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# II. SILYLATION OF POLYANIONS OF 2-ALKYNOIC ACIDS

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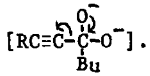
In the preceding communication we recorded that the selective γ-alkylation/silylation of 2-butynoic acid was attained using the base n-butyllithium and tetramethylethylenediamine (BuLi-TMEDA), and that α-alkylation resulted via the base lithium diisopropylamide (LDA). We now report a study of the possible extension of this regiospecificity using the substituted acetylenic acids 2-pentynoic acid (1) and 4-methyl-2-pentynoic acid (2) and the agent chlorotrimethylsilane (CTMS).

Surprisingly, acids 1 and 2 with BuLi-TMEDA in tetrahydrofuran (THF) followed by CTMS, did not silylate regularly but underwent an addition-cleavage reaction in 50 and 70% yields, respectively.

$$RC{\equiv}C\text{-}CO_2H \xrightarrow[\text{pentane, -78°}]{\text{2BuLi-TMEDA/CTMS}} RC{\equiv}C\text{-}SiMe_3 + BuCO_2SiMe_3 \qquad R = Et,\ isoPr$$

Presumably the initial adduct[1] was cleaved in the following way  $[RC{\equiv}C\text{-}\overset{O^-}{\underset{Bu}{C}}\text{-}O^-]$. In addition to the cleavage products a small amount of mono, di and trisilylated compounds were formed.

Acid 1 with 3 equiv[2] of LDA gave a trisilylated product. Spectral data and solvolysis studies showed that the product is $Me_3Si(Me)C{=}C{=}C(SiMe_3)CO_2SiMe_3$, compound 3: $H^1NMR(CDCl_3)$ δ0.15(S,18H), 0.27(S,9H), 1.5(S,3H); IR(neat) 1950(C=C=C), 1730 $cm^{-1}$(C=O); mass spectrum m/e (rel intensity) 314($M^+$, 1.1), 228(52), 75(79), 73(100), 44(91.7). The formation of product 3 most likely involves isomerization followed by polyanion formation. Craig[3b] has reported the rapid transformation of $C_5$-$C_9$ 2-alkynoic acids to the corresponding 3-isomers.

$$\underline{1} \xrightarrow[\text{2. } H_3O^+]{\text{1.}NaNH_2} CH_3C{\equiv}C\text{-}CH_2CO_2H$$

Thus in our system the following transformations might be involved[4b].

$$CH_3CH_2C{\equiv}C\text{-}CO_2H \xrightarrow{3LDA} [CH_3C^-{=}C{=}C^-\text{-}CO_2^-] \xrightarrow{CTMS} \underline{3}$$

The dianion of acid 2, formed with LDA in THF and treated with CTMS, exclusively gave the α-silyl product $Me_2C{=}C{=}C(SiMe_3)CO_2SiMe_3$ (4) in 60% yield. Compound 4: $H^1NMR(CDCl_3)$ δ0.16(S,9H), 0.3(S,9H), 1.8(S,6H); IR(neat) 1950(C=C=C), 1730 $cm^{-1}$(C=O); mass spectrum m/e (rel intensity) 256($M^+$,9), 241(8), 147(51), 124(29), 94(14), 73(100).

$$Me_2CHC{\equiv}CCO_2H \xrightarrow[\text{-78°,THF}]{3LDA^2} [Me_2C{=}C{=}C^-\text{-}CO_2^-] \xrightarrow{CTMS} \underline{4}$$

A preliminary study was done to test the combination of LDA-TMEDA[5a,b] as a possible promoter of γ-alkylation. Compound 2 and LDA-TMEDA (1:1) in pentane gave GLC evidence of approximately 50% γ-isomer[6]. Apparently the explanation for this variation lies in the different ion pair reactivities.

Polysilylation of 2-butynoic acid was accomplished using 6 equiv of BuLi-TMEDA and gave a 70% yield of the allenic compound 5[7a]: $H^1NMR(CDCl_3)$ δ0.15(S,27H), 0.27(S,9H); IR(neat) 1940(C=C=C), 1730(C=O), 1410, 1310, 1250, 1230(Si-$CH_3$), 1050 $cm^{-1}$(Si-O, C-O).

$$CH_3C{\equiv}CCO_2H \xrightarrow[\text{pentane, }-78^\circ]{\text{6BuLi-TMEDA/CTMS}} \underset{\underline{5}}{(Me_3Si)_2C{=}C{=}C(SiMe_3)CO_2SiMe_3}$$

We undertook this investigation on the premise that dianions of 2-alkynoic acids would undergo silylation to give cumulogs[8] of trimethylsilylketene ketals[9] of the type $R_2C{=}C{=}C{=}C(OSiMe_3)_2$. Under our reaction conditions no products of this type were observed presumably because of high energy pathways for their formation.

Acknowledgment:

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References:

1. M. Jorgenson, Org. React., 18, 1 (1970).
2. Use of 2 equiv of LDA gave mainly monosilylation.
3. (a) J. C. Craig and M. Moyle, J. Chem. Soc., 4402 (1963).
   (b) Craig found that $C_5$-$C_9$ αβ-acetylenic acids having two γ-hydrogen atoms underwent rearrangement to their βγ-acetylenic isomers with sodamide in liquid ammonia -- ref 3a.
4. (a) G. A. Gornowicz and R. West. J. Am. Chem. Soc., 93, 1714 (1971).
   (b) There also exists the possibility that anion formation - silylation is stepwise. West[4a] has observed this in the polysilylation of acetonitrile. Thus in our system, by analogy, the dianion only would be formed initially followed by a mono anion after initial silylation.

   $$CH_3C{\equiv}C\text{-}\bar{C}HCO_2^- \xrightarrow{\text{CTMS}} CH_3C{\equiv}CCH(SiMe_3)CO_2SiMe_3 \xrightarrow{\text{LDA}} CH_3C{\equiv}C\text{-}C^-(SiMe_3)CO_2SiMe_3 \longrightarrow \underline{3}$$
5. (a) T. A. Whitney and A. W. Langer, Jr., U.S. Patent 3,787,496 (Chem Ab. 80, 82364k (1974)), claim that metalated amine complexes are displacement reagents in the formation of substituted aromatic compounds via benzyne intermediates.
   (b) P. L. Creger, J. Am. Chem. Soc., 92, 1396 (1970), reported that the combination LDA-THF-heptane formed the dianion of o-toluic acid. We found that LDA-THF and toluic acid formed a monoanion only and the hydrocarbon was necessary for dianion formation.
6. The retention times of the γ product and the α isomer 4 corresponded with those of the respective isomers from 2-butynoic acid.
7. (a) The product was most likely formed by stepwise silylation[7b]. It was not formed via rearrangement of 2-butynoic acid to 3-butynoic or allenic acids. See following communications.
   (b) T. L. Chwang and R. West, J. Am. Chem. Soc., 95, 3324 (1973).
8. First International Conference on Organic Synthesis, Louvain-la-Neuve, Belgium 1974.
9. C. Ainsworth and Y.-N. Kuo, J. Organomet. Chem., 46, 73 (1972).

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