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-diynes 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 reported[4] on the extraordinary efficiency of the heterogeneous catalyst KNH_2–Al_2O_3 for the isomerization of αω-diynes even when the triple bonds are separated by more than two methylene groups, compared with previous systems, such as $KOBu^t$–$HOBu^t$, 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-diynes (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.

$RCH_2{\cdot}CH_2{\cdot}C{\vdots}C{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH_2R$ (I)
$R{\cdot}[CH{:}CH]_4{\cdot}R$ (II)
$RC{\vdots}C{\cdot}C{\vdots}C{\cdot}[CH_2]_4{\cdot}R$ (III)
a; $R = Ph$
b; $R = 2,3,5,6\text{-}Me_4C_6H$
c; $R = 2,4,6\text{-}Me_3C_6H_2$

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 $C_\alpha H_2$ of the intermediate allene (IV).

$RC_\alpha H_2{\cdot}CH{:}C{:}CH{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH_2R$ (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

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

[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.

both catalytic systems, probably owing to inductive effects.

We have also studied the isomerization of the acetylenes (Va and b), in which the triple bond migrates readily into conjugation with the trimethylphenyl group giving the pent-1-ynes (VI). No conjugated diene was formed in either case. It is very unlikely, therefore, that the formation of the tetraene (IIb or c) would occur *via* an intermediate of the type $\cdot C{:}C{\cdot}C{:}C{\cdot}CH_2R$ (R = Ph or 2,4,6-$Me_3C_6H_2$). During the formation of the pent-2-ynes (Va and b) in liquid ammonia, substantial rearrangement of the acetylenes was not observed. On the other hand, a complex mixture of rearranged products was obtained (as expected from the known sensitivity of the $C{:}C{\cdot}CH_2{\cdot}C{:}C$ system toward base) with benzyl bromide instead of 2,4,6-trimethylbenzyl bromide (VIII). This is another example of the steric protection provided by two *o*-methyl groups of a doubly-activated benzylic methylene group.

$RCH_2{\cdot}CH_2{\cdot}C{:}C{\cdot}CH_2{\cdot}C_6H_2Me_3$-2,4,6 (V)
$RCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}C{:}C{\cdot}C_6H_2Me_3$-2,4,6 (VI)
a; R = Ph
b; R = 2,4,6-$Me_3C_6H_2$

$$\underset{\text{(VII)}}{RCH_2{\cdot}CH_2{\cdot}C{:}CNa} + \underset{\text{(VIII)}}{BrCH_2{\cdot}C_6H_2Me_3\text{-2,4,6}} \longrightarrow \text{(V)}$$

EXPERIMENTAL

4-Phenylbut-1-yne and 4-(2,3,5,6-tetramethylphenyl)but-1-yne were prepared as previously described.[1] 1,8-Bis-(2,3,5,6-tetramethylphenyl)octa-3,5-diyne (Ib) and 1,8-diphenylocta-3,5-diyne (Ia) were prepared as reported[1] by oxidative coupling of the corresponding 4-arylbut-1-yne.

4-(2,4,6-*Trimethylphenyl*)*but*-1-*yne*.— 2,4,6-Trimethylbenzyl bromide was added to prop-2-ynylmagnesium bromide in ether.[1] The mixture was poured into water, the organic layer was washed with dilute HCl and water, and was dried (Na_2SO_4). After evaporation, the residue was distilled under reduced pressure to leave the but-1-yne.

1,8-*Bis*-(2,4,6-*trimethylphenyl*)*octa*-3,5-*diyne* (Ic).—This was prepared by heating the corresponding 4-arylbutyne during 30 h at 70 °C in the presence of copper(II) acetate–pyridine (yield 54%), m.p. 144 °C (Found: C, 90·8; H, 9·1. $C_{26}H_{30}$ requires C, 91·2; H, 8·8%), $\lambda_{max.}$ 4·5s μm ($C{:}C{\cdot}C{:}C$), δ 2·24 (*p*-Me), 2·36 (*o*-Me), 2·48 ($CH_2{\cdot}C{:}C$), 2·80 ($ArCH_2$), and 6·56 p.p.m. (ArH).

5-*Phenyl*-1-(2,4,6-*trimethylphenyl*)*pent*-2-*yne* (Va).—This was obtained by adding 4-(2,4,6-trimethylphenyl)but-1-yne (0·2 mol) to a solution of sodamide (0·2 mol) in liquid ammonia (1·5 l). Benzyl chloride (0·2 mol) in ether (50 ml) was then added. The ammonia evaporated overnight, the residue was taken up in ether–crushed ice, and the organic layer was washed and dried (Na_2SO_4) to yield the product (35%), m.p. 44° (Found: C, 91·4; H, 8·4. $C_{20}H_{22}$ requires C, 91·6; H, 8·4%), δ 2·26 and 2·32 (2 × Me), 2·60 ($CH_2{\cdot}C{:}C$), 2·72 ($PhCH_2$), 3·32 ($ArCH_2$), and 6·80 p.p.m. (ArH).

1,5-*Bis*-(2,4,6-*trimethylphenyl*)*pent*-2-*yne* (Vb).—This was prepared similarly (yield 24%), m.p. 80° (Found: C, 90·9; H, 8·5. $C_{23}H_{28}$ requires C, 90·8; H, 9·2%), δ 2·28 and 2·36—2·96 (Me and $CH_2{\cdot}C{:}C$), 3·36 ($ArCH_2$), and 6·72—6·84 p.p.m. (ArH).

In an attempt to prepare 1,5-diphenylpent-2-yne, the sodium salt of 4-phenylbut-1-yne was treated with benzyl chloride under the same conditions as before, but a complex mixture of at least four compounds which could not be isolated by g.l.c. was obtained.

Techniques of Isomerization.—*With potassium t-butoxide*. The acetylene (0·5 g) was added to a solution of potassium t-butoxide (5 g) in t-butyl alcohol at 75 °C. The reaction was followed by u.v. spectroscopy.

With potassamide–alumina. A suspension of potassamide (0·7 g) and alumina (10 g) in hexane (50 ml) containing the acetylene (0·5 g) was prepared at room temperature.[1,4] The reaction was followed by u.v. spectroscopy.

1,8-*Bis*-(2,4,6-*trimethylphenyl*)*octa*-1,3-*diyne* (IIIc).—1,8-Bis-(2,4,6-trimethylphenyl)octa-3,5-diyne (Ic) was isomerized in the presence of potassium t-butoxide as above to yield (8·6%) light yellow crystals of the 1,3-*diyne*, m.p. 75° (from ethanol) (Found: C, 90·8; H, 8·6. $C_{26}H_{30}$ requires C, 91·2; H, 8·7%), $\lambda_{max.}$ 266 (ε 14,000), 281 (22,300), and 294 nm (18,500) (typical for a conjugated diyne), δ 1·28 (4H, 6- and 7-H), 2·2 [6H, 1-(2,6-$Me_2C_6H_2$)], 2·30 [9H, 1-(4-MeC_6H_2) and 8-(2,6-$Me_2C_6H_2$)], 2·40 (4H, 5- and 8-H), 2·44 [3H, 8-(4-MeC_6H_2)], and 6·8 p.p.m. (4H, 1- and 8-$Me_3C_6H_2$).

1,8-*Bis*-(2,4,6-*trimethylphenyl*)*octa*-1,3,5,7-*tetraene* (IIc).—The diyne (Ic) was isomerized on the heterogeneous catalyst, potassamide–alumina, to yield the *tetraene* (IIc) (*ca*. 30%), m.p. 201° (decomp.) (Found: C, 90·7; H, 8·5. $C_{26}H_{30}$ requires C, 91·2; H, 8·8%), $\lambda_{max.}$ 350 nm (ε 54,400), δ 2·08 (*p*-Me), 2·15 (*o*-Me), 6·4 (olefinic H), and 6·8 p.p.m. (ArH).

5-*Phenyl*-1-(2,4,6-*trimethylphenyl*)*pent*-1-*yne* (VIa).—The formation of this compound was observed by u.v. spectroscopy during the isomerization of the pent-2-yne (Va) by both catalysts. It could not be isolated in a pure state, but its u.v. spectrum was identical to that of (VIb) (see later).

1,5-*Bis*-(2,4,6-*trimethylphenyl*)*pent*-1-*yne* (VIb).—The isomerization of the pent-2-yne (Vb) by either catalyst gave the isomer (VIb), which was isolated by pouring into water and extracting the acetylenic material with hexane. The solvent was evaporated and the residue was recrystallized from ethyl acetate (20%), m.p. 59—61 °C (Found: C, 90·75; H, 9·3. $C_{23}H_{28}$ requires C, 90·7; H, 9·3%), $\lambda_{max.}$ 241sh (ε 16,700), 248 (22,700), and 258 nm (21,700). As expected, this spectrum shows a bathochromic shift relative to the spectrum of phenylacetylene.

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