Acetylene–Allene Isomerisations. Part I. Base Catalysis by Potassium t-Butoxide in t-Butyl Alcohol

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Isomerisation of hex-1-, -2-, and -3-yne, and hexa-1,2- and -2,3-diene catalysed by potassium t-butoxide in t-butyl alcohol (concentrating on the first 20% or so of isomerisation of the pure compounds) is reported. The experimental results are discussed as better evidence for the accepted stepwise acetylene–allene isomerisation than has been previously reported. Kinetic acidity of protons and stability of carbanions in this system is discussed.

THE base-catalysed isomerisation of acetylenes and allenes, first described by Favorskii,[1] has since been the subject of a number of investigations, as indicated in recent reviews.[2,3] The most important contribution to an understanding of homogeneous catalysis in solution came from Jacobs and his co-workers[4] who postulated mesomeric carbanion intermediates in a stepwise acetylene–allene–acetylene transformation (1).

$$\begin{aligned} &HC{\equiv}C{-}CH_2R + B \rightleftharpoons \{HC{\equiv}C{-}\bar{C}HR \leftrightarrow \\ &\quad H\bar{C}{=}C{=}CHR\} + BH^+ \rightleftharpoons H_2C{=}C{=}CHR + B \rightleftharpoons \\ &\quad \{H_2C{=}C{=}\bar{C}R \leftrightarrow H_2\bar{C}{-}C{\equiv}CR\} + BH^+ \rightleftharpoons \\ &\qquad H_3C{-}C{\equiv}CR + B \textit{ etc.} \quad (1) \end{aligned}$$

Jacobs and his co-workers studied the pentyne–pentadiene system (catalyst KOH–EtOH) and observed no hexa-1,3- or -2,3-diene formation. They concluded that isomerisation involved only C-1 and C-2. There is disagreement about this aspect of acetylene–allene isomerisation. Wojtkowiak and Romanet[5] report that oct-1- and -2-yne and octa-1,2-diene equilibrate with no formation of octa-2,3-diene, oct-3-yne, or beyond (catalyst KOH–EtOH at 125—175°) whereas Smadja[2] reports isomerisation beyond the alk-2-yne with the same system. Workers who have observed no migration of a triple bond to C-3 and beyond have implied that acetylene–allene isomerisations are only significant between C-1 and C-2.

However if acetylene–allene isomerisations are stepwise, and if the rate of isomerisation of alk-2-ynes is particularly slow (as has been frequently observed[2,4]) then isomerisations commencing with alk-1- or -2-ynes or with alka-1,2-dienes will proceed beyond alk-2-ynes only very slowly. It seems also inappropriate to study isomerisations of alk-3-ynes by looking only for alk-1-ynes in product mixtures, as has been reported.[6] More importantly, the slowness of the reaction alk-2-yne ⟶ alka-2,3-diene should not be taken to imply that other reactions are therefore slow. (We will report reaction rates for isomerisation of hexa-2,3-diene which are much faster than those for hex-2-yne.)

Investigations employing a number of catalytic systems have been reported. Four categories of base catalysis can be identified. (a) Potassium hydroxide–ethanol (125—175°): isomerisation beyond alk-2-yne has been stated not to occur,[1,4,5] but this view has been contradicted.[2] (b) Alkali metal alkoxides in alcohol solvents (below 200°): isomerisation beyond alk-2-ynes has been observed.[2] (c) Metal amides in liquid ammonia or amine solvents (at moderate temperatures): extensive isomerisations beyond alk-2-ynes has been reported.[7] Alk-1-ynes predominate in reaction mixtures where the catalyst is in molar excess due to their conversions to anions. A number of outstanding problems in this field are reviewed in the following paper. (d) Catalysts (b) and (c) (at more elevated temperatures): isomerisation to conjugated dienes has been demonstrated.[2]

The catalysts are increasingly more basic from (a) to (d) and, providing that the formation of carbanions is rate determining, these observations can be rationalised in terms of carbanion stability. In the alk-1-yne ⇌ alka-1,2-diene ⇌ alk-2-yne system the mesomeric carbanions leading to isomerisation are (I) and (II).

$$(H{-}C{\equiv}C{-}\bar{C}H{-}R \leftrightarrow H{-}\bar{C}{=}C{=}CH{-}R)$$

from alk-1-yne ‡ and alka-1,2-diene

(I)

$$(H_2C{=}C{=}\bar{C}{-}R \leftrightarrow H_2\bar{C}{-}C{\equiv}C{-}R)$$

from alka-1,2-diene and alk-2-yne

(II)

Referring to carbanions with a triple bond adjacent to the negative carbon as acetylenic, and to those with the negative carbon as part of an allene system as allenic, we note that (II) has a contribution from a *primary* acetylenic carbanion, which can be predicted to lower the energy of this carbanion. [Further, alka-1,2-dienes

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‡ $\bar{C}{\equiv}C{-}CH_2{-}R$ cannot lead to isomerisation, although it is the more stable anion which can be formed from an alk-1-yne.

[1] A. Favorskii, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 414, 553.

[2] W. Smadja, *Ann. Chim. (France)*, 1965, **10**, 105.

[3] R. J. Bushby, *Quart. Rev.*, 1970, **24**, 585.

[4] T. L. Jacobs, R. Akawie, and R. G. Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 1273.

[5] B. Wojtkowiak and R. Romanet, *Bull. Soc. Chim. France*, 1962, 805.

[6] T. H. Vaughn, R. R. Vogt, and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1934, **56**, 2120.

[7] J. H. Wotiz, W. E. Billups, and D. T. Christian, *J. Org. Chem.*, 1966, **31**, 2069.

react much faster than alk-2-ynes, forming predominantly alk-2-ynes rather than alk-1-ynes. This implies that (II) is more easily formed than (I) from an alka-1,2-diene, and that the acetylenic carbanion contributes predominantly to the mesomeric carbanion (II). Alk-2-ynes reacting *via* (II) would therefore reform rather than isomerise, and should undergo rapid hydrogen exchange adjacent to the triple bond.] The apparent ease of formation of (I) is less easy to rationalise; the allenic contribution is most likely to explain the kinetic acidity since the acetylenic contribution is implicated in the slower isomerisation of internal acetylenes. The allenic contribution is undoubtedly stabilised by the adjacent hydrogen atom, rather than an alkyl group, and the greater *s* character of the orbital on the negative carbon atom in $C=\bar{C}-$ may lower the energy of this carbanion to some extent.

Isomerisations of -3- and higher alkynes in (b) and (c) require formation of less stable carbanions: $R^1-C\equiv C-\bar{C}H-R^2 \leftrightarrow R^1-\bar{C}=C=CH-R^2$. Here the destabilising influence of alkyl groups is apparent. Internal allenes would isomerise through the same carbanions.

Isomerisations (d) to conjugated dienes can involve carbanion intermediates if alternative deprotonation of allenes is considered: $R^1-CH=C=CH-CH_2-R^2 \rightleftharpoons R^1-CH=C=CH-\bar{C}H-R^2 \leftrightarrow R^1-CH=\bar{C}-CH=CH-R^2$. The experimental observations suggest that this deprotonation is slower than those previously described; the lack of obvious relative stabilisation of these carbanions supports this view. No simple pathway to conjugated dienes directly from alkynes can be described.

Thermodynamic considerations should now be briefly mentioned. From published data[8] the stability sequence is roughly alk-1-yne < alka-1,2-diene < alka-2,3-diene, alka-3,4-diene, *etc.* < alk-3-yne, alk-4-yne, *etc.* < alk-2-yne < alka-1,3-diene < alka-2,4-diene, alka-3,5-diene, *etc.* Any experiment in which conjugated dienes are not the major products is not under thermodynamic control and should not be described as an equilibration. Systems (a)—(c) provide product mixtures which may represent 'sub-equilibria' meaning that components are present in amounts reflecting their relative stabilities. However the invariance over a temperature range 125—175° of one 'equilibrium mixture'[5] is surprising. Previous work on acetylene–allene isomerisations has over-emphasised the importance of the approach to these 'sub-equilibria'. Where a number of components are changing concentration in a complicated and interdependent manner the number of kinetic variables prevents any satisfactory kinetic resolution, and the thermodynamic information obtained is of doubtful value. Permutation of catalyst, catalyst concentration, temperature, and isomer concentration have all been reported; what is lacking is a study of a series of initially pure isomers undergoing a small change in composition under identical experimental conditions. This would provide a proper test of the stepwise acetylene–allene mechanism. To this end we have prepared a series of pure isomers and examined carefully the first 20% or so of their isomerisation under homogeneous catalysis, with the catalyst in molar excess.*

RESULTS

We have synthesised hex-1-, -2-, and -3-yne, and hexa-1,2-, -2,3-, -1,3-, and -2,4-diene. (For convenience these compounds will often be referred to as 1-, 2-, 3-, 1,2-, 2,3-, 1,3-, and 2,4- in the following discussion.) The

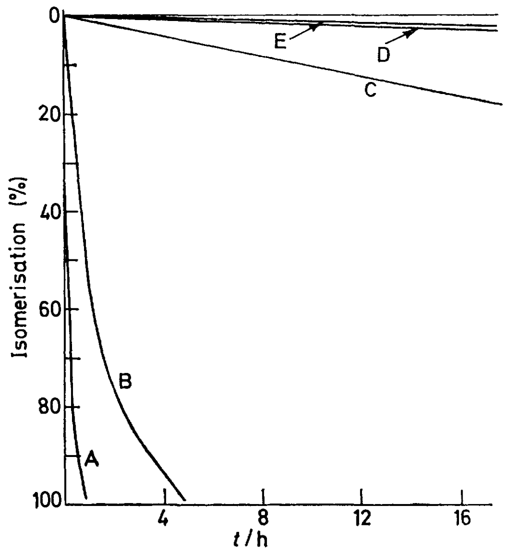

FIGURE 1 Observed isomerisation: A, hexa-1,2-diene; B, hex-1-yne; C, hexa-2,3-diene; D, hex-3-yne; E, hex-2-yne

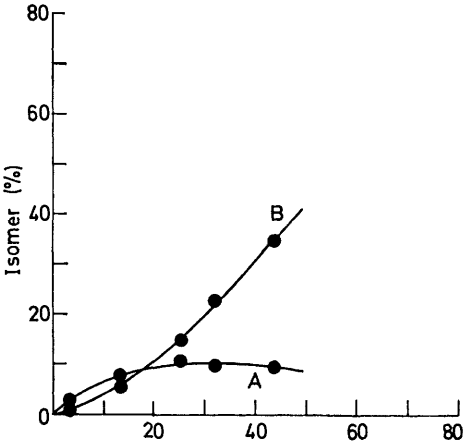

FIGURE 2 Isomerisation of hex-1-yne: A, hexa-1,2-diene; B, hex-2-yne

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* Experimental conditions chosen by other workers have often resulted in heterogeneous mixtures in which a hydrocarbon layer separates from the catalyst, and in which the isomer was in considerable molar excess. These conditions are inappropriate for a kinetic study of homogeneous catalysis.

[8] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.

isomerisation of these compounds (0·066M) in solutions of potassium t-butoxide (1·07M) in t-butyl alcohol at 85° has been studied for the first 20% or so of reaction.

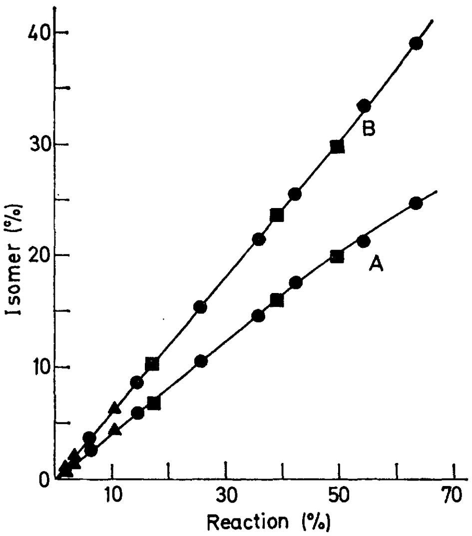

FIGURE 3 Isomerisation of hexa-2,3-diene: A, hex-3-yne; B, hex-2-yne; ▲, concn. of KOBu^t halved; ■, concn. of hex-2,3-diene doubled

Figure 1 shows the observed isomerisations. Figures 2—4 show isomerisations of hex-1-yne, hexa-2,3-diene, and hex-3-yne respectively.* Hexa-1,2-diene reacted to form hex-2- (65%) and -1-yne (6%) in 15 min. Before this time the starting material and hex-1-yne were not separable by the analytical technique used. Results for hex-2-yne isomerisation are in the Table.

Isomerisation of hex-2-yne (0·066M) in KOBu^t (1·07M)–Bu^{t}OH at 85°

t/h	2- (%)	1,2- (%)	2,3- (%)	3- (%)
0	100			
7	99·0	0·64	0·20	0·12
21·5	98·2	0·73	0·89	0·18
44·5	97·1	0·79	0·81	0·32
68·5	96·6	2·6 [a]		0·86
117	95·0	3·5 [a]		1·46
171	93·9	3·9 [a]		2·2
215	92·3	4·7 [a]		3·0

[a] The analytical procedure could not separate these two isomers when in this quantity.

DISCUSSION

A clearer vindication than previously of the stepwise acetylene–allene isomerisation suggested by Jacobs *et al.*[4] is now possible.

Figure 1 shows that rates of isomerisation are in the sequence 1,2- $>$ 1- $\gg$ 2,3- $\gg$ 3- $>$ 2-.

Consider now the isomerisation of hex-1-yne (Figure 2). The stepwise mechanism requires the sequence 1- $\rightleftharpoons$ 1,2- $\rightleftharpoons$ 2- in which 1,2- is a precursor to formation of 2-. Since 1,2-, in a separate experiment, is shown to isomerise faster than 1- or 2-, and to give 2- as a major product, Figure 2 is precisely of the form expected. The allene is initially formed more rapidly than 2-, then the amount of 1,2- remains approximately constant as 2- builds up considerably. The slow initial production of 2- and the gradually increasing slope of this curve argues for 1,2- being a precursor and for absence of a direct pathway from 1- to 2-.

Figure 3 shows the isomerisation of 2,3-. According to the stepwise mechanism 2- and 3- can be formed directly, and since these isomers are shown, in separate experiments, to isomerise more slowly than 2,3- they should be formed in a uniform manner, as was found. (Halving the catalyst concentration was shown roughly to halve the rate of isomerisation. Halving the isomer concentration made no discernible difference to the rate of isomerisation. Neither of these changes, however, affected the relative ratio of 2- : 3-).

Figure 4 shows isomerisation of 3-, and again supports the stepwise mechanism. We note that the slope of the line representing production of 2,3- is continually decreasing whereas that representing production of 2- is continually increasing. Again 2,3- appears to be a precursor to formation of 2- although in this case since 2,3- itself isomerises relatively slowly the amount of this isomer does not become approximately constant during the amount of reaction studied.

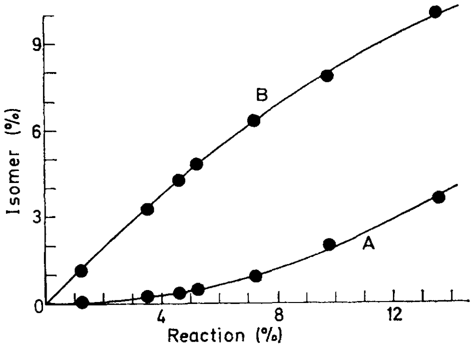

FIGURE 4 Isomerisation of hex-3-yne: A, hex-2-yne; B, hexa-2,3-diene

Due to analytical difficulties the results for isomerisation of 2- and 1,2- must be discussed more qualitatively. In the case of isomerisation of 2- it is clear that the initially formed products are the expected allenes, 1,2- and 2,3-, and that 3- is being formed slowly at first and then more rapidly; the expected behaviour if a precursor is required. The absence of 1- at first is readily understood since 1,2- forms 2- in considerable excess over 1-, whereas 2,3- forms 2- and 3- in approximately equal proportions. 1,2-Hexadiene as starting material is clearly reacting to give only the expected 1- and 2-, the latter in excess. In the reaction time studied 1- will react to give 2- to some extent, hence the falling

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* We plot % isomer *vs.* extent of isomerisation rather than time since the relative amount of isomer formed is of prime importance. These graphs are invariant with isomer and catalyst concentration (see Figure 3).

amount of 1- observed. The initial ratio of 2- : 1- would appear to be roughly 10 : 1.

The results combine to give good evidence for a stepwise isomerisation 1- $\rightleftharpoons$ 1,2- $\rightleftharpoons$ 2- $\rightleftharpoons$ 2,3- $\rightleftharpoons$ 3-. The relatively slow rate of isomerisation of 2- enables 'equilibration' between 1-, 1,2-, and 2- to be achieved, but it must be noted that 2,3- isomerises very much more rapidly than 2-. Thus, although starting from 1- isomerisation appears to stop at 2- this cannot be taken to imply that more internal isomers such as 2,3- and 3- are stable under the same conditions. There is good reason for believing that this observation in the hexyne–hexadiene system would be general to longer chain isomers as the relative stability of intermediates is unlikely to be affected by addition of further carbon atoms at some remove from the negative carbon atom.

The stepwise mechanism involves carbanion intermediates and is more properly written as 1- $\rightleftharpoons$ (I) $\rightleftharpoons$ 1,2- $\rightleftharpoons$ (II) $\rightleftharpoons$ 2- $\rightleftharpoons$ (III) $\rightleftharpoons$ 2,3- $\rightleftharpoons$ (IV) $\rightleftharpoons$ 3- [where (III) is $CH_3{-}C{\equiv}C{-}\bar{C}H{-}CH_2CH_3 \longleftrightarrow CH_3{-}\bar{C}{=}C{=}CHCH_2CH_3$ and (IV) is $CH_3{-}\bar{C}H{-}C{\equiv}C{-}CH_2CH_3 \longleftrightarrow CH_3CH{=}C{=}\bar{C}{-}CH_2CH_3$], a system with sixteen separate kinetic processes. We can reasonably assume that the deprotonation processes are slow and therefore rate determining compared to protonation, since the solvent is a much stronger acid than the hydrocarbons, but this nevertheless leaves an intractable system without further independent experimental results (such as isotopic studies leading to rates of hydrogen exchange in unreacted starting materials). The observed rates of isomerisation (Figure 1) very roughly parallel thermodynamic instability in that the least stable isomers are seen to isomerise most rapidly, and this could be assumed to imply more rapid carbanion formation from the least stable isomers. However it must be recognised that the observed rate of isomerisation may not depend simply on the rate of deprotonation of the starting material. Thus in the case of the slow isomerisation of hex-2-yne carbanion (II) is likely to be formed more easily than carbanion (III), but since the negative charge in the mesomeric ion (II) would be predominantly on C-1 protonation results in reformation of starting material. Even fast deprotonation would result in slow isomerisation in this case. Isotope exchange reactions coupled with the experimental results here could lead to an understanding of kinetic acidity and carbanion stability in this system which would be a valuable addition to our knowledge of acetylenes and allenes.

EXPERIMENTAL

Preparation of Reagents.—Hex-1-, -2-, and -3-yne were prepared by standard methods.[9] Hexa-1,2- and -2,3-diene were prepared by standard methods.[10,11] All these compounds after distillation through a spinning-band column were >99·5% pure by g.l.c. Hexa-1,3-diene was prepared by the method of Butler *et al.*,[12] hexa-2,4-diene was prepared by the method of Adams and Geissman.[13] t-Butyl alcohol was purified by distillation under dry nitrogen from sodium (3 g per 100 ml of solvent) after refluxing until *ca.* 2/3 of the sodium had dissolved. Solutions of potassium t-butoxide were prepared by adding potassium to the solvent in a dry box flushed with dry nitrogen (the potassium being first rinsed with two lots of dry ether and two lots of anhydrous solvent) and then refluxing the mixture for 12 h. The catalyst was stored in the dry box, and its concentration determined by titration with standard acid.

Isomerisations.—The catalyst (2 ml) and the appropriate isomer (0·015 ml) were pipetted into dry test-tubes in a dry box continuously flushed with dry nitrogen. The test-tubes were sealed and stored at *ca.* −15° until they were added to a thermostat at 85°. After the appropriate time, reaction was stopped by rapidly chilling to −15° and the contents were added to ice–water (*ca.* 10 ml). The hydrocarbons were extracted with purified light petroleum (b.p. 40—60°) * (*ca.* 1 ml). t-Butyl alcohol which interferes with g.l.c. analysis was removed by successive washings with water (10, 10, 5 ml). The composition of hydrocarbon mixtures was determined by g.l.c.

G.l.c. Analysis.—Separate experiments demonstrated that hex-1-, -2-, and -3-yne, and hexa-1,2- and -2,3-diene could be separated on a 12 ft × $\frac{1}{8}$ in stainless steel column packed with 20% polypropylene glycol (LB–550–X) on Chromosorb W 60/80, and that optimum separation was achieved when the flow rate was in the range 15—25 ml min^{-1} of nitrogen near 50°. Retention times relative to hex-2-yne (*ca.* 50 min) = 1·00 were hexa-2,3-diene 0·65, hexa-1,2-diene 0·68, hex-1-yne 0·71, and hex-3-yne 0·84. Mixtures containing large quantities of hexa-2,3- and -1,2-diene, or hexa-1,2-diene and hex-1-yne, or containing one component in these pairs in considerable excess over the other, could not always be analysed, as has been noted in results.

Chromatograms were analysed by relating the product (peak height × retention time[14] × attenuation) to the amount of isomer present. Calibration experiments showed that detector response (flame ionisation) was not identical for each of these compounds, so a further factor by which the above product must be multipled was experimentally determined (mean of 10 separate investigations). Again if we assign hex-2-yne = 1·00, then hexa-2,3-diene = 0·97, hexa-1,2-diene = 1·04, hex-1-yne = 0·84, and hex-3-yne = 0·96.

The small amount of impurity (<0·5% in all cases) present before each isomerisation has been allowed for in the results given, by assuming that impurities would isomerise at the same rate as the appropriate pure isomer separately studied, and correcting the experimental composition accordingly. This correction was usually small and often within experimental error.

Conjugated Dienes.—Smadja[2] reports that conjugated dienes are not formed in isomerisations of the heptynes and allenic heptadienes, catalysed by potassium t-butoxide in

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[9] E. A. Bried and G. F. Hennion, *J. Amer. Chem. Soc.*, 1937, **59**, 1310.

[10] G. F. Hennion and J. J. Sheehan, *J. Amer. Chem. Soc.*, 1949, **71**, 1964.

[11] M. Gaudemar, *Ann. Chim. (France)*, 1956, **1**, 161.

* Purified by fractional distillation. Fractions with no g.l.c. peaks in the hexyne–hexadiene region were used.

[12] C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, 1963, **28**, 372.

[13] R. Adams and T. A. Geissman, *J. Amer. Chem. Soc.*, 1939, **61**, 2083.

[14] R. L. Pecsok, 'Principles and Practice of Gas Chromatography,' Wiley, New York, 1959, p. 145.

t-butyl alcohol in the temperature range 82—196°. The absence of conjugated dienes in our isomerisations is inferred from the absence of appropriate peaks on chromatograms. Our prepared hexa-2,3-diene gave two peaks, the major peak (*ca.* 89%) with retention time relative to hex-2-yne of 0·62, the minor peak (*ca.* 11%) with relative retention time 0·69.* Our sample of hexa-2,4-diene gave four peaks, one of which (*ca.* 9%) we assume to be from hexa-1,3-diene since it had relative retention time of 0·62. The other three peaks † were (*ca.* 45%) relative retention time 0·82, (*ca.* 43%) relative retention time 0·91, and (*ca.* 3%) relative retention time 0·98. Only the minor peak in hexa-1,3-diene would be obscured completely in chromatograms.

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* The major peak is presumably the *trans*-3-isomer, the minor peak the *cis*-3-isomer.

† Hexa-2,4-diene has three geometrical isomers; *trans–trans*, *trans–cis*, and *cis–cis*. Since the but-2-enal used in the preparation is almost 100% *trans* [15] we assume that the peak with relative retention time 0·98 is the *cis–cis* isomer.

[15] W. G. Young, *J. Amer. Chem. Soc.*, 1932, **54**, 2498.