

IV. SILYLATION STUDIES OF 3-BUTYNOIC ACID
 AND 2,3-BUTADIENOIC ACID

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In conjunction with our studies outlined in preceding communications, of the treatment of 2-butyneic acid with various strong bases followed by silylation, we also investigated the isomeric acids 3-butyneic acid¹(1) and 2,3-butadienoic acid(2) (allenic acid),² under similar conditions (Table I). Acid 1 and 2 equiv of lithium diisopropylamide (LDA) treated with chlorotrimethylsilane (CTMS) gave the unrearranged silylation product 3.³ Substitution of acid 2 for 1 also gave compound 3. ¹H¹NMR(CCl₄) δ0.15(S,9H), 0.28(S,9H), 3.2(S,2H); IR(neat) 2200(C≡C), 1730 cm⁻¹(C=O). Surprisingly, this relationship between compounds 1 and 2 was found throughout the investigation.

Table I

3-Butyneic Acid and 2,3-Butadienoic Acid Treated with Base and CTMS^a

<u>Acid</u>	<u>Base</u>	<u>Product</u>	<u>Yield, %^a</u>
HC≡CCH ₂ CO ₂ H (<u>1</u>)	2LDA	Me ₃ SiC≡CCH ₂ CO ₂ SiMe ₃ (<u>3</u>) ^b	67
or			
CH ₂ =C=CHCO ₂ H (<u>2</u>)			
<u>1</u> , <u>2</u>	4LDA	(Me ₃ Si) ₂ C=C=C(SiMe ₃)CO ₂ SiMe ₃ (<u>4</u>)	60
<u>1</u>	4LDA	Me ₃ SiC≡C-C=C(OSiMe ₃) ₂ (<u>5</u>) SiMe ₃	unstable ^c
<u>1</u> , <u>2</u>	2 BuLi-TMEDA	H ₂ C=C=CHCO ₂ SiMe ₃ (<u>6</u>)	80

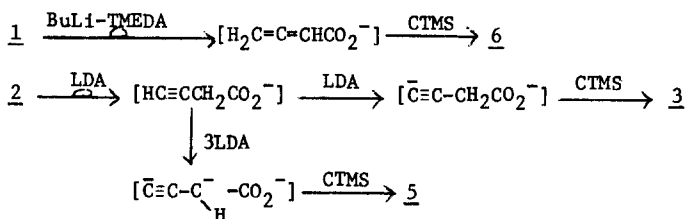
a. See ref. 4.

b. See ref. 3.

c. See ref. 6.

Acid 1 and 4 equiv of LDA with CTMS at -78°, allowed to warm to room temperature,⁴ gave the polysilylated product 4.⁵ Acid 1 and 4 equiv of LDA with CTMS at -78°, allowed to warm to zero degrees only, gave the polysilylated ketene ketal compound 5. It rearranged⁶ on standing at room temperature to give compound 4.

Unexpectedly, acid 1 and 2 BuLi-TMEDA with CTMS (-78°, room temp 1 hr) gave mainly the monosilylated compound trimethylsilyl allenate (6).⁷ When a large excess (7 equiv) of base was used compound 6 was still the only product. Allenic acid (2) as starting material behaved the same. These results are interpreted in the following way:



That is, BuLi-TMEDA brings about the rearrangement of the anion of 1 to the anion of 2⁸ while LDA does the opposite. The anion of 2 is stable to strong base but protons can be abstracted stepwise from the anion of 1.

Acknowledgment:

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References:

1. I. Heilbron, E. R. H. Jones and F. Sondheimer, J. Chem. Soc., 606 (1949).
2. G. Eglinton, E. R. H. Jones, G. H. Mansfield and M. C. Whiting, ibid, 3197 (1954).
3. Compound 3, in the crude reaction mixture, underwent change on standing at 0° for approximately 1 week.
4. Experimental conditions and procedures similar to those recorded in preceding communications.
5. This compound was also obtained by the polysilylation of 2-butynoic acid using BuLi-TMEDA as base and recorded in a preceding communication.
6. Although compounds 4 and 5 had different GLC retention times we were not able to isolate 5 free of 4. Initially the IR spectrum showed double and triple bond absorptions which were lost, on standing at room temperature, with corresponding increase of allenic absorption. The NMR data were consistent with the conversion of 5 to 4. The rearrangement of 5 may be 6-centered.
7. A small amount of disilylated product was observed.
8. The isomerization of 3-butynoic acid with potassium carbonate has been reported -- ref. 2.

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