

Base-catalysed Prototropic Isomerization. Part VI.¹ The Isomerization of Acetylenic Hydrocarbons

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The isomerization of substituted 1,8-diphenylocta-3,5-diyne by potassium t-butoxide-t-butyl alcohol and by potassamide on alumina (a homogeneous catalyst) has been studied. The course of the reaction depends strongly on the catalyst and on the diyne. Conjugated tetraenes are obtained with both catalysts in the case of 1,8-diphenylocta-3,5-diyne. In contrast, 1,8-bis-(2,4,6-trimethylphenyl)octa-3,5-diyne gives a conjugated tetraene on the heterogeneous catalyst, but migration of the triple bonds takes place in the homogeneous system giving 1,8-bis-(2,4,6-trimethylphenyl)octa-1,3-diyne.

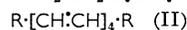
THE isomerization of acetylenes to polyenes has been studied extensively during the last decade, and is the key step for the preparation of annulenes.² The study of base-catalysed migration of triple bonds in cycloalkadiynes has shown the existence of conformational effects in macrocycles.³

We have reported⁴ on the extraordinary efficiency of the heterogeneous catalyst $\text{KNH}_2\text{-Al}_2\text{O}_3$ for the isomerization of $\alpha\omega$ -diynes even when the triple bonds are separated by more than two methylene groups, compared with previous systems, such as $\text{KOBU}^t\text{-HOBU}^t$, which are effective only when two methylene groups lie between the triple bonds. These results prompted us to investigate some cases where the base-catalysed isomerization of unsaturated compounds is difficult or does not follow the normal path.

We have reported on a steric effect in the isomerization of substituted 1,8-diphenylocta-3,5-diyne (I).¹ The 1,8-diphenyl compound (Ia) gave the tetraene (IIa) with potassium t-butoxide, whereas a migration of the triple bonds was observed in the 2,3,5,6-tetramethylphenyl compound (Ib) resulting in the formation of the conjugated diyne (IIIb) in high yield, and no tetraene.

We have now examined the influence of the nature of the base on this reaction. The diyne (Ia) gives the tetraene (IIa) with both catalysts, while the diyne (Ic)

gives the 'conjugated' ‡ diyne (IIIc) with the butoxide catalyst and the tetraene (IIc) with potassamide-alumina.



a; R = Ph

b; R = 2,3,5,6-Me₄C₆H

c; R = 2,4,6-Me₃C₆H₂

The u.v. spectrum of the tetraene (IIc) shows a large band at 350 nm, the absence of fine structure in which signifies that steric interaction between the 2,6-methyl groups and the β -olefinic proton prevents coplanarity of the aromatic rings and the tetraene system.

The formation of the tetraene (IIc) can be explained by the mechanism suggested for the formation of (IIa) (see ref. 1); potassamide, being a less hindered base than potassium t-butoxide, would attack the benzylic methylene group $\text{C}_\alpha\text{H}_2$ of the intermediate allene (IV).



It is interesting to note that the diyne (IIIc) is not isomerized under the conditions which give the tetraene (IIc); it follows that (IIIc) is not an intermediate in the isomerization of the diyne (Ic). The tetramethylphenyl-diyne (Ib) gave the same product (IIIb) with

¹ Part V, A. J. Hubert and A. J. Anciaux, *Bull. Soc. chim. belges*, 1968, **77**, 513.

² F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.*, 1959, **81**, 1771, 4755.

³ A. J. Hubert and J. Dale, *J. Chem. Soc. (C)*, 1965, 3118.

⁴ A. J. Hubert, *Chem. and Ind.*, 1968, 975.

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‡ Conjugation of the diyne with the phenyl group is implied by the term 'conjugate.'

