Table I

MX_2	$(R^2S)_2$	Crude Bz-Leu-Gly-OEt Yield, %	Crude Bz-Leu-Gly-OEt $[\alpha]^{20}D$, deg[a]	Crude Bz-Leu-Gly-OEt L isomer, %
Di-*p*-anisylmercury	$(p\text{-}ClC_6H_4S)_2$	88	−30.5	90
Di-*p*-anisylmercury	$(o\text{-}O_2NC_6H_4S)_2$	92	−32.4	95
2*p*-Anisylmercuric bromide	$(o\text{-}O_2NC_6H_4S)_2$	92	−32.0	94

[a] *c* 3.1, EtOH.

effective in maintaining optical purity, but phenol (75%, 0% L isomer), *p*-nitrophenol (90%, 11% L isomer), and pivalic acid[5] (57%, 39% L isomer) were ineffective.

In reactions of type B, HCl is produced along with the peptide by the reaction of the supposed key intermediate of acyloxyphosphonium salt $(Ph_3P^+OCOR^1)^-SR^2$, ethyl glycinate, and mercuric chloride. Therefore, a basic substance such as triethylamine must be used as a HCl scavenger.

In order to eliminate bases from the reaction system, reactions were tried using various kinds of metal compounds in place of the metal halide and triethylamine. These compounds should yield mercaptides and chemical species which are not concerned with the deprotonation.

For this purpose, two kinds of metal compounds can be considered, namely (a) mercuric salts of urea, succinimide, *p*-nitrophenol, etc., and (b) di-*p*-anisylmercury and *p*-anisylmercuric bromide. It was found that the former group of compounds rapidly affords mercaptides on treatment with triphenylphosphine and disulfide probably through the direct attack of the R^2S^- anion of the phosphonium salt produced, while the latter compounds can react only with R^2SH to yield mercaptides and anisole, but cannot react with the R^2S^- anion.

In the cases of group a compounds (MX), the acyloxyphosphonium mercaptide readily reacts with the metal compounds to produce metal mercaptides and the second acyloxyphosphonium salts by the reference anion exchange. The stabilities of X^- anions involved in the salts would be expected to have a great effect on racemization and, in accordance with this, the optical purity increased as the X^- anion stability increased, except in the case of N-hydroxysuccinimide: mercuric salt of urea, 81% yield (23% L isomer); succinimide, 91% (46% L isomer); phthalimide, 85% (47% L isomer); *p*-nitrophenol, 82% (51% L isomer); 2,4-dinitrophenol, 92% (73% L isomer); N-hydroxysuccinimide, 89% (59% L isomer).

More favorable results were obtained by the use of group b compounds as shown in Table I.

In a typical experiment, ethyl glycinate (10 mmol) in methylene chloride was added at room temperature to a stirred mixture of equimolar amounts of di-*p*-anisylmercury, triphenylphosphine, di-*o*-nitrophenyl disulfide, and N-benzoyl-L-leucine in methylene chloride. After stirring for 2 days, the precipitated mercury mercaptide was filtered off and the solvent was evaporated *in vacuo*. From the residue, Bz-Leu-Gly-OEt was separated by chromatography on silica gel, 2.94 g (92%), mp 142–148°, $[\alpha]^{20}D$ −32.4° (*c* 3.1, EtOH), and was recrystallized from ethyl acetate–petroleum ether (bp 30–50°), mp 156–157°, $[\alpha]^{20}D$ −34.2° (*c* 3.1, EtOH).

The high optical purity obtained in the above experiment may due to the absence of oxazolone formation. In this reaction system the intermediate acyloxyphosphonium salt is attacked only by ethyl glycinate to produce the peptide and R^2SH which yields mercaptide and anisole by reaction with mercuric compounds. Since anisole is produced directly by the protonation of R^2SH to the mercuric compound, anisyl anion is absent during this mercaptide formation reaction and oxazolone formation can be prevented.

Teruaki Mukaiyama, Rei Matsueda
Hiroshi Maruyama, Masaaki Ueki
Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo, Japan
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Carbon Skeletal Rearrangement of Butene Ions

Sir:

The lability of the double bond in alkene ions, as suggested by the similarity of the mass spectra of isomeric C_4H_8 compounds,[1] has been well known for some time. The migration is usually written as a hydrogen randomization involving a 1,2 and/or a 1,3 hydride or hydrogen atom shift.[2] The randomness of deuterium atom retention in $C_3(H,D)_5^+$ from 1-butene-4-d_3 ion near its appearance potential excludes a pure 1,3-shift mechanism,[3] a conclusion supported by the mass spectrum of 2-butene-1,4-d_2 at a nominal ionizing voltage of 70 V.[4] The mass spectra of specifically deuterium-labeled pentenes can also be interpreted by a series of 1,2 shifts competing with dissociation without the participation of cyclic intermediates.[4] However, the mechanism of the deuterium atom randomization has not been established, and the possibility that carbon atom migration contributes has not been investigated.

We have examined this question using 1-butene-4-d_3 and 1-butene-4-^{13}C, prepared by the method of Regier and Blue.[5] The mass spectra of these compounds were determined on an Atlas CH4 mass spectrometer at 0.2-V intervals of nominal electron accelerating potentials between 9.0 and 15 V. Representative results for the deuterated compound are given in Table I; relative abundances compare well with those reported by Bryce and Kebarle,[3] confirming the conclusion that the hydrogens randomize. In our investigation the mass values shown in Table I can

(1) Catalog of Mass Spectra Data, American Petroleum Institute Project 44, Texas A&M College, College Station, Texas, 1964.
(2) K. Biemann, "Mass Spectrometry-Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 83; H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 55.
(3) W. A. Bryce and P. Kebarle, *Can. J. Chem.*, **34**, 1249 (1956).
(4) B. J. Millard and D. F. Shaw, *J. Chem. Soc., B*, 664 (1966).
(5) R. B. Regier and R. W. Blue, *J. Org. Chem.*, **14**, 505 (1949).

Table I. Distribution of $C_3(H,D)_5^+$ Ions from $CD_3CH_2CHCH_2$

m/e	Ion	% expected from 1,3 shift	% expected, random	% observed at nominal ionizing voltage[a] 9.9 V	10.5 V	11.1 V	11.5 V	13.1 V[b]	13.0 V[c]
41	$C_3H_5^+$	12.5	1.8	5.5	6.3	7.3	8.1	12.4	9.1
42	$C_3H_4D^+$	37.5	26.8	26.9	26.3	25.7	25.5	25.3	27.3
43	$C_3H_3D_2^+$	..	53.6	48.5	47.9	46.8	45.9	40.9	45.3
44	$C_3H_2D_3^+$	50.0	17.8	19.1	19.7	20.2	20.5	21.4	18.1

[a] Calibration of the energy scale with Xe indicates that these voltages differ less than 0.3 V from the most probable value of the electron energy distribution. [b] At this energy unlabeled 1-butene shows 5.9% of the ions in this group to be $C_3H_3^+$ and $C_3H_4^+$. [c] Reference 3.

be almost entirely associated with $C_3(H,D)_5^+$ ions since the mass spectra of unlabeled 1-butene show that the intensities of neighboring mass peaks are less than 5% of that at *m/e* 41 at nominal energies less than 11.5 eV. Formation of the $C_3H_5^+$ ion at these energies is observed even though its appearance potential is 11.4 eV[6] because of the exponential high-energy tail of the electron energy distribution, whose width at half-height was 0.65 eV.

The participation of skeletal rearrangement in the randomization would lead to a loss of carbon identity as well. When 1-butene-4-^{13}C with an isotopic purity of 38.5% was subjected to electron bombardment, the resultant $C_3H_5^+$ ion contained 28.5% ^{13}C at ionizing voltages where other fragment ions did not contribute materially. This abundance corresponds to 75% retention of the ^{13}C label in the allyl ion, demonstrating loss of carbon identity and rearrangement of the carbon skeleton. Methyl loss involving solely the terminal carbons would lead to a retention of only 50% of the label in the $C_3H_5^+$ ion.

The early work of Rylander and Meyerson[6] suggests the methylcyclopropane cation as the intermediate responsible for the skeletal randomization. Thermodynamic arguments would also lead one to prefer this entity since rearrangement of 1-butene ion to that structure requires only 0.83 eV while formation of the cyclobutane ion demands 1.2 eV.[7] Wagner[8] suggested a substituted cyclopropane ion structure to account for the radiation-induced skeletal isomerization of solid pentenes and hexenes at 77 °K. Lastly, fragmentation of propene-1-^{13}C to $C_2H_3^+$ induced by 75-eV electrons is preceded by *ca.* 25% skeletal isomerization.[9] This evidence strongly supports a sequence of 1,3 ring closures to methylcyclopropane ion and reopenings as the mechanism for loss of carbon atom identity and much of the hydrogen atom randomization. It obviates the necessity to invoke an unattractive series of 1,2 hydrogen atom or hydride shifts.

The tendency toward decreasing deuterium randomization with increasing electron energy suggested by Bryce and Kebarle[3] appears to be supported by the data in Table I, whose trend could not be materially affected by any plausible correction for labeled $C_3H_3^+$ and $C_3H_4^+$.[10] Similarly, ^{13}C retention in the $C_3H_5^+$ ion from butene-1-^{13}C is decreased to 69% at a nominal ionizing voltage of 15.1 V. Even the maximum reasonable correction for contributions of labeled $C_3H_4^+$ to the peak at *m/e* 41 leads to a calculated retention of only 70% at that energy. The rate of fragmentation thus appears to become competitive not only with that of deuterium atom migration but also with that of skeletal rearrangement at higher excitation energies of the precursor ion.

(6) P. W. Rylander and S. Meyerson, *J. Am. Chem. Soc.*, **78**, 5799 (1966).
(7) G. G. Meisels, J. Y. Park, and B. G. Giessner, 16th Annual Meeting on Mass Spectrometry, Pittsburgh, Pa., May 1968.
(8) C. D. Wagner, *J. Phys. Chem.*, **71**, 3445 (1967).
(9) H. H. Voge, C. D. Wagner, and D. D. Stevenson, *J. Catalysis*, **2**, 58 (1963).
(10) S. Meyerson, *J. Chem. Phys.*, **34**, 2046 (1961).

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G. G. Meisels, J. Y. Park, B. G. Giessner
Department of Chemistry, University of Houston
Houston, Texas 77004
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A New Method of Forming the Carbon–Silicon Bond. Reductive Silylation of Carbonyl Compounds

Sir:

In a previous communication[1] we described some aspects of the reducing power exhibited by the trichlorosilane–tertiary amine combination. In the course of further experiments with this reagent system, we have observed a novel reaction in which certain carbonyl compounds like aromatic ketones, aldehydes, and acid chlorides can be converted in excellent yields to organosilicon derivatives, *via* replacement of the carbonyl oxygen. One of the important aspects of this discovery is that it constitutes an entirely new preparative method for forming a carbon–silicon bond. The over-all process, "reductive silylation," can be represented by eq 1.

$$R'\overset{\overset{O}{\|}}{C}R'' + 2HSiCl_3 + R_3N \rightarrow R'\underset{\underset{H}{|}}{\overset{\overset{SiCl_3}{|}}{C}}R'' + R_3N\cdot HCl + (1/x)(SiCl_2O)_x \quad (1)$$

I

Thus, when equimolar quantities of benzophenone and tri-*n*-propylamine were combined with 3 equiv of trichlorosilane, a vigorously exothermic reaction ensued. After refluxing for 1 hr at 55–75° and treating the mixture with pentane, tri-*n*-propylamine hydrochloride (99%), melting at 136–138°, precipitated. Distillation of the filtrate afforded (95%) benzhydryltrichlorosilane (bp 141–145° (2.5 mm); mp 48–49°[2] after glpc purification). The distillation residue was a resinous material (suggesting

(1) R. A. Benkeser and W. E. Smith, *J. Amer. Chem. Soc.*, 90, 5307 (1968).
(2) This compound has been reported as melting at 55–56°. See E. A. Chernyshev and N. G. Tolstikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 7, 1223 (1962).