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THE MONOMETALATION OF 3-BUTENENITRILE

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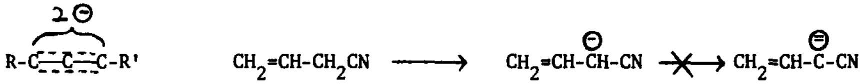
In our study on the metalation of 1,4-enynes we have shown$^{1)}$ that their mono- and dilithium derivatives can be easily obtained when n-butyllithium in ether was used as the metalating agent. Special stability was attributed to the dianions of the type I which were named sesquiacetylenes. We were interested to find out whether 3-butenenitrile (allylcyanide II), the cyano analogue of 1,4-enyne can follow the same pattern of behavior to produce the monoanion III$^{2)}$ and then, the dianion, the vinylsesquiazacetylene (IV)$^{2)}$.



$CH_2=CH-CH_2CN \longrightarrow CH_2=CH-\overset{\ominus}{C}H-CN \not\longrightarrow CH_2=CH-\overset{\ominus}{C}-CN$

I II III IV

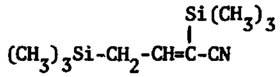
The metalation of the position α to a nitrile group was investigated$^{3-7)}$ under various conditions and the degree of metalation (mono- or polymetalation) was established on the basis of the analysis of the products from reactions of the respective anions with, for example, alkyl halides or carbonyl groups. However, in a recent publication,$^{8)}$ Gornowicz and West have shown that at least in some cases where n-butyllithium was used as the metalating agent, previous interpretations were incorrect and that the formation of dimetalation products was due to a secondary step of metalation after the reaction of the monoanion took place; therefore, a direct investigation of the reaction mixture is necessary in order to acquire the right information on the course of the reaction.

Early experiments on the metalation of II with n-butyllithium in hexane/THF or hexane/TMEDA failed to bring about positive results, because the reactions were very exothermic even at very low temperature (-100°) and led to polymerizations. When 2 equivalents of MeLi in ether/THF (Ca. 1.5M) were used to react with II at -100°, a smooth reaction occurred and an orange solution was formed after a few minutes. Subsequent treatment of this solution with either trimethylsilyl chloride (V) or benzyl bromide (VI) led to the formation of the "dimetalation" products VII and

VIII respectively (both in yields of 70-80%).

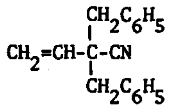
2,4-bis(trimethylsilyl)-2-butenenitrile (VII) was purified by GLC (SE 30, 15%, 2m at 160°); NMR (CCl_4): 6.51/t (j=8), 1H (vinyl); 2.09/3 (j=8), 2H (allylic); 0.21/s, 9H ($(CH_3)_3Si\text{-}\overset{|}{C}\text{=}$); 0.08/s, 9H ($(CH_3)_3Si\text{-}\underset{|}{\overset{|}{C}}\text{-}$). MS: M^+ 211 m/e and IR: 2250 cm^{-1} (nitrile group[9]).

2,2-dibenzyl-3-butenenitrile (VIII) m.p. 69° was purified by crystallization from hexane; NMR (CCl_4): 7.03/s, 10H (aromatic); 5.44/q (j_1=8, j_2=18), 1H (vinyl);4.91/d (j=8), 1H (olefinic) 4.90/d (j=18), 1H (olefinic); 2.73/s, 4H (benzylic). MS: M^+ 247 m/e and IR: 2245 cm^{-1} (nitrile group[9]).



$$(CH_3)_3Si\text{-}CH_2\text{-}CH\text{=}\overset{\overset{\displaystyle Si(CH_3)_3}{|}}{C}\text{-}CN$$

VII



$$CH_2\text{=}CH\text{-}\underset{\underset{\displaystyle CH_2C_6H_5}{|}}{\overset{\overset{\displaystyle CH_2C_6H_5}{|}}{C}}\text{-}CN$$

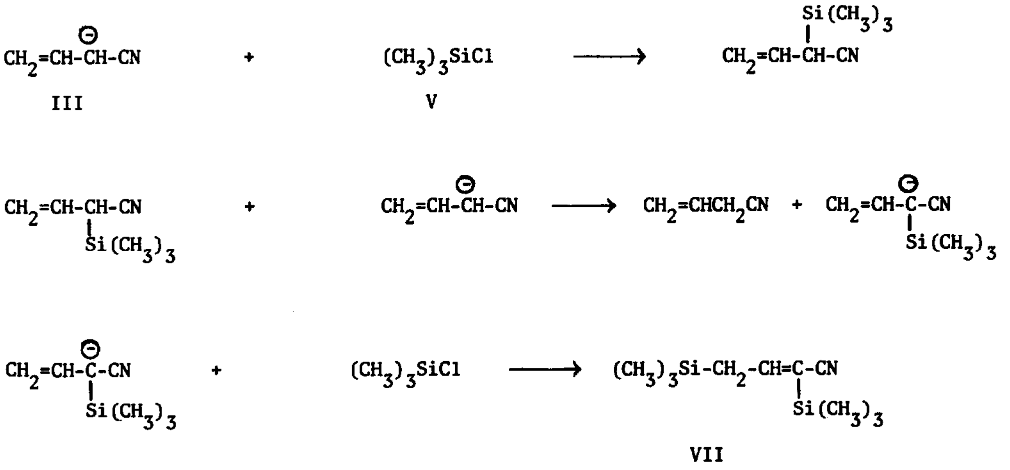
VIII

No products of monometalation were isolated from these reactions.

When II reacted with only 1 equivalent of MeLi and the resulting solution was then reacted with trimethylsilyl chloride, the starting material II and VII were produced in a 1:1 ratio (by NMR and GLC).

The NMR spectrum of the reaction mixture was recorded before the treatment with trimethylsilyl chloride, and while all the signals of the starting material disappeared two distinct regions of absorption were revealed. Two triplets are centered at δ 5.82 with j_1=17 Hz and j_2=10 Hz (one proton as was proved by the use of toluene as an internal standard) and the other absorption, a doublet, at δ 2.32 with j=10 Hz. There was no change in these absorptions when either an excess of MeLi was used in the reaction or after the addition, to the sample, of n-butyllithium in hexane. Also, we could not observe any change in the spectrum in the temperature range of -80 to +40°.

We have concluded that the species in the solution is the monoanion III, the absorption at δ 2.32 is that of the proton on carbon 2 while the source of the absorption at δ 5.82 is the proton on carbon 3. Only six lines appear in the spectrum of the last proton, this degeneracy is a result of similar coupling between the proton on carbon 3 with the proton on carbon 2 and the cis proton on carbon 4. Apparently most of the charge in III is located on the nitrogen[10] and the rotation in the C_3-C_4 bond is restricted in the temperature range studied. The same phenomenon was also observed in the monoanions generated from the 1,4-enynes[1]. The absorptions of the two terminal protons of III are masked by the signals of the solvent. The results indicate that only III is produced from II in the reaction with MeLi in ether/THF. When no excess of MeLi is present the reaction of III with V to form II and VII follows Scheme I. When more than 1 equivalent of MeLi is present in the reaction mixture the same process occurs again probably because the reaction between MeLi and V is too slow to interfere and VII is formed in a high yield.



$$\underset{\text{III}}{CH_2{=}CH{-}\overset{\ominus}{C}H{-}CN} + \underset{\text{V}}{(CH_3)_3SiCl} \longrightarrow CH_2{=}CH{-}\overset{\overset{Si(CH_3)_3}{|}}{C}H{-}CN \qquad (1)$$

$$CH_2{=}CH{-}\underset{\underset{Si(CH_3)_3}{|}}{CH}{-}CN + CH_2{=}CH{-}\overset{\ominus}{C}H{-}CN \longrightarrow CH_2{=}CHCH_2CN + CH_2{=}CH{-}\underset{\underset{Si(CH_3)_3}{|}}{\overset{\ominus}{C}}{-}CN \qquad (2)$$

$$CH_2{=}CH{-}\underset{\underset{Si(CH_3)_3}{|}}{\overset{\ominus}{C}}{-}CN + (CH_3)_3SiCl \longrightarrow \underset{\text{VII}}{(CH_3)_3Si{-}CH_2{-}CH{=}\underset{\underset{Si(CH_3)_3}{|}}{C}{-}CN} \qquad (3)$$

Scheme I

(The rate of reaction (2) must be greater than the rate of reaction (1)).

In VIII the two benzyl groups are bonded to the same carbon probably because of less severe steric requirements of these groups in comparison to the trimethylsilyl groups. Even though it might seem reasonable to predict that the electron attracting groups: the nitrile and the double bond, will render the methylene hydrogens in II, at least as acidic as in the 1,4-enynes, the formation of a lithium-nitrogen bond$^{8)}$ in the monoanion III reduces the acidity of the second hydrogen at position 2 and inhibits further metalation under the conditions studied.

References

1) J. Klein and S. Brenner, J. Am. Chem. Soc., 91, 3094 (1969).

2) Only one resonance form is written here.

3) D.E. Whyte and A.C. Cope, J. Am. Chem. Soc., 65, 1999 (1943).

4) W.I. O'Sullivan, F.W. Swamer, W.J. Humphlett and C.R. Hauser, J. Org. Chem., 26, 2306 (1961).

5) E.M. Kaiser and C.R. Hauser, J. Am. Chem. Soc., 88, 2348 (1966).

6) E.M. Kaiser and C.R. Hauser, J. Org. Chem., 33, 3402 (1968).

7) D.N. Crouse and D. Seebach, Chem. Ber., 101, 3113 (1968).

8) G.A. Gornowicz and R. West, J. Am. Chem. Soc., 93, 1714 (1971).

9) D.J. Curran and S. Siggia in "The Chemistry of the Cyano Group", Z. Rappoport (Editor), p. 194, Interscience Publishers (1970).

10) A.C. Cope, H.L. Holmes and H.O. House, Organic Reactions, Vol. 9, 107 (1957).