Proton-catalysed Isomerization of Cumulenic Amines

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Cumulenic amines $R^1CH{=}C{=}C{=}C(R^3)NR^2{}_2$ (R^1 and R^2 = H or alkyl, R^3 = H or Me) are converted rapidly at 20 °C into enyne amines $R^1C{\equiv}C{-}CH{=}C(R^3)NR^2{}_2$ with methanol or water under neutral conditions.

Recently, amines with the $C{=}C{=}C{=}C{-}N$ structure have been prepared for the first time.[1,2] The parent compounds $H_2C{=}C{=}C{=}CH{-}NR^2{}_2$ were assumed to be intermediates in the base-catalysed isomerization[3] of $H_2C{=}CH{-}C{\equiv}C{-}NR^2{}_2$ into $HC{\equiv}C{-}CH{=}CH{-}NR^2{}_2$. The successful synthesis[2] of butatriene derivatives permitted the direct demonstration that bases such as potassium t-butoxide in tetrahydrofuran or dimethyl sulphoxide, or alkali amides in liquid ammonia effected their smooth isomerization into $HC{\equiv}C{-}CH{=}CH{-}NR^2{}_2$.[4]

We now report that cumulenic amines (**1**) isomerize into enyne amines (**3**) in methanol or water. The mechanism is different from that of the base-catalysed conversion.

Addition at 20 °C of a small amount (*ca.* 10 mol %) of neutral methanol to (**1**) resulted in a fast conversion into (**3**), which could be isolated in 80% or higher yields by distillation at low pressure (0.1—0.5 mmHg). Shaking ethereal solutions of (**1**)

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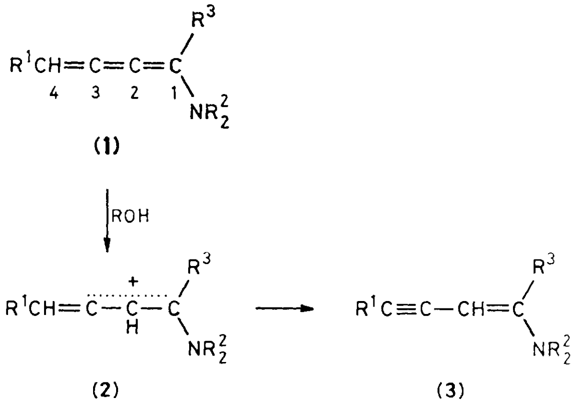


(1)

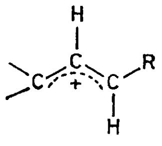
(2)

(3)

with water gave similar results. The enyne amines (**3**) ($R^1 = H$ or Me and $R^3 = H$) were obtained in at least 98% of the *E* form (according to ^{1}H n.m.r.; for spectral data see ref. 3); the *Z*-isomers were present in traces only. By monitoring the reaction with ^{1}H n.m.r. spectroscopy, it was shown that the preferred formation of the *E*-isomer is kinetically controlled and apparently not the result of a thermodynamically controlled $Z \rightarrow E$-isomerization.

The conversion into (**3**) did not take place in t-butyl alcohol. In a molar solution of potassium methoxide in methanol this reaction was markedly slower than in neutral methanol. Isomerization of $H_2C=C=C=C(Me)NEt_2$ by water or methanol into the corresponding enyne proceeded even more easily than that of the parent compound $H_2C=C=C=CH{-}NEt_2$. The trimethylsilyl-derivative $H_2C=C=C=C(SiMe_3)NEt_2$, however, did not undergo any isomerization with water (methanol gave tars).

These experimental facts can be explained by assuming protonation of C-2 in (**1**) to give the allylic carbocation (**2**); this subsequently loses one of the methylene protons at C-4. Alkyl substituents (*e.g.* $R^3 = Me$) stabilize (**2**) and cause (**1**), $R^3 = Me$ to isomerize more easily than (**1**), $R^3 = H$. Trimethylsilyl-groups are known to destabilize adjacent positive charges (compare ref. 5), and hence the greater stability of (**1**), $R^3 = SiMe_3$ towards water may be due to more difficult protonation. Similar differences in water-stability have been noted in the allenic series.[6] While $H_2C=C=CH{-}NMe_2$ and $H_2C=C=C$-(alkyl)NMe_2 hydrolyse in water rapidly, $H_2C=C=C(SiMe_3)$-Me_2 remains unchanged.



(4)

The almost exclusive, and kinetically controlled, formation of *E*-(**3**), for $R^3 = H$, may be rationalized by considering the geometry of the intermediate allylic cation (**2**). The *E*-configuration of an allylic carbocation with a donor substituent (*e.g.* $R = NR^2_2$) (**4**) is likely to be the most stable. Deprotonation on C-4 should then lead to predominant formation of *E*-(**3**).

The interrelation between cumulenic amines (**1**) and enyne amines (**3**) described in this communication represents a novel isomerization of unsaturated compounds under mild conditions.

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