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ISOMERIZATION OF MONO- AND DIACETYLENIC HYDROCARBONS

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Abstract—The acetylenic hydrocarbons, 1-hexyne, 2-hexyne, 3-hexyne, 2-butyne, 2,4-hexadiyne and 3,5-octadiyne have been isomerized in dimethylsuphoxide (DMSO) using the methylsulphinyl carbanion as a base-catalyst. No products containing allenic or other dienic functionalities were observed. The mechanism of the rearrangement is discussed and NMR studies of hydrogen-deuterium exchange in 2-butyne and 2,4-hexadiyne in d_6-DMSO are described.

Base-catalyzed isomerization of acetylenes has been studied extensively.[1] It has been reported that 1-alkynes isomerize[2] to internal alkynes as well as the reverse isomerization of internal alkynes to the corresponding terminal acetylenes.[3,4] Such reactions were frequently accomplished at elevated temperatures or other drastic conditions. For example, isomeric pentynes were equilibrated[5] at 175° and heptynes and decynes, near 200°.[6,7] The isomerization of hexynes in liquid ammonia utilizing sodium amide as base was found to be very slow and a sealed autoclave was employed.[8] Furthermore, rearrangements of acetylenes were also accompanied by side reactions to give polymerization and/or addition of solvent to the unsaturated bonds.[5]

Figure 1 describes the rate of disappearance of each monohexyne under the same reaction conditions. Figure 2 shows the isomerization of **1** to isomers **2** and **3**. According to Fig. 1, all three hexynes require about 60 hr to reach the stationary quasi-equilibrium state, when 1:1 molar ratio of substrate to catalyst was employed. It is noteworthy that under different isomerization conditions,[8] 1-hexyne was found to require 1100 hr whereas the other two isomers reached "equilibrium" within less than 1 hr.

Like similar prototropic rearrangements, the base-catalyzed isomerization of acetylenes is probably best represented by a simple carbanion mechanism through an allene intermediate,[10,11] as follows:

$$\mathrm{RC{\equiv}CCH_2CH_2R'} \xrightleftharpoons{-\mathrm{H}^+} \mathrm{RC{\equiv}C\bar{C}HCH_2R'} \longleftrightarrow \mathrm{R\bar{C}{=}C{=}CHCH_2R'} \xrightarrow{+\mathrm{H}^+} \underset{\mathbf{4}}{\mathrm{RCH{=}C{=}CHCH_2R'}}$$

$$\mathbf{4} \xrightarrow{-\mathrm{H}^+} \mathrm{RCH{=}C{=}\bar{C}CH_2R'} \longleftrightarrow \mathrm{R\bar{C}HC{\equiv}CCH_2R'} \xrightarrow{+\mathrm{H}^+} \mathrm{RCH_2C{\equiv}CCH_2R'} \qquad (\text{route } a)$$

$$\mathbf{4} \xrightarrow[-\mathrm{H}^+]{} \mathrm{RCH{=}C{=}CH\bar{C}HR'} \rightleftharpoons \mathrm{RCH{=}\bar{C}{-}CH{=}CHR'} \xrightarrow{+\mathrm{H}^-} \mathrm{RCH{=}CH{-}CH{=}CHR'} \qquad (\text{route } b)$$

RESULTS AND DISCUSSION

The present study has been conducted on the isomerization of acetylenic hydrocarbons in DMSO at ambient temperatures, utilizing Corey's base (methylsulphinyl carbanion) as catalyst. 1-Hexyne (**1**), 2-hexyne (**2**) and 3-hexyne (**3**) were isomerized independently and the reaction followed by removing aliquots at specified time intervals and quenching them with ice-water. After extraction into ether and distillation, the products were analyzed by using vapor phase chromatography (VPC), IR and NMR spectroscopy. The reactions were allowed to proceed until no further change in their composition could be determined. All three normal hexynes were found to rearrange and give the same stationary quasi-equilibrium* mixture at the same catalyst concentration. The composition of each mixture consisted of 82% of **2**, 11% of **3** and 7% of **1**, without detecting any conjugated diene or allenic isomers. No change was observed in the composition of the products in each mixture when the molar amount of the catalyst relative to substrate was increased from 0.2 to 1.1. (Evidently, at lower catalyst concentrations longer periods of time were needed for reaching the quasi-equilibrium state). The quasi-equilibrium constants and the Gibb's free energy for the isomerization processes are summarized in Table 1.

The migration of the triple bond (route *a*) or the isomerization to conjugated diene (route *b*) depends on the relative acidity of the allenic and the allylic hydrogens in the allene **4**. If R′ is a phenyl group, a double or triple bond, then the allylic hydrogens are more acidic than the allenic ones and a mechanism through route *b* will be favoured. When no activating group is present the allenic hydrogens are more acidic and the isomerization will proceed via route *a* to give only acetylenic compounds. On studying the isomerization of the three n-hexynes by dynamic NMR, no allenic intermediate was detected. This observation may be ascribed to the very small concentration of the allene in the quasi-equilibrium states due to rapid isomerization. Furthermore, analysis of the product mixtures showed no evidence of the formation of products other than acetylenes. Therefore, it is presumed that the mechanism of the isomerization of **1**–**3** with Corey's base in DMSO,

Table 1. Quasi-equilibrium constants (K) and Gibb's free energy (ΔG°) data

Reaction	K (at 25°)	ΔG° (cal.mol^{-1})
$3 \rightleftharpoons 2$	7.46	−1196.0
$2 \rightleftharpoons 1$	0.085	−1467.6
$3 \leftrightharpoons 1$	0.64	+269.4

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*The term "quasi-equilibrium" is used here since isomerization of the anion of 1-hexyne may be involved.

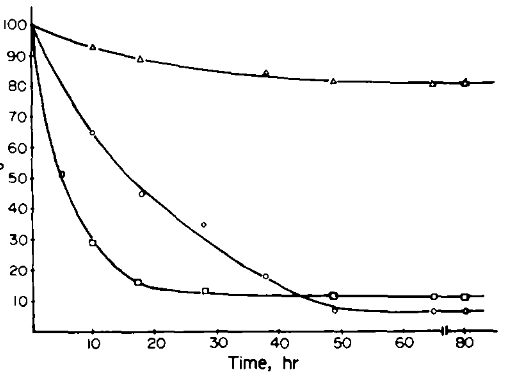


Fig. 1. The rate of isomerization of 1-, 2- and 3-hexynes in DMSO-$MeSOCH_2^-Na^+$ at 25°. ○, 1-hexyne; △, 2-hexyne; □, 3-hexyne.

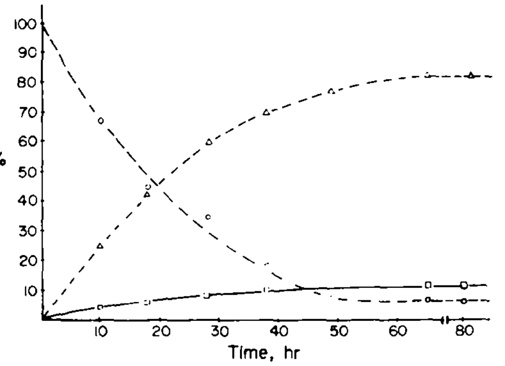


Fig. 2. Isomerization of 1-hexyne to 2- and 3-hexynes in DMSO-$MeSOCH_2^-Na^+$ at 25°. ○, 1-hexyne; △, 2-hexyne; □, 3-hexyne.

proceeds via route *a* which also eliminates the formation of conjugated dienes (they are known to be kinetically unfavored and formed only under extreme conditions[1]).

It is of interest to compare our experimental results with those of others, conducted under different conditions. Wotiz *et al.*[8] studied the isomerization of n-hexynes in ethylenediamine using sodamide as catalyst. Besides the hexynes they also observed 2,3-hexadiene in the "equilibrium" mixtures. Upon changing the molar quantity of the base, amination and polymerization was found to take place. Isomerization of octynes[12] with KOH-EtOH yielded an "equilibrium" mixture, containing 97.5% of 2-octyne, 0.2% of 1-octyne and 2.3% of 1,2-octadiene. An equilibrium mixture of heptynes[13] with t-BuOK-t-BuOH was found to contain 2- and 3-heptynes in 46% and 42% yield, respectively, and small amounts of 2,3-, 3,4- and 1,2-heptadienes. The "equilibrium" mixtures of pentynes consisted of 1.3% 1-pentyne, 3.5% 1,2-pentadiene and 95.2% 2-pentyne.[5] These data indicate that dienes were also formed in contrast to the reaction employed by us, in which high selectivity is obtained.

The predominance of 2-hexyne in the quasi-equilibrium mixture may be attributed to a greater degree of stabilization of this isomer due to hyperconjugation as a result of its five α hydrogens. Thus, 3-hexyne is more stable than 1-hexyne because the electron deficient triple bond "prefers" to be disubstituted with electron donating groups. We have examined this tendency also by studying the isomerization of 2-butyne (**5**) in DMSO using methylsulphinyl carbanion as a base catalyst. As expected, no other isomers were formed as indicated by NMR and IR spectroscopy even when the amount of catalyst was increased from 0.01 to an equimolar quantity relative to the substrate. Another example for this tendency was demonstrated effectively in the isomerization[3] of diethyl acetal of but-2-yne-1-al (**6**) which yielded the terminal acetylene (**7**). In this case, the acetylenic group tends to migrate away from the electron-withdrawing acetal groups:

$$\underset{\mathbf{6}}{CH_3C{\equiv}CCH(OEt)_2} \longrightarrow \underset{\mathbf{7}}{HC{\equiv}CCH_2CH(OEt)_2}$$

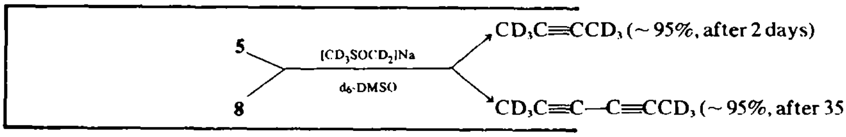
The effect of introducing an additional ethynyl group in conjugation to the first one was also studied. On treating 2,4-hexadiyne (**8**) with Corey's base in DMSO, no isomerization was observed, in analogy to the behaviour of **5**. However, isomerization of 3,5-octadiyne (**9**) resulted in the exclusive formation of 2,4-octadiyne (**10**), in yields of 70% and 82% after 20 and 36 hr, respectively. Thus, it seems that conjugated diacetylenes,

$$\underset{\mathbf{9}}{CH_3CH_2C{\equiv}C{-}C{\equiv}CCH_2CH_3}$$

$$\xrightarrow[\text{DMSO}]{MeSOCH_2^-Na^+} \underset{\mathbf{10}}{CH_3C{\equiv}C{-}C{\equiv}CC_3H_7}$$

likewise monacetylenic hydrocarbons, are also more stable when they are alkyl disubstituted and consequently with the highest degree of hyperconjugation.

Base-catalyzed rearrangements of acetylenes were found to proceed from low (18%) to high (85%) intramolecularity.[14] Several groups[14–17] found that the extent of intramolecularity is low in DMSO when a negatively charged base was used as catalyst. On the basis of this observation a dynamic NMR study of compounds **5** and **8** in d_6-DMSO was carried out. The experiments resulted with an exchange of all hydrogens with deuterium atoms in both compounds. Thus, there is full agreement with Cram's and Klein's findings[14–16] of a high degree of intermolecular interaction between the solvent and the substrate. Moreover, we observed that the second ethynyl group in **8** has a considerable effect on the rate of H–D exchange relative to that of **5**. The following scheme demonstrates qualitatively the relative acidity of their propargylic hydrogens toward the H–D exchange, as followed by NMR, when 20:1 molar ratio of substrate to catalyst, respectively, was employed:



It is noteworthy that this characteristic in which the additional triple bond makes the molecule more electron-deficient and consequently, the hydrogens more acidic, also affected the course of the metalation reaction. On reacting n-butyllithium with **5** only monolithiation took place[18] whereas with **8**, a tetralithio derivative was obtained,[19] under the same conditions.

EXPERIMENTAL

All acetylenes used were commercial products (Farchan Ltd.) except for compound **10**. Methylsulfinyl carbanion was prepared according to a known procedure.[9] DMSO was twice distilled from calcium hydride at 64°/4 mm and used immediately.

Isomerization of 1-, 2- *and* 3-*hexynes* (**1**, **2** *and* **3**, *respectively*). Three 100 ml flasks, each fitted with a rubber-capped injection port and connected through a 3-way stopcock to an Argon source, were purged with the innert gas. All three flasks immersed in a water bath whose temp. was constant (25°) and stirred with a magnetic stirrer. The methylsulfinyl carbanion, which was prepared in advance (2.4 g sodium hydride 50% in mineral oil and 25 ml of dry DMSO) was divided into equally three portions. Each portion contained 16.6 mmole of the catalyst and was transferred by a syringe to one of the flasks. Then, 16 mmoles of each of the n-hexynes was introduced slowly into the base. Aliquots of 1 ml each were taken from the flasks at specified time intervals and quenched with ice-water. Each sample was extracted into 3–5 ml of methylene chloride and the organic layer washed about ten times with water, to get rid of DMSO. After drying over $MgSO_4$ and filtering, the sample was ready for VPC analyzation using 10% Apeizon L column, on Chromosorb W, 5 m × 1/4", at 70°.

Isomerization of 3,5-*octadiyne* (**9**). Under the same procedure and apparatus described before for **1**–**3** 0.7 mmoles of the catalyst was added dropwise (by a syringe) to a cold soln (−10°) of 30 mmoles of **9**, in 25 ml of DMSO. Then the mixture was left overnight for 20 hr, at room temp. After the same work-up, the mixture was distilled (24–26°/6 mm) and the distilate yield was 70% of the rearranged product, **10**. (The relative ratio was based on NMR integration of the mixture and VPC analysis). Preparative separation was available by using VPC on Carbowax 20M 10%, on Chromosorb W, 2 m × 1/4", at 140°. The ratio of **10** to **9** in the distilate was increased to 82% to 18% when the mixture was allowed to stand for 36 hr. (Found: C, 90.80; H, 9.40. Calc. for **10**: C, 90.57; H, 9.43%). IR: 2100, 2200 cm^{-1}; UV (EtOH): 226(490), 237(290). NMR (ppm): 1.03(t, 3H), 1.53(quint., 2H), 1.95(t, 3H, J = 1 Hz), 2.23(t, 2H).

Isomerization of 2-butyne (**5**) *in* d_6-DMSO. The reaction was carried out in NMR tube fitted with a rubber-capped injection port. After purging the tube with Argon, 8 mmoles of the catalyst (0.4 ml of a soln containing 0.1 g of the NaH in 1 ml of d_6-DMSO) were injected into the tube to an equimolar quantity of **5**. The reaction was followed by NMR and the rate of H–D exchange was determined by the relative integrations in different time intervals. Under these conditions, ~95% of exchange lasted after 315 min.

Isomerization of 2,4-*hexadiyne* (**8**) *in* d_6-DMSO. The same technique as for **5** except that here, 0.05 mmoles of the catalyst were added to the NMR tube already contained 0.4 ml of d_6-DMSO and 1 mmole of **8**.

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