283 (1966).
(8) See, for example, ref 1e,i and R. E. Wolff, M. Greff, and J. A. McCloskey, *Adv. Mass Spectrom.*, **4**, 193 (1968).
(9) G. A. Olah and J. R. DeMember, *J. Amer. Chem. Soc.*, **92**, 718 (1970).
(10) E. White, V, and J. A. McCloskey, unpublished experiments.
(11) P. M. Krueger and J. A. McCloskey, *Anal. Chem.*, **41**, 1930 (1969).

mg of alcohol or acid with bis(trimethylsilyl)acetamide (BSA),[12] [bis(perdeuteriotrimethylsilyl)acetamide[13] for TMS-d_9 derivatives] or bis(trimethylsilyl)trifluoroacetamide[14] (BSTFA) at 100° for 1 hr in a screw-cap vial. The TMS ether of 2-bromoethanol (**6c**) was prepared by heating the alcohol with a 10% solution of trimethylchlorosilane[12] in benzene (rather than BSA or BSTFA) at 100° for 1 hr in order to obtain a peak well separated from reagents on gas chromatography.

The halo alcohols and halo acids were obtained from commercial sources[15] except for those whose preparation is described below.

11-Fluoroundecanol.—The procedure used was basically that applied by Pattison and Norman to the synthesis of ω-fluoroalkenes.[16] A mixture of 11-bromoundecanol (250 mg) and dry powdered KF (95 mg) in diethylene glycol (600 μl) was heated in a sealed vial at 120° for 24 hr. The cooled reaction mixture was diluted with water and extracted with ether, the organic layer washed with water and dried over $CaSO_4$, and the ether was removed by evaporation to give crude 11-fluoroundecanol (300 μl). A sample was converted to the TMS derivative (**10a**). Gas chromatography indicated a purity of about 50%. A sample subjected to gas chromatography–mass spectrometry gave for **10a** an exact mass for M − H[17] of 261.2062 (261.2050 required for $C_{14}H_{31}OFSi$) and for M − F of 243.2119 (243.2144 required for $C_{14}H_{31}OSi$).

11-Fluoroundecanoic Acid and 10-Fluorodecanoic Acid.—Crude 11-fluoroundecanol (10.3 mg) was added with stirring to concentrated HNO_3 (2 ml). After 1 hr the mixture was heated to 100° in 1 hr and then held at 80–100° for 1.5 hr. After cooling, ether and water were added, the organic layer was separated, washed twice with water, and dried over $CaSO_4$, and the ether was removed by evaporation. The entire residue was treated with BSTFA (300 μl) and subjected to gas chromatography–mass spectrometry. Mass measurements for the two major gas chromatographic peaks gave, in order of decreasing retention time, an exact molecular mass for **5a**, 276.1923 (276.1921 required for $C_{14}H_{29}O_2FSi$), for **4a**, 262.1776 (262.1764 required for $C_{13}H_{27}O_2FSi$).

6-Chlorohexanoic Acid.—6-Chlorohexanol (4.1 g) was added in 45 min to concentrated HNO_3 (8.8 ml) with stirring and cooling to maintain the temperature below 31°. The two phase mixture was stirred at room temperature for 4 hr and then heated slowly to 90° and held at 90° for 1 hr. After cooling, water (50 ml) was added and the mixture was extracted with ether. The organic layer was washed twice with water and dried over $CaSO_4$, and the ether was removed by evaporation to give crude 6-chlorohexanoic acid. A small sample was converted to the TMS derivative **3b** and subjected to gas chromatography–mass spectrometry. The mass spectrum of **3b** showed the following characteristic ions: mass (relative intensity) of M, 222 and 224 (0.3, 0.1%); M − CH_3, 207 and 209 (8.0, 2.1%). A high resolution spectrum gave an exact molecular mass of 224.0842 and 222.0871 (224.0816 and 222.0843 required for $C_9H_{19}O_2{}^{37}ClSi$ and $C_9H_{19}O_2{}^{35}ClSi$).

11-Chloroundecanoic Acid.—A mixture of 11-bromoundecanoic acid (5.3 g), AgCl (5.7 g), and LiCl (5.0 g) in acetonitrile (50 ml) was stirred for 10 days. An additional 5.7 g of AgCl was added and stirring continued for 30 days. Gas chromatography of the TMS derivatives prepared from a small portion of the reaction mixture showed about 92% conversion of **10c** to **10b**. Acetic acid (1 ml) was added to the reaction mixture and the salts were removed by filtration and washed with acetonitrile (30 ml). The volume of the combined filtrate and wash was reduced to 10 ml by evaporation and water (100 ml) and ether (100 ml) were added. The ethereal layer was separated, washed with water, and dried over $CaSO_4$, and the ether was removed by evaporation to give 4.3 g (98%) of crude 11-chloroundecanoic acid. A small sample was converted to the TMS derivative **5b** and subjected to gas chromatography–mass spectrometry: exact molecular mass, 292.1628 (292.1625 required for $C_{14}H_{29}O_2{}^{35}ClSi$).

11-Chloroundecanol.—An approximately 1 *M* solution of borane in tetrahydrofuran (10 ml) was added with stirring under nitrogen to 11-chloroundecanoic acid (1.1 g) in tetrahydrofuran (5 ml) in 10 min. The solution was stirred for 1 hr and then heated under reflux for 10 min. After cooling to room temperature, acetic acid (1 ml) was added slowly and the mixture heated under reflux for 10 min. The reaction mixture was poured into water (50 ml) and ether (50 ml). The ethereal layer was separated, washed successively with water, 5% aqueous $NaHCO_3$, and water, and dried over $CaSO_4$. Removal of the ether by evaporation gave crude 11-chloroundecanol, a small sample of which was converted to the TMS derivative **10b** and examined by gas chromatography–mass spectrometry. The mass spectrum showed the following characteristic ions: mass (relative intensity) of M, 278 and 280 (<0.1%); M − H, 277 and 279 (0.2, 0.4%);[18] M − CH_3, 263 and 265 (1.7, 0.6%).

6-Bromohexanol, 10-bromodecanol, and 11-bromoundecanol were prepared from the corresponding acids by the same procedure used to prepare 11-chloroundecanol. Samples of the crude bromo alcohols were converted to the TMS derivatives and subjected to gas chromatography–mass spectrometry.

The mass spectrum of **8c** showed the following characteristic ions: mass (relative intensity) of M, 252 and 254 (absent); M − H, 251 and 253 (0.1, 0.1%); M − CH_3, 237 and 239 (1.3, 1.3%).

The mass spectrum[18] of **9c** showed the following characteristic ions: mass (relative intensity) of M, 308 and 310 (0.03, 0.02%); M − H, 307 and 309 (0.06, 0.08%); M − CH_3, 293 and 295 (0.9, 0.9%).

The mass spectrum[18] of **10c** showed the following characteristic ions: mass (relative intensity) of M, 322 and 324 (0.05, 0.06%); M − H, 321 and 323 (0.10, 0.24%); M − CH_3, 307 and 309 (1.7, 1.7%). A high resolution mass spectrum from which the molecular ion was absent gave the exact masses for M − CH_3 of 307.1108 and 309.1103 (307.1092 and 309.1073 required for $C_{13}H_{28}O^{79}BrSi$ and $C_{13}H_{28}O^{81}BrSi$).

11-Bromo-1,1-dideuteriundecanol.—11-Bromoundecanoic acid (265 mg) in tetrahydrofuran (8 ml) was added to $LiAlD_4$[13] (44 mg) in tetrahydrofuran (5 ml) with stirring. The reaction mixture was stirred for 0.5 hr, then hydrolyzed by the addition of ethyl acetate (0.5 ml) and acetic acid (0.2 ml) followed after 10 min by water (100 ml). The mixture was extracted with ether and the organic layer washed three times with water and dried over $CaSO_4$. Removal of the ether by evaporation gave 198 mg (78%) of crude product. A small sample was converted to the TMS derivative **10c**-1,1-d_2 and subjected to gas chromatography–mass spectrometry. The mass spectrum showed an isotopic composition of 97.7% d_2 and 2.3% d_1.

Iodo Compounds.—All iodo compounds (except **1d** which was prepared from iodoacetic acid[15]) were prepared from the TMS derivatives of the corresponding bromo compounds. Sodium iodide (about 5 mg/100 μl) was added to each reaction mixture from the preparation of the TMS derivatives of the bromo compounds, and the mixtures were heated at 100° for 18–24 hr. Exchange was observed to be more rapid in samples prepared with BSA than in those prepared with BSTFA.

The mass spectra of the iodo compounds showed the following characteristic ions: mass (relative intensity) for **3d** of M, 314 (3.1%), M − CH_3, 299 (26.0%); for **4d** of M, 370 (4.9%), M − CH_3, 355 (38.0%); for **5d** of M, 384 (3.7%), M − CH_3, 369 (43.0%); for **6d** of M, 244 (0.3%), M − H, 243 (0.2%), M − CH_3, 229 (78.0%); for **8d** of M, 300 (0.1%), M − H, 299 (0.2%), M − CH_3, 285 (25.4%); for **9d** of M, 356 (0.4%), M − H, 355 (0.2%), M − CH_3, 341 (19.8%); and for **10d** of M, 370 (0.7%), M − H, 369 (0.3%), M − CH_3 355 (36.0%).

Registry No.—**3b**, 26305-94-2; **3d**, 26305-95-3; **4a**, 26305-85-1; **4d**, 26305-96-4; **5a**, 26305-97-5; **5b**, 26305-98-6; **6d**, 26305-99-7; **8c**, 26306-00-3; **8d**, 26306-01-4; **9c**, 26306-02-5; **9d**, 26305-80-6; **10a**,

(12) Purchased from the Pierce Chemical Co., Rockford, Ill., and distilled before use.

(13) Obtained from Merck Sharp and Dohme of Canada, Ltd., Montreal.

(14) Obtained from Peninsular ChemResearch, Inc., Gainesville, Fla.

(15) 2-Bromoethanol, 3-bromopropanol, 6-chlorohexanol, 3-bromopropionic acid, 6-bromohexanoic acid, and 11-bromoundecanoic acid were purchased from the Eastman Kodak Co., Rochester, N. Y. 10-Chlorodecanol and 3-bromobutyric acid were obtained from K & K Laboratories, Inc., Plainview, N. Y., 10-bromodecanoic acid from Chemicals Procurement Laboratories, Inc., College Point, N. Y., and iodoacetic acid from the Aldrich Chemical Co., Milwaukee, Wis.

(16) F. L. M. Pattison and J. J. Norman, *J. Amer. Chem. Soc.*, **79**, 2311 (1957).

(17) The M − H ion was characteristic of the TMS derivatives of all of the haloalcohols examined. The molecular ions of these compounds were often absent and always less intense than the M − H ion except in the iodides.

(18) The relative intensities are not corrected for the overlap which occurs among M + H, M, and M − H ions. The observed pattern for **10b** was 277 (0.20), 278 (0.08), 279 (0.39), 280 (0.10), 281 (0.12%).

26305-81-7; **10b**, 26305-82-8; **10c**, 26305-83-9; **10d**, 26305-84-0.

Acknowledgment.—This work was supported by the National Institutes of Health (GM 13901) and the Robert A. Welch Foundation (Q-125), and computer facilities by NIH Grant RR 259. E. W. is grateful to the Robert A. Welch Foundation for postdoctoral financial support. We are indebted to Miss P. F. Crain and Mr. K. Lyman for determination of some of the mass spectra.

Reaction of Ethyl Azidoformate with Dimethyl- and Diethylketen-*N*-(*p*-tolyl)imine

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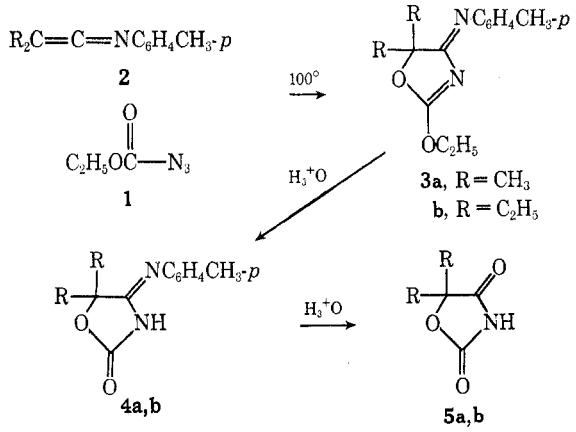
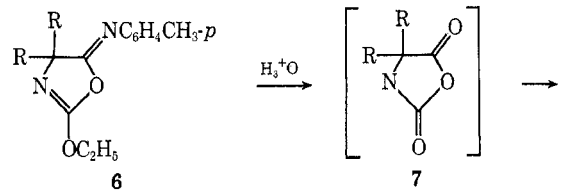
Received February 9, 1970

The formation of heterocyclic ring systems from cycloaddition reactions of ketenimines has recently received attention.[1,2] Since detailed studies on carbethoxynitrene from ethyl azidoformate have been reported,[3,4] and a variety of methods for preparing ketenimines are available,[5-7] the previously unreported cycloaddition reaction of ethyl azidoformate with two ketenimines was investigated. Reaction occurred under thermal but not photolytic conditions.

Thermolysis of a mixture of ethyl azidoformate (**1**) and ketenimines (**2a** or **2b**) at 100° led to the formation of the corresponding 4-*N*-(*p*-tolyl)imino-2-ethoxy-2-oxazolines (**3**) in 70% yields. The products were isolated by distillation at 0.01 mm; analyses and spectral data were consistent with structure **3**.



Mild acid hydrolysis of the adducts **3a,b** gave the tautomeric oxazolidinones **4a,b**; the latter compounds were isolated directly when the crude thermolysis products were chromatographed on neutral alumina. Vigorous acid hydrolysis of **4a,b** gave 5,5-dimethyl-2,4-oxazolidindione (**5a**), identified by comparison with an authentic sample, and 5,5-diethyl-2,4-oxazolidindione (**5b**), identified by comparison of spectral and physical data reported in the literature.[8] This hydrolytic sequence establishes the 4-imino structure **3** of the adducts as opposed to the alternate 5-imino oxazolidinones (**6**). Hydrolysis of the latter would lead to the 2,5-oxazolidinediones (**7**) which are unstable under the conditions used and would be subject to further degradation.[9]



6 **7**

The formation of the adducts **3** suggests that the adducts may arise by rearrangement of an acyltriazoline or aziridine. In view of the polarity of a ketenimine, cycloaddition of singlet carbethoxynitrene would be expected to give **6** rather than **3**.

Experimental Section

Melting points are uncorrected. Elemental analyses and molecular weight determinations were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared absorption spectra were obtained with a Perkin-Elmer spectrophotometer, Model 337. The nmr spectra were determined on a JOEL Company 100 Mc nmr. Chemical shifts are given in δ (ppm) downfield from TMS as an internal standard. The uv spectra were run on a Beckman DK-2A spectrophotometer. Ethyl azidoformate was prepared and purified as previously reported.[3] The 5,5-dimethyl-2,4-oxazolidinedione was purchased from Chemical Procurement Laboratories, Inc.

Preparation of Dimethyl- and Diethylketene-*N*-(*p*-tolyl)imine (2a, 2b).—The ketenimines (**2**) were prepared according to the method of Stevens and French[5] from the corresponding imidoyl chlorides in 65% yields. Proof of structure was accomplished by ir, nmr, and hydrolysis to the corresponding amides. Dimethylketene-*N*-(*p*-tolyl)imine (**2a**) had a bp of 63–65° (0.05 mm) [lit.[5] 64–65° (0.05 mm)]: nmr (neat) δ 7.03 (m, 4 H), 2.18 (s, 3 H), 1.61 (s, 6 H). Diethylketene-*N*-(*p*-tolyl)imine (**2b**) had a bp of 62–64° (0.01 mm): nmr (neat) δ 7.07 (m, 4 H), 2.19 (s, 3 H), 1.97 (quartet, 4 H), 1.01 (t, 6 H).

Preparation of 2-Oxazolines (3a and 3b).—A mixture of ethyl azidoformate (5.5 g, 0.047 mol) and dimethylketene-*N*-(*p*-tolyl)imine (8.05 g, 0.047 mol) was placed in an oil bath at 100 ± 1°. The mixture was stirred, and after 24 hr, it was cooled to room temperature. Distillation *in vacuo* gave 8.2 g (70%) of light yellow liquid, bp 103–104° (0.01 mm). This material was placed in a refrigerator and after 4 hr it solidified. The solid was low melting and could not be recrystallized. A second distillation gave an analytical sample of the 2-oxazoline (**3a**): uv max (cyclohexane) 283 mμ (ϵ −9530) and conjugated aromatic band 207 mμ (ϵ −13,000); ir (neat) 1710 (C=N exocyclic) and 1675 (C=N cyclic); nmr (DMSO-d_6) δ 7.04 (m, 4 H), 4.35 (quartet, 2 H), 2.24 (s, 3 H), 1.53 (s, 6 H), 1.27 (t, 3 H). *Anal.* Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.36; N, 11.37. Found: C, 68.16; H, 7.10; N, 11.10.

The procedure was repeated for the reaction with diethylketene-*N*-(*p*-tolyl)imine. Distillation *in vacuo* gave a 70% yield

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