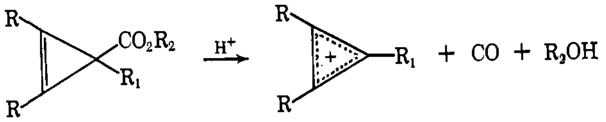
Breslow[2] demonstrated the further value of the reaction. We now show that a yet simpler and more powerful modification of the decarbonylation conditions permits the preparation of the parent cyclopropenium ion IIc and its mono- (IId) and dimethyl (IIe) derivatives from the corresponding esters Ic–e.



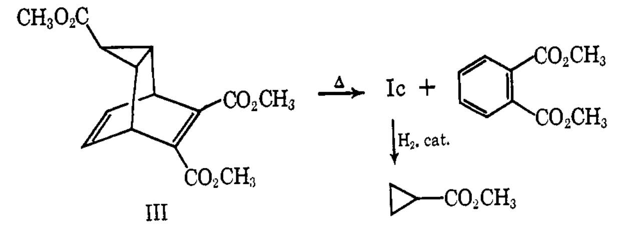
I II

a, R = $C_6H_5$; $R_1$ = H; $R_2$ = H
b, R = $C_3H_7$; $R_1$ = H; $R_2$ = H
c, R = H; $R_1$ = H; $R_2$ = $CH_3$
d, R = H; $R_1$ = $CH_3$; $R_2$ = $C_2H_5$
e, R = $CH_3$; $R_1$ = H; $R_2$ = $C_2H_5$

Solution of ethyl 1,2-dimethylcyclopropene-3-carboxylate (IIe)[3] in 25% sulfur trioxide in sulfuric acid or, more simply, in chlorosulfonic or fluorosulfonic acid at room temperature, proceeded with gas evolution and the formation of dimethylcyclopropenium ion in solution in near-quantitative yield as judged from the appearance of characteristic peaks at $\tau$ 6.96 (singlet, area 6.0) and $-0.04$ (singlet, area 1.0).[4] The ion could be precipitated in low yield from chlorosulfonic acid as the hexachloroantimonate by the addition of 10% antimony pentachloride in acetyl chloride followed by dilution with ether. The colorless crystalline salt thus obtained ($\lambda_{\max}^{\text{Nujol}}$ 3.20, 5.55 $\mu$. *Anal.* Found: C, 15.01; H, 1.76; Cl, 51.96) was identical with that obtained in 75% yield by reaction of 1,2-dimethylcyclopropene-3-carboxylic acid (mp 76.5–77.5°; $\lambda_{\max}^{\text{CHCl}_3}$ 2.9–4.0, 5.25, 5.95 $\mu$. *Anal.* Found: C, 64.30; H, 7.18) with 10% antimony pentachloride in acetyl chloride at 0° (*cf.* ref 1). The salt was converted to the ether by shaking it with aqueous sodium bicarbonate and ether. When the ethereal solution thus obtained was extracted with sulfuric acid, the strong peaks characteristic of dimethylcyclopropenium ion appeared in the nmr spectrum of the acid solution.

When a solution of ethyl 3-methylcyclopropene-3-carboxylate[5] in methylene chloride was added to cold, well-stirred chlorosulfonic acid, gas evolution was evident. The nmr spectrum of the resultant solution exhibited strong peaks at $\tau$ $-0.58$ and 6.87[4] in area ratio 2.0:3.0 for the methylcyclopropenium ion IId. The rest of the spectrum was quite clean, exhibiting only multiplets for the ethyl group at $\tau$ 5.4 and 8.5 in addition to solvent peaks.

Although the very unstable methylcyclopropene-3-carboxylate Ie has not been reported as isolated in pure form, Doering[6] has obtained evidence for its presence in the pyrolysate of Diels–Alder adduct III by low-temperature hydrogenation to the methylcyclopropanecarboxylate. Passage of the effluent vapors from pyrolysis of III in a helium stream into cold ($-40$ to $-70°$) chlorosulfonic or fluorosulfonic acid gave clear solutions which evolved gas on warming. The nmr spectra of these solutions were quite complicated, but in addition to peaks characteristic of solvents and dimethyl phthalate, a persistent sharp singlet at $\tau$ $-0.80$ appeared. Blank solutions containing either adduct III or dimethyl phthalate in the acids gave no gas evolution on warming and gave no nmr resonance near $\tau$ $-0.80$.



The species responsible for this peak was very stable in chlorosulfonic acid, since the solutions could be evaporated by heating under vacuum to a syrup with reappearance of the nmr peak upon dilution to the fluid stage. The chemical consistency of our results as well as the agreement of the resonance peak at $\tau$ $-0.80$ with that observed by Breslow for solutions of cyclopropenium hexachloroantimonate in fluorosulfonic acid ($\tau$ $-0.87$)[7] suggest that this species is the cyclopropenium ion (IIc).

**Acknowledgments.** We are pleased to acknowledge support of this work by the Petroleum Research Fund administered by the American Chemical Society under Grant 742-A-4 and the National Science Foundation under Grant GP 6378. We also appreciate valuable early discussions with Professor M. J. Goldstein.

---

(2) R. Breslow and H. Höver, *J. Am. Chem. Soc.*, **82**, 2644 (1960).

(3) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); R. G. Silberman, M.S. Thesis, Cornell University, 1963.

(4) Nmr spectra are referenced to internal tetramethylammonium tetrafluoroborate taken as $\tau$ 6.87.

(5) M. J. Jorgensen and C. H. Heathcock, *J. Am. Chem. Soc.*, **87**, 5264 (1965). We are grateful to Dr. Jorgensen for a sample of the ester.

(6) W. von E. Doering, G. Laber, R. Bonderwahl, N. F. Chamberlain, and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956); R. Gevirtz, Ph.D. Thesis, Cornell University, 1965.

(7) R. Breslow, J. T. Groves, and G. Ryan, *J. Am. Chem. Soc.*, **89**, 5048 (1967).

(8) Fellow of the Alfred P. Sloan Foundation 1962–1965. Address correspondence to Department of Chemistry, Michigan State University, East Lansing, Mich. 48823.

**D. G. Farnum,[8] G. Mehta, R. G. Silberman**
*Department of Chemistry, Cornell University*
*Ithaca, New York 14850*
*Department of Chemistry, Michigan State University*
*East Lansing, Michigan 48823*

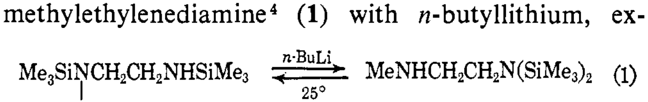
*Received July 31, 1967*

---

## New Anionic Rearrangements. VI.[1] Condensation of Organosilylethylenediamines to Silaimidazolidines[2]

*Sir:*

A new condensation reaction has been discovered in experiments designed to extend our studies of the 1,2-anionic rearrangement of organosilylhydrazines[1,3] to 1,4 systems. We treated N,N′-bis(trimethylsilyl)-N-methylethylenediamine[4] (1) with *n*-butyllithium, ex-



$$\underset{\text{Me}}{\text{Me}_3\text{Si}\underset{|}{\text{N}}\text{CH}_2\text{CH}_2\text{NHSiMe}_3} \underset{25°}{\overset{n\text{-BuLi}}{\rightleftharpoons}} \text{MeNHCH}_2\text{CH}_2\text{N(SiMe}_3)_2 \quad (1)$$

1 2

---

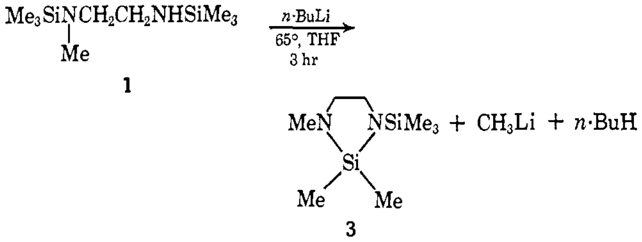
(1) Previous paper in this series: R. West and M. Ishikawa, *J. Am. Chem. Soc.*, **89**, 4981 (1967).

(2) Research sponsored by Air Force Office of Scientific Research (SRC), O.A.R., U.A.S.F. Grant No. AF-AFOSR 1061-66.

(3) R. E. Bailey and R. West, *J. Am. Chem. Soc.*, **86**, 5369 (1964); R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966); **89**, 4068, 4072 (1967).

(4) Satisfactory elemental analyses for C, H, Si, and N were obtained for all compounds described in this communication.

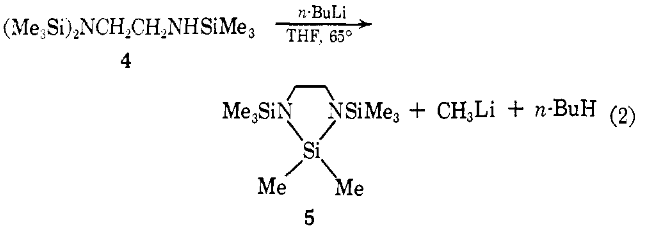
pecting to observe rearrangement to the N,N-bissilyl isomer **2**. When little or no rearrangement was found at 25° in ether, the reaction was repeated in tetrahydrofuran at 65°. Under these conditions, a quite unexpected condensation took place, with the formation of a silamidazolidine ring and *elimination of methyllithium.*



In a typical experiment 21 ml of 1.8 *M* *n*-butyllithium in cyclohexane was added to 8 g (0.037 mole) of **1** dissolved in 30 ml of tetrahydrofuran, with cooling to −70°. Butane is evolved immediately as **1** is converted to its N-lithio derivative. The mixture was slowly warmed to room temperature and then heated to 65° to reflux for 48 hr. The mixture was cooled and pyrrole (2.5 g) was added as a protonating agent. Solvents were removed and the product was obtained by fractional distillation as a colorless liquid, bp 80–83° (22 torr), $n^{22}\text{D}$ 1.4413, yield 6.5 g (81%). The proton nmr spectrum showed sharp peaks at $\tau$ 7.55, 9.94, and 9.89 with relative intensity 1:2:3 attributed to N–C$H_3$, >Si-(C$H_3$)$_2$, and –Si(C$H_3$)$_3$ protons, respectively, as well as a complex pattern attributed to the methylene bridge protons at $\tau$ 6.84–7.35.

The methyllithium by-product was identified qualitatively by its nmr spectrum and quantitatively by protonation with pyrrole to give methane. The condensation reaction also takes place with *catalytic* quantities of *n*-butyllithium; in this case methane is evolved continuously as silaimidazolidine formation takes place.

The nature of the condensation product was confirmed by carrying out the reaction using N,N,N′-tris-(trimethylsilyl)ethylenediamine (**4**) to give the known[5] compound 1,3-bis(trimethylsilyl)-2,2-dimethyl-2-silaimidazolidine (**5**). The properties of **5** obtained in this reaction are fully consistent with the proposed structure and agree with those reported for the same substance by Kummer and Rochow.[5]



The condensation reaction can be viewed as taking place by nucleophilic attack of the anionic amide nitrogen on silicon, perhaps with simultaneous electrophilic attack on methyl carbon by lithium cation.[6] The surprising fact about this condensation reaction is that a C–Li bond in methyllithium is formed from an N–Li bond in the N-lithioethylenediamine. The C–Li bond is expected to be much less stable than N–Li, so other factors, as yet unidentified, must more than compensate for the energy gain involved in the formation of methyllithium from N-lithioethylenediamine.

Later experiments showed that the rearrangement indicated in eq 1 does in fact take place. No rearrangement was observed starting with **1** only because equilibrium in this particular reaction lies >95% toward **1**. If **2** is the starting material nearly complete rearrangement is observed. Moreover, the anionic rearrangement of N-silylethylenediamines appears to be a general reaction.[7] Numerous examples which have been studied in our laboratories will be described in forthcoming papers.[8]

**Acknowledgment.** The authors thank the U. S. Educational Commission/Japan for a travel grant to M. I.

---

[5] D. Kummer and E. G. Rochow, *Z. Anorg. Allgem. Chem.*, **321**, 21 (1963).

[6] High-temperature condensation reactions leading to silaimidazolidines have been described by Fink, and these reactions may be related mechanistically to the condensations described here. See W. Fink, *Ber.*, **99**, 2267 (1966).

[7] M. Ishikawa and R. West, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967, Paper L-132.

[8] The silylethylenediamine rearrangements provide the first examples of anionic rearrangement between N atoms in diamines and can be viewed as a new class of Smiles rearrangements.[9]

[9] J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 362 (1951).

**Robert West, Mitsuo Ishikawa**
*Department of Chemistry, University of Wisconsin*
*Madison, Wisconsin 53706*

*Received June 26, 1967*

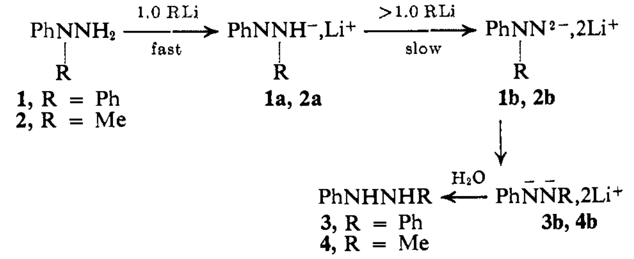
---

## New Anionic Rearrangements. VII.[1] Rearrangement of Dianions of Arylhydrazines[2]

*Sir:*

The 1,2-anionic rearrangement of organosilylhydrazines, in which organosilyl groups migrate from one nitrogen atom to the other, has been described in a series of recent papers.[1,3,4] We now wish to report the base-catalyzed, 1,2 migration of the phenyl moiety in two phenylhydrazines. However, these rearrangements are strikingly different from the silylhydrazine rearrangements.

When up to 1 equiv of an alkyllithium compound is added to 1,1-diphenylhydrazine (**1**) or 1-phenyl-1-methylhydrazine (**2**), rapid proton transfer takes place to give the monoanion of the hydrazine (as its lithium salt). The monoanions **1a** and **2a** do *not* rearrange even on long heating at temperatures up to 100° in bis-



---

[1] Previous paper in this series: R. West and M. Ishikawa, *J. Am. Chem. Soc.*, **89**, 5049 (1967).

[2] Research sponsored by Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. AF-AFOSR-1061-66.

[3] R. E. Bailey and R. West, *J. Am. Chem. Soc.*, **86**, 5369 (1964); R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966); **89**, 4068 (1967); R. West and M. Ishikawa, *ibid.*, **89**, 4981 (1967).

[4] R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4072 (1967).