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A CONVENIENT SYNTHESIS OF 1- AND 2-ALKYNES

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Abstract—Terminal olefins are transformed by bromination and subsequent dehydrobromination at room temperature with a solution of sodamide or sodium hydride in DMSO to pure terminal acetylenes. *trans* Dehydrobromination of vinylic bromides proceeds faster than the *cis*. Conditions were found, where the 1-alkynes are converted into 2-alkynes.

TERMINAL acetylenes are prepared generally from sodium acetylide and alkyl halides in liquid ammonia.[1] Although good results were obtained from lower alkyl halides, insignificant yields of terminal acetylenes were recorded for higher alkyl bromides and higher temperatures, requiring the use of an autoclave, were recommended in these cases.[2] A second method of preparation of acetylenes using the bromination-dehydrobromination procedure leads in the aliphatic series to rearrangements[2] due to the high reaction temperatures during the second step involving strong bases. No rearrangements[3] were obtained in the dehydrobromination by sodamide in liquid ammonia, which is a very inconvenient solvent.

Terminal olefins are now prepared in large amounts on a technical scale in the petrochemical industry and are commercially available. These compounds present excellent starting material for 1-alkynes if the base-catalyzed isomerizations can be avoided in the dehydrobromination step. DMSO, as a solvent, accelerates[4] base catalyzed reactions, such as isomerization of olefins, by several powers of 10 relative to non-polar solvents. The Wolff-Kishner reaction can be conducted at room temperature in this solvent.[5] It was therefore chosen as the medium for the base-promoted elimination. Two strong bases, sodamide and methylsulphinylcarbanion were chosen as dehydrobrominating agents. Higher olefins, such as 1-decene, 1-tridecene, 1-tetradecene, 1-pentadecene and 1-hexadecene were used as starting materials in view of the difficulties encountered in the preparation of long-chain 1-alkynes.[2]

Bromination of these olefins in CCl_4 gave the 1,2-dibromoalkanes. Treatment of these compounds with an excess (3·3 moles) of methylsulphinylcarbanion in DMSO[6] gave excellent yields of 1-alkynes after 1 hr reaction at room temperature. The action of a solution of sodamide in DMSO was much slower and only proceeded satisfactorily with application of heat giving the 1-alkynes in a very good yield after 9 hr at 65–70°. GLC showed the presence in the product of one fraction only, corresponding to the known 1-alkynes. Since other possible products of the reaction were not always available to test their separability from the 1-alkynes, we relied on the IR and NMR spectra which showed the absence of allenic, vinylic or $\equiv C—CH_3$ bands in the products. These methods determined the upper limit of isomers at approximately 5%.

Continued heating of dibromodecane with sodamide in DMSO initially gave a product which showed in the IR an allenic as well as an acetylenic band. However, after 30 hr heating, 2-alkynes, either free of or containing very small amounts of 1-alkynes (GLC IR and NMR) and allenes (IR, NMR) only were obtained. The 2-alkynes were characterized by analysis, IR and in the NMR by the presence of three protons in the $\equiv CCH_3$ triplet and two protons in the $-CH_2C\equiv$multiplet. A similar pattern for the propargylic protons was observed in the case of 2-pentyne.[7]

The isomerization of the 1-alkynes with methylsulphinylcarbanion in DMSO was less rewarding. No reaction occurred at room temperature, but at 65–70° mixtures of 1-, 2- and 3-alkynes, which could be separated by GLC, were obtained from 1-decyne. Thus, the proportion of these compounds obtained after 0·5, 1·5 and 3 hr were 27:54:19; 17:44:39 and nil:42:58 respectively. As the 3-decyne was characterized by the presence of four $-CH_2-C\equiv$ protons in the NMR spectrum, it could also contain 4- or 5-decyne, if this had not been separated by GLC under the conditions used.

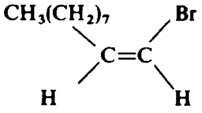
Our results show that 1-alkynes may be prepared smoothly from terminal olefins by the action of a solution of sodamide or sodium hydride in DMSO. These terminal acetylenes are transformed into pure 2-alkynes by the action of sodamide. Methylsulphinylcarbanion is not a satisfactory isomerizing agent for this purpose, since both 2- and 3-alkynes are produced at the same time. The 1-alkynes are formed first during the dehybromination, but they are isomerized into 2-alkynes, even in the presence of strong bases such as sodamide and sodium hydride which transforms them into sodium acetylides. Isomerization of 2- into 1-alkynes in the presence of sodamide has been observed[6, 8] and attributed to the higher stability of the acetylides. This does not seem to be the reason for the 2- to 1-alkyne isomerization since, in our experiments, the preferred reaction is in the reverse direction. The observed isomerizations[6, 8] may be the result of the precipitation of the acetylides from the reaction mixture, thus shifting the equilibrium in the direction of the 1-alkynes. In our conditions, all the components were in solution and the isomerization reflects the "true" equilibrium. This seems to be similar to the equilibrium between 1- and 2-alkynes.[9]

Our results also confirmed the claim[10] that 2-alkynes can be isomerized into 3-alkynes. This isomerization requires a more basic agent than the 1- to 2-alkyne isomerization and this could explain the failure, of other authors[11, 12] to obtain the 2- to 3-alkyne rearrangement. The relatively fast sodamide-catalyzed isomerization of 1- to 2-alkynes reflects their entalphy[9] which is lower by 4·8 kcal/mole for the second relative to the first compound. The 2- and 3-alkynes have comparable energies. The propargylic anions, (intermediates in all these rearrangements) of the 2- and 3-alkynes are of higher or at least the same energy as those of the 1-alkynes. Relative rates of metallation, which are larger for 1-phenylpropyne than for 1-phenylbutyne[13] support this estimate in view of the relation between rates of metallation and equilibria.[14] The formation of the anion intermediate for the 2- to 3-alkyne rearrangement is therefore approximately 4·8 kcal/mole more endothermic than the 1- to 2-alkyne transformation. Only very strong bases like methylsulphinylcarbanion, which produce appreciable amounts of intermediate anions, could establish a relatively fast equilibrium between the 2- and 3-alkynes. No 1,3-dienes were found in the reaction mixture despite their having the lowest energy of all the isomers.[9] This finding confirms the hypothesis[9] that their formation proceeds by a different mechanism[10] than the interconversion of the alkynes and allenes.

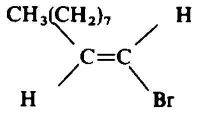
The intermediate vinyl bromides formed during the preparation of 1-alkynes and the stereochemistry of their dehydrohalogenation are of interest. They were prepared by dehydrohalogenation of 1,2-dibromodecane with sodium hydroxide in boiling ethanol or by sodamide in DMSO at room temperature for 1 hr. A similar mixture of three compounds A,B,C in the ratio of 50:28:22, as analyzed by GLC, was obtained in both reactions. Compound A showed in its NMR spectrum two broadened singlets at τ 4·45 and 4·7 for the two olefinic protons and was assigned structure I. The two other compounds showed NMR spectra, which could not be submitted to a first order analysis. They were distinguished by their IR spectra, in which C shows a band at 940 cm^{-1}, which is absent in B. Compound B is therefore the *cis*-(II) and C the *trans*-vinyl bromide (III). The base did not discriminate between the terminal and internal carbon in the abstraction of a proton, since equal amounts of the 1- and 2-bromoalkenes were obtained. A very slight preferential formation of the *cis* relative to the *trans*-vinyl bromide was observed. No proton was abstracted from the carbon at the 3-position to give an allene apparently because of the higher acidity of the protons α-to the bromine substituents.

$CH_3(CH_2)_7CBr = CH_2$

I



II



III

Treatment of the mixture of vinylic bromides with a solution of sodamide in DMSO for 45 min at 65–70° led first to the disappearance of I and II and formation of 1-decyne. The bromide III was completely transformed to this acetylene after 9 hr under these conditions. Two conclusions may be drawn from these results: (1) Formation of the acetylene does not proceed by way of an α-elimination[15] in view of the larger reactivity of I relative to III, and (2) *trans*-Elimination is faster than *cis*. This is consistent with an E2 mechanism, although our preliminary results show a rather small rate difference between the two isomers II and III. Other authors[16, 17] reported much higher ratios[16, 17] of *syn*/*anti* E2 rates (10^2–10^6) for similar reactions. It should be pointed out, that the larger reactivity of the *cis* isomer II does not eliminate the possibility of an Elcb mechanism for this reaction in view of the known ability of vinylic organometallics to retain their configuration[18] in contrast to the saturated compounds. It is possible that the *trans*-anion eliminates the bromide ion faster than the *cis*-anion, or the latter has to undergo the isomerization to the *trans*-ion before elimination occurs. The preferred *syn*-elimination assumed recently for Elcb reactions in saturated systems[19, 20] is not necessarily an argument against this mechanism in vinylic bromides in view of the different electronic structures in these systems.

It is of interest that no allenes were obtained from I. The vinylic hydrogen is much more reactive in this system than the allylic one, in spite of the somewhat lower energy of the 1,2-diene relative to the 1-alkyne.[9]

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ soln on a Varian T60 and A100 instruments. IR spectra were taken neat on a Perkin–Elmer 337.

Bromination. Br_2 in a slight excess was added dropwise with stirring to a soln of the commercial olefin (0·1 mole) in CCl_4 (200 ml) at a temp not higher than 35°. The soln was washed with $NaHSO_3$ aq and water and distilled giving yields higher than 95%.

1,2-*Dibromodecane*, b.p. 110–112°, 0·1 mm. (Found: C, 40·2; H, 6·4; Br, 53·3; $C_{10}H_{20}Br_2$ requires: C, 40·0; H, 6·7; Br, 53·3%).

1,2-*Dibromotridecane*, b.p. 123–127°, 0·3 mm. (Found: C, 45·1; H, 7·44; Br, 46·8; $C_{13}H_{26}Br_2$ requires: C, 45·6; H, 7·6; Br, 46·8%).

1,2-*Dibromotetradecane*,[21] b.p. 140–142°. 0·3 mm. (Found: C, 47·6; H, 8·02; $C_{14}H_{28}Br_2$ requires: C, 47·2; H, 7·9%).

1,2-*Dibromopentadecane*, b.p. 157–160°, 0·3 mm. (Found: C, 49·4; H, 8·34; $C_{15}H_{30}Br_2$ requires: C, 48·6; H, 8·1%).

1,2-*Dibromohexadecane*,[22] b.p. 175°, 1 mm. (Found: C, 49·9; H, 8·5; $C_{16}H_{32}Br_2$ requires: C, 50·0; H, 8·3%).

Bromodecenes I, II *and* III. KOH (0·2 mole) in water (10 ml) was added to a soln of 1,2-dibromodecane (0·15 mole) in EtOH (100 ml). The soln was refluxed for 2 hr, then concentrated *in vacuo*, poured into water, extracted with ether and distilled at b.p. 90–92°, 0·8 mm. (Found: Br, 36·1; $C_{10}H_{19}Br$ requires: Br, 36·5%). GLC on a 2 m × ¼ column of 20% SE 30 on chromosorb P. acid washed separated three compounds I, II, III. The same mixture of products was obtained by the action of sodamide (5 equivs) in DMSO on the dibromide.

Reactions with sodamide. Sodamide (8 g) was pulverized under parafin oil then added to DMSO (80 ml) and heated under N_2 at 65–70° for 1 hr. This soln was used in dehydrobrominations. The dibromoalkane was added to 8 mole-equivs of sodamide and reacted the required time. 1-Alkynes were obtained after 9 hr heating at 65–70°. The soln was then left overnight at room temp, and poured into ice-water. The product was extracted with ether and the ether soln washed with 5 consecutive portions of water (50 ml). Distillation gave the 1-alkyne.

1-*Decyne*, b.p. 60–62°, (0·8 mm), 94% yield. (Found: C, 87·04; H, 12·95; $C_{10}H_{18}$ requires: C, 86·96; H, 13·04%).

1-*Tridecyne*, b.p. 72–74° (0·8 mm), 90% yield. (Found: C, 86·7; H, 13·5; $C_{13}H_{24}$ requires: C, 86·8; H, 13·2%).

1-*Tetradecyne*, b.p. 78–81° (0·8 mm), 94% yield. (Found: C, 86·7; H, 13·1; $C_{14}H_{26}$ requires: C, 86·6; H, 13·4%).

1-*Pentadecyne*, b.p. 108–112° (1 mm), 77% yield. (Found: C, 86·8; H, 13·2; $C_{15}H_{28}$ requires: C, 86·5; H, 13·5%).

1-*Hexadecyne*, b.p. 114–116° (0·3 mm), 72% yield. (Found: C, 86·8; H, 13·4; $C_{16}H_{30}$ requires: C, 86·5; H, 13·5%).

All these 1-alkynes show in the IR a band at 2120 cm^{-1} and in the NMR $\equiv CH$ at τ 8·3 (t), $-CH_2-C\equiv$ at τ 7·8–8·0 (m), CH_3-C at τ 9·1 (t). They were compared by GLC and spectra with commercial products (Farchan Research Laboratory).

2-*Decyne* was obtained in a similar manner after heating the reaction mixture for 21 hr, b.p. 61° (0·8 mm), 94% yield. (Found: C, 86·6; H, 13·2; $C_{10}H_{18}$ requires: C, 86·96; H, 13·04%); NMR; $\equiv C-CH_3$ at τ 8·29 (t) (J 2·5 H_2).

2-*Tridecyne*, b.p. 73–75° (0·7 mm); $\equiv C-CH_3$ at τ 8·3 (t) (J 2·5 Hz). (Found: C, 86·4; H, 13·4. $C_{13}H_{24}$ requires: C, 86·8; H, 13·2%).

2-*Tetradecyne*, b.p. 80–83° (1 mm); $\equiv C-CH_3$ at τ 8·29 (t) (J 2·5 Hz). (Found: C, 86·97; H, 13·55. $C_{14}H_{26}$ requires: C, 86·6; H, 13·4%).

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