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# THE REARRANGEMENT OF 1,5-HEXADIYNE AND 1,6-HEPTADIYNE*

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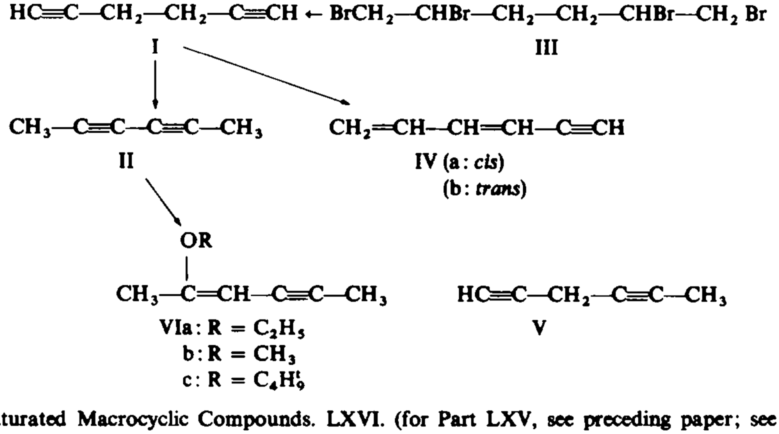
**Abstract**—The rearrangement of 1,5-hexadiyne (I) with potassium t-butoxide in t-butyl alcohol led mainly to a ca. 2:1 mixture of *cis*-1,3-hexadien-5-yne (IVa) and *trans*-1,3-hexadien-5-yne (IVb), and a minor amount of 2,4-hexadiyne (II). Both IVa and IVb were isolated and characterized. Contrary to previous reports, a similar result was obtained when the rearrangement of I was carried out with ethanolic potassium hydroxide, and in this case 2-ethoxy-2-hexen-4-yne (VIa) (derived from II) was also formed. The rearrangement of 1,6-heptadiyne (VIII) with potassium t-butoxide in t-butyl alcohol gave toluene and *trans*-1,3-heptadien-5-yne (Xb) in about equal amounts, but no *cis*-1,3-heptadien-5-yne (Xa) was detected. Authentic samples of Xa and Xb were prepared by methylation of IVa and IVb.

## *The rearrangement of* 1,5-*hexadiyne* (I)

THE rearrangement of 1,5-hexadiyne (I)[1] with various bases has been studied by several investigators, and different products have been isolated depending on the base employed. Faworsky[2] treated I with KOH in EtOH at 100° in a sealed tube, and obtained 2,4-hexadiyne (II), as well as an ether (now shown to be VIa) in poor yields. Faworksy[2] also reinvestigated Henry's synthesis of I[3] [involving dehydrobromination of 1,2,5,6-tetrabromohexane (III) with hot solid KOH, and then with KOH in boiling EtOH] and showed that the reaction gave the rearrangement product II in addition to I. Griner[4] treated III directly with KOH in boiling EtOH, and obtained evidence for the formation of a hydrocarbon containing only one terminal acetylene group in addition to I. The new substance, presumably a rearrangement product of I,



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* Unsaturated Macrocyclic Compounds. LXVI. (for Part LXV, see preceding paper; see also first footnote in that paper).

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was considered to be 1,4-hexadiyne (V), but this structure is very unlikely in view of the now well known facile rearrangement of 1,4-diynes to 1,3-diynes with base.[5] Griner's work was reinvestigated by Lespieau,[6] who isolated II in addition to I. Eglinton *et al.*[7] reported that treatment of I with $KOBu^t$ in boiling diglyme gave a vinyl ether of unknown structure. Finally, our own group[8] found that rearrangement of I with $KOBu^t$ in boiling $Bu^tOH$ leads to 1,3-hexadien-5-yne (IV) [ca. 65% *cis* (IVa), 35% *trans* (IVb)] in reasonably good yield.

We decided to reinvestigate the rearrangement of I both with $KOBu^t$ in $Bu^tOH$ and with KOH in EtOH, in order to determine whether the reactions in fact take fundamentally different courses. The diyne I[1] was treated with $KOBu^t$ in boiling $Bu^tOH$ and the product was isolated with pentane, as described previously.[8] GLC analysis on a 10% SE 30 silicon rubber-Chromsorb W column showed that the product contained I, II and IV in a ratio of ca. 3:2:20.* The diyne II was identified by comparison of the retention time with that of an authentic sample (prepared as described by Conn *et al.*[9]). The yield of IV was ca. 50% (determined spectroscopially), and the yield of II was therefore ca. 5%. The column did not separate IVa and IVb. However, GLC analysis on a tri-*o*-tolylphosphate-Chromsorb W column effected this separation, and confirmed our previous finding that IV consists of a ca. 2:1 mixture of the *cis* (IVa) and *trans* (IVb) isomers.[8,10]

Both IVa and IVb have now been isolated in the pure state by preparative GLC. The IR spectrum (in $CS_2$) of IVb showed a strong band at 10·63 μ, the out-of-plane vibration of a conjugated *trans*-olefin,[11] while IVa exhibited only a weak band in this region (10·62 μ). Other conjugated *cis* olefins have been found to show absorption in this region (e.g., *cis*-2-penten-4-yne,[12] *cis*-3-hexene-1,5-diyne[13]). The UV spectra (in EtOH) were also in agreement with the assigned structures, IVa exhibiting $\lambda_{max}$ 252·5 mμ (ε 22,400), and IVb $\lambda_{max}$ 252·5 mμ (ε 34,500), ca. 264 sh mμ (ε 26,800). It has been found in other pairs of conjugated *cis–trans* isomers that the UV maxima occur at essentially the same wavelengths but the intensities of those of the *trans* isomer are considerably higher than those of the *cis* isomer; e.g. *cis*-3-hexene-1,5-diyne

$$HC{\equiv}C{-}CH{=}CH{-}C{\equiv}CH$$

VII (a: *cis*)
(b: *trans*)

(VIIa): $\lambda_{max}^{MeOH}$ 250 mμ (ε 14,500) and 262 mμ (ε 12,500);[13] *trans*-3-hexene-1,5-diyne (VIIb): $\lambda_{max}^{MeOH}$ 251 mμ (ε 20,400) and 263 mμ (ε 18,100).[13]

The rearrangement of I with KOH in EtOH was studied under several conditions, in attempts to reproduct the early work,[2,4,6] and two experiments are described. In experiment A, I was boiled with a ca. 20% solution of KOH in absolute EtOH. UV spectral examination of aliquots removed at intervals revealed the appearance of a maximum at 252–253 mμ, indicative of IV. The solution obtained after 5 hr boiling and extraction with pentane on GLC analysis was found to consist of I (60%), II (10%), IV (26·5%), the ether VIa (2%, see below), and an unidentified substance (1·5%), pentane, high boiling and involatile material being neglected. The dienyne

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* The compositions of mixtures estimated from GLC analyses in this paper are approximate, and no corrections for variations in thermal conductivity of the components have been made.

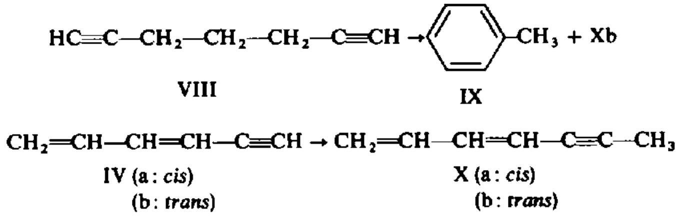
IV was again a mixture of *cis* (IVa) and *trans* (IVb) isomers, as evidenced by GLC analysis and the IR spectrum, but the ratio was not determined in this case. In experiment B, I was boiled with a relatively large amount of very concentrated KOH in 95% EtOH for 5 hr. The resulting solution now showed a UV maximum at 235 mμ, due to the ether VIa (see below). GLC analysis indicated the presence of VIa (isolated by preparative GLC) and two unidentified substances, but no I, II or IV.

The above-mentioned 2-ethoxy-2-hexen-4-yne (VIa) was obtained most conveniently (in ca. 50% yield) by boiling II with KOH in 95% EtOH for 5 hours. This reaction (conducted at 100–130° in a sealed tube) had already been shown by Griner[4] to give rise to an EtOH adduct. The latter was expected to possess structure VIa, since Bohlmann and Viehe[14] subsequently showed that treatment of I with KOH in MeOH (at 120° in a sealed tube) leads to the corresponding methoxy-compound VIb. The structure VIa was confirmed by the IR, UV and NMR spectra, as well as by the elemental composition. The NMR spectrum indicated that VIa consists of one stereoisomer, the olefinic proton quartet appearing at τ 5·45. By comparison, the olefinic proton signal in VIb appears at τ 5·40 for the "*cis*" isomer and at τ 5·49 for the "*trans*" isomer.[15] Unfortunately, these values are too similar to allow a stereochemical assignment to be made to VIa in the absence of the other isomer. Treatment of II with KOBu$^t$ in boiling Bu$^t$OH led to the corresponding t-butyl ether VIc, as evidenced by the UV spectrum, but this substance was not isolated.

From the above described experiments, it is clear that treatment of I either with KOBu$^t$ in Bu$^t$OH or with KOH in EtOH gives rise initially to IVa, b in major amounts and to II in minor amounts. IVa, b and II must be formed from I by independent paths, since they were not interconverted under any of the basic conditions. When the rearrangement of I is carried out with KOH in EtOH, the initially formed II subsequently undergoes addition of EtOH to give the ether VIa, while IVa, b is gradually destroyed. These results are not incompatible with the early literature.[2,4,6] Only the minor components II and VIa were detected in the rearrangement of I with KOH in EtOH, presumably because both these substances could easily be separated from unchanged I in view of their much higher boiling points and because II is a crystalline substance at room temperature. By comparison, the boiling point of IVa, b (b.p. 82–83°)[8] is very similar to that of I (b.p. 85–86°).[4] Moreover, the hydrocarbon containing only one terminal acetylene obtained by Griner[4] from I with KOH in EtOH (considered to be V) is presumably IVa, b.

### *The rearrangement of* 1,6-*heptadiyne* (VIII)

The rearrangement of 1,6-heptadiyne (VIII)[16] was of interest, since, if this reaction were to give a linear conjugated compound, then it was probable that similar rearrangement of the cyclic oligomers of VIII[17] would give rise to cyclic conjugated



systems. In the same way, the rearrangement of 1,5-hexadiyne (I) to 1,3-hexadien-5-yne (IV)[8] had served as a model for the synthesis of a variety of cyclic conjugated compounds from the cyclic oligomers of I.[18] However, when we commenced our study in 1963, the only reported rearrangement of VIII (with KOBu$^t$ in boiling diglyme) had led to toluene (IX) instead of a linear conjugated product.[7, 19]

We decided to study the rearrangement of VIII with KOBu$^t$ in Bu$^t$OH, since this reagent had smoothly given linear conjugated compounds from linear 1,4-enynes,[20] 1,5-enynes[21] and 1,5-diynes.[8] As expected, the rearrangement of the 1,6-diyne VIII proceeded less readily than that of the previously studied 1,4- and 1,5-diunsaturated systems, and required heating for 6 hr at 80° for most of the starting material to be consumed. GLC analysis of the product showed that toluene and *trans*-1,3-heptadien-5-yne (Xb) were essentially the only volatile products formed, each in ca. 30% yield. These substances were isolated by preparative GLC and identified by comparison with authentic samples (for Xb, see below). Toluene and Xb appear to be formed from VIII by independent paths, since Xb was not converted to toluene under the basic conditions used for its formation.

In order to obtain comparison samples, the above-described mixture of *cis*- and *trans*-1,3-hexadien-5-yne (IVa, b), obtained by rearrangement of 1,5-hexadiyne (I), was converted to the sodium salts by treatment with sodamide in liquid ammonia, and then alkylated with methyl iodide. Preparative GLC of the product gave both *cis*-1,3-heptadien-5-yne (Xa) and the *trans* isomer (Xb). The relative stereochemical assignments are based mainly on the facts that the IR spectrum of Xb showed a strong *trans* olefin band at 10·61 μ[11] (absent in Xa), and that the intensity of the UV maximum at 258 mμ is considerably higher in Xb (ε 31,800) than in Xa (ε 21,700). The *trans* isomer Xb obtained in this way proved to be identical to the substance formed in addition to toluene in the rearrangement of VIII. Moreover, comparison of the total rearrangement product from VIII with Xa (GLC retention times, IR spectra) showed that this product contained no appreciable amount of Xa.

The rearrangement of VIII under the conditions of Eglinton *et al.*[7, 19] (KOBu$^t$ in boiling diglyme) was also reinvestigated, in order to find out whether Xb is formed in addition to toluene. GLC analysis of the product showed the presence of toluene contaminated with ca. 5% of an unidentified impurity, but no Xb. It is possible, of course, that Xb is formed as an intermediate, but is destroyed under the very vigorous conditions.

Some preliminary experiments have been carried out (by Drs. P. K. Grant, H. J. Luthardt and R. Wolovsky) involving the rearrangement of the cyclic dimer[17a] and the cyclic trimer[17b] of VIII under the conditions used with VIII, but no monocyclic conjugated systems could be obtained.

After completion of this work, Hubert[22] reported that rearrangement of VIII with potassium amide on alumina in light petroleum at 25° gives X in 75% yield, but the stereochemistry was not discussed.

## EXPERIMENTAL*

### *Treatment of* 1,5-*hexadiyne* (I) *with potassium* t-*butoxide in* t-*butyl alcohol*

Compound I[1] (12 g) was rearranged with a satd soln of KOBu$^t$ in Bu$^t$OH (4 ml), essentially as described

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* For general procedures, see preceding paper.

previously.[8] The dried and filtered pentane extract (50 ml) showed UV $\lambda_{max}$ (EtOH) 253 mμ due to IVa and IVb; the spectroscopic yield was ca. 50% based on the ratio and ε values of the pure isomers (see below) GLC analysis (column S2, 65°) showed peaks due to I, II and IV in the ratio of ca. 3:2:20 (retention times: I < IV < II; I and II were identified by comparison of the retention times with those of authentic samples[9]). Columns S2 did not separate IVa and IVb. However, both isomers were shown to be present by GLC on column Y (20°), when two incompletely separated peaks due to IVa and IVb in the ratio ca. 2:1 were apparent (retention times: IVa < IVb).

Distillation of the brown extract (45 ml) at 50° (bath temp) (30 mm) into a receiver cooled in liq air gave a colourless soln (32·5 ml). Samples (ca. 1 ml each) were subjected to preparative GLC on column Y (20°; He flow rate 200 ml/min); IVa and IVb were collected in receivers cooled in liq air, and the physical properties were measured as quickly as possible.

IVa is a colourless liquid, homogeneous by GLC (column Y, 20°), $n_D^{28}$ 1·4919; IR $\lambda_{max}$ ($CS_2$) μ: 3·01(s), 4·76(w) ($HC{\equiv}C$), 10·02(s), 10·98(s) (monosubst $C{=}C$) and following bands different from IVb: 10·32(w), 10·62(w), 12·82(s), 14·47(w); UV $\lambda_{max}$ (EtOH): 252·5 mμ (ε 22,400).

IVb is a colourless liquid, homogeneous by GLC (column Y, 20°), $n_D^{28}$ 1·5099; IR $\lambda_{max}$ ($CS_2$) μ: 3·00(s), 4·74(w) ($HC{\equiv}C$), 10·03(s), 11·00(s) (monosubst $C{=}C$) and following bands different from IVa: 10·63(s) (*trans* $C{=}C$), 11·87(m); UV $\lambda_{max}$ (EtOH) mμ (ε): 252·5 (34,500), ca. 264 sh (26,800).

Both IVa and IVb are unstable. On standing at room temp without protection from air or day light, they became yellow within a few min and then gradually polymerized.

*Treatment of* 1,5-*hexadiyne* (I) *with potassium hydroxide in ethyl alcohol*

(a) *Experiment* A. A mixture of I (5·17 g), KOH (2·2 g) and abs EtOH (10 ml) was boiled under reflux, moisture being excluded. Aliquots were withdrawn at intervals (10 min–5 hr). The product in each case was isolated with pentane, and the soln [UV (EtOH): $\lambda_{max}$ 252–253 mμ due to IVa, b in every case] was examined by GLC. Use of column S2 at 65° in each case revealed the presence of I, IV, an unidentified substance and II (in order of increasing retention times), while column S2 at 160° showed the presence also of VIa (identified by comparison of the retention time with that of the sample obtained from II). After being boiled for 5 hr, the remaining material was isolated with pentane. GLC analysis as above showed the presence of I (60%), II (10%), IV (26·5%), VIa (2%) and the unidentified substance (1·5%), pentane and involatile material being neglected. The amount of IV present after boiling for 5 hr was ca. 8 times that present after boiling for 10 min, as determined by the optical density of the 252–253 mμ UV maximum.

The yellow pentane extract deposited insoluble polymeric material on standing at −15° for 3 days. Evaporation and preparative GLC (column S2, 65°; He flow rate 180 ml/min) gave samples of IV and the unidentified substance (UV: end absorption only). The resulting IV was a mixture of IVa and IVb, as evidenced by GLC (column Y, 20°) and the IR spectrum ($CS_2$), but the ratio was not determined.

(b) *Experiment* B. A mixture of I (2 g), powdered KOH (15 g) and 95% EtOH (10 ml) was boiled under reflux for 5 hr. The black mixture was cooled, poured into ice–$H_2O$, and extracted with pentane. The brown pentane extract (70 ml) showed UV $\lambda_{max}$ (EtOH) mμ (opt dens after dilution × 2000): 235 (0·76), ca. 265 sh (0·50), ca. 280 sh (0·43). The extract, which gave no ppt with $AgNO_3$–$NH_3$ soln, deposited insoluble polymeric material on standing at −15° for 2 days. Filtration and evaporation led to a dark green liq (1·36 g), which by GLC analysis (column S2, 65–160°) was shown to contain the unidentified substance obtained in Experiment A, VIa and another unidentified substance (in order of increasing retention times), but no I, II or IV. Preparative GLC (solumn S2, 160°; He flow rate 220 ml/min) gave a sample of VIa; homogeneous by GLC (column S2, 160°); identical GLC retention time as that of the sample obtained from II; UV $\lambda_{max}$ (EtOH): 236 mμ (ε 13,700). The IR spectrum (neat) showed all the bands of VIa obtained from II, and additional bands at 7·61, 8·29, 8·59, 9·01, 10·73 sh and 13·72 μ; it was not determined whether the additional bands are due to the presence of the other stereoisomer or of an impurity with identical GLC retention time.

*Treatment of* 2,4-*hexadiyne* (II) *with potassium hydroxide in ethyl alcohol*

A mixture of II[9] (0·63 g), powdered KOH (15 g) and 95% EtOH (20 ml) was boiled under reflux for 5 hr. The light brown soln was cooled, poured into ice–$H_2O$ and extracted with pentane. The pentane extract was washed with $H_2O$ and dried over $Na_2SO_4$. The soln showed UV $\lambda_{max}$ (EtOH) 236 mμ due to VIa, the spectroscopic yield being 53%. Evaporation gave a yellow liquid (0·74 g), IR spectrum (neat) essentially identical to that of pure VIa, and showing only a single peak due to VIa on GLC analysis (column S2, 160°). Preparative GLC (column S2, 160°; He flow rate 220 ml/min) gave pure VIa as a colourless liquid.

homogeneous by GLC; b.p. 167–169° (determined by the micro-method of Garcia;[23] lit[4] b.p. 169–170°), $n_D^{28}$ 1·4791; IR $\lambda_{max}$ (neat) μ: 4·47(w), 4·79(w) ($C \equiv C$), 6·13(s) ($C = C$), 8·10(s) ($= \overset{|}{C} - OR$), 9·36(s) ($-OR$); UV $\lambda_{max}$ (EtOH): 236 mμ (ε 14,200); NMR (A-60, $CDCl_3$) τ: 1H q ($J$ = 2 c/s) at 5·45 ($-C\underline{H} = \overset{|}{C} - O$),[15] 2H q ($J$ = 7 c/s) at 6·28 ($-C\underline{H}_2 - O -$), 3H s at 7·98 ($C\underline{H}_3 - C \equiv$), 3H d ($J$ = 2 c/s) at 8·03 ($C\underline{H}_3 - \overset{|}{C} =$) and 3H t ($J$ = 7 c/s) at 8·71 ($C\underline{H}_3 - CH_2 - O -$). (Found: C, 77·30; H, 9·94; $C_8H_{12}O$ requires: C, 77·37; H, 9·74%).

*Treatment of* 2,4-*hexadiyne* (II) *with potassium* t-*butoxide in* t-*butyl alcohol*

A satd soln of $KOBu^t$ in $Bu^tOH$ (10 ml) was added to II[9] (100 mg), moisture being excluded. The mixture was then boiled under reflux, aliquots being removed every hr. The product in each case was isolated with pentane, and the UV spectrum was determined (against pentane). A maximum at 237 mμ gradually appeared, presumably due to VIc; the spectroscopic yield after 7 hr boiling was 9%, assuming that VIa and VIc possess the same ε values.

cis-1,3-*Heptadien*-5-*yne* (Xa) *and* trans-1,3-*heptadien*-5-*yne* (Xb) *from* cis-1,3-*hexadien*-5-*yne* (IVa) *and* trans-1,3-*hexadien*-5-*yne* (IVb)

A suspension of $NaNH_2$ in liq $NH_3$ (ca. 100 ml) was prepared at ca. −50° from Na (1 g, 0·043 g atom), $Fe(NO_3)_2 \cdot 6H_2O$ being used as catalyst.[24] A pentane soln of a ca. 2:1 mixture of IVa and IVb [1·98 g (0·025 mole, estimated spectroscopically) in 25 ml; the soln, obtained from the above described rearrangement of I with $KOBu^t$, also contained I and II] was added dropwise with stirring during 10 min. The mixture was stirred for another 15 min, and MeI (3·55 g, 0·025 mole) in ether (12 ml) was then added during 10 min. The mixture was stirred at ca. −30° for 3 hr, $NH_4Cl$ and ether were then added, followed by $H_2O$ and ice. The aqueous layer was washed with ether, and the combined ether extracts were washed with 10% $H_2SO_4$ aq, 10% $NaHCO_3$ aq and $H_2O$. Evaporation of the dried extract through a Vigreux column gave a liquid residue; IR $\lambda_{max}$ (neat): bands of Xa and Xb (see below) and 3·02(w) ($HC \equiv$); UV $\lambda_{max}$ (EtOH): 256 mμ. GLC analysis (column S2, 107°) showed the presence mainly of Xa and Xb (ca. 2:1, Xa eluted before Xb, separation incomplete), as well as smaller amounts of I, II and IVa, b.

Preparative GLC (column S2, 107°, He flow rate 185 ml/min) readily gave a liquid containing only Xa and Xb; the ratio was ca. 1:1, as estimated from the IR and UV spectra, the $n_D$ value and GLC analysis. The mixture was separated by several successive preparative GLC separations, as before.

Xa is a colourless liquid, contaminated with no more than 3% of Xb (GLC on column S2, 107°), m.p. < −75° (it crystallized on cooling in liq air, but melted in an acetone–solid $CO_2$ bath), b.p. 115–117° (determined by the micro-method of Garcia[23]), $n_D^{28}$ 1·5180; IR $\lambda_{max}$ (neat) μ: 4·33(w), 4·45(m), 4·85(w) ($C \equiv C$), 9·98(s), 10·99(s) (monosubst $C = C$) and following band different from Xb: 12·77(s); UV $\lambda_{max}$ (EtOH): 258 mμ (ε 21,700). (Found: C, 91·42; H, 8·62. $C_7H_8$ requires: C, 91·25; H, 8·75%).

Xb is a colourless liquid contaminated with no more than 2% of Xa (GLC on column S2, 107°), m.p. −54 to −52°, b.p. 122–124° (determined by the micro-method of Garcia[23]), $n_D^{28}$ 1·5322; IR $\lambda_{max}$ (neat) μ: 4·46(m), 4·85(w) ($C \equiv C$), 9·98(s), 11·03(s) (monosubst $C = C$) and following bands different from Xa: 10·61(s) (*trans* $C = C$), 11·83(m), 12·55(w); UV $\lambda_{max}$ (EtOH) mμ (ε): 258 (31,800), 268 sh (24,800). (Found: C, 91·65; H, 9·00. $C_7H_8$ requires: C, 91·25; H, 8·75%).

Both Xa and Xb are reasonably stable and remained colourless after standing for several days, unlike IVa and IVb.

*Treatment of* 1,6-*heptadiyne* (VIII) *with potassium* t-*butoxide in* t-*butyl alcohol*

Compound VIII[16] (1·03 g) was added dropwise to a satd soln of $KOBu^t$ in $Bu^tOH$ (10 ml), and the brown mixture was stirred for 6 hr in an oil bath at 80° under a reflux condenser (moisture exclusion). The mixture was cooled, poured into ice–$H_2O$, and extracted with pentane. The pentane extract was washed with $H_2O$, dried over $Na_2SO_4$ and evaporated through a Vigreux column. The resulting yellow liquid (690 mg) on GLC analysis (column S2, 107°) was found to consist essentially of IX and Xb (ca. 1:1), while Xa was absent (comparison of retention times with authentic samples). The IR spectrum (neat) was very similar to that of a 1:1 mixture of IX and Xb, but a weak band at 3·02 μ ($HC \equiv C$) was also present. The UV spectrum showed $\lambda_{max}$ (EtOH) mμ (rel opt dens): 258 (0·60), 267 sh (0·49), 286 (0·06), 302 (0·05). The yield of Xb was 326 mg (32%), based on the intensity of the 258 mμ band (IX can be neglected in the calculation, since the ε value of pure IX is <300 in this region). Preparative GLC (column S2, 107°; He flow rate

150 ml/min) gave two fractions as colourless liquids. The one eluted first proved to be IX contaminated with ca. 15% of Xb and 1·5% of VIII (GLC analysis on column S2, 107°; comparison of retention times with authentic samples); the IR and UV spectra were in agreement with this composition, and essentially pure IX was obtained by repeating the preparative GLC separation. The second fraction was Xb, contaminated with ca. 4% of a substance of longer retention time (GLC analysis on column S2, 107°). It showed m.p. −55 to −52° (undepressed on admixture with the sample obtained from IVb), $n_D^{28}$ 1·5307; UV $\lambda_{max}$ (EtOH) mμ (ε): 258 (31,100), 268 sh (24,500). The IR spectrum (neat) was essentially identical to that of the sample obtained from IVb, but contained additional weak bands at 3·03 μ ($HC{\equiv}C$) and 10·38 μ.

Experiments in which the treatment of VIII with KOBu$^t$ in Bu$^t$OH at 80° was carried out for shorter times resulted in lower yields of IX and Xb. When the reaction was carried out at room temp for 2 hr, <1% of Xb was formed (determined by the UV spectrum).

*Treatment of* 1,6-*heptadiyne* (VIII) *with potassium* t-*butoxide in diglyme*[7,19]

A satd soln of KOBu$^t$ in Bu$^t$OH (20 ml) was evaporated under reduced pressure, finally at 160°. The residue (3·7 g), diglyme (37 ml) and VIII (600 mg) was boiled under reflux for 4 hr, moisture being excluded. The mixture was cooled, poured into ice–$H_2O$ and extracted with pentane. The extract was washed with $H_2O$, dried ($Na_2SO_4$) and evaporated through a Vigreux column. The UV spectrum of the residue was very similar to that of IX. GLC analysis (column S2, 101°) indicated it to consist of IX contaminated with ca. 5% of a substance of longer retention time. Preparative GLC (column S2, 101°; He flow rate 185 ml/min) gave pure IX (identified by the IR and UV spectra) and then the minor component. The latter showed UV $\lambda_{max}$ (EtOH) 261 mμ (and strong end absorption below 220 mμ) and was not identified.

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