211. *Allenes. Part I. The Rearrangement of Prop-2-ynyl Acetates.*

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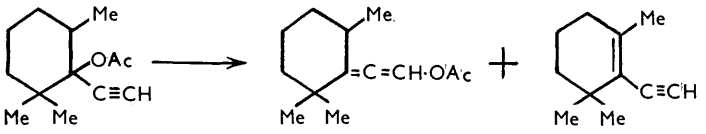
The pyrolysis of 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexyl acetate has been shown to give the allene, 2 : 2 : 6-trimethyl*cyclo*hexylidenevinyl acetate, besides the 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexene previously isolated. In the tetramethyl series the allenic acetate was isolated as the sole product in high yield. The mechanism of this rearrangement is discussed. Hydrolysis of the allenic acetates gave unsaturated aldehydes.

THE work described in this paper originated in the discovery that one of the main products from the pyrolysis of 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexyl acetate [1] (I) was the allenic acetate (II) while 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexene (III) was formed at the same time in smaller yield.

The *cyclo*hexene (III), required by us for other purposes, was prepared by pyrolysis from the crystalline acetate (I) (free from hydroxylic impurities as shown by its infrared

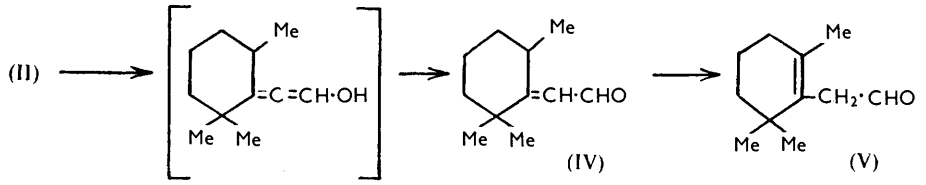
[1] Attenburrow, Cameron, Chapman, Evans, Hems, Jansen, and Walker, *J.*, 1952, 1094.

spectrum); it formed a lower-boiling fraction: the higher-boiling fraction had a fruity odour distinct from the typical acetylenic odour of the starting material and was isomeric with the latter. The higher-boiling material gave no ultraviolet absorption maximum, so the presence of a conjugated chromophore such as the enyne system in (III) was excluded; its infrared spectrum contained no acetylenic C–H stretching band near 3300

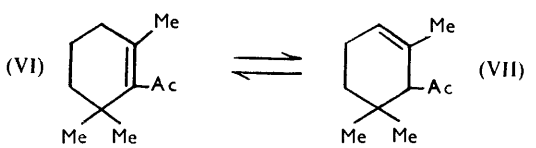


(I) (II) (III)

cm.$^{-1}$, but a strong C=O stretching band at 1750 cm.$^{-1}$ indicating the acetate group (original acetate band at 1745 cm.$^{-1}$) and a strong allene C=C stretching band at 1970 cm.$^{-1}$. This evidence strongly suggested the allenic structure (II). Adding the 2 : 4-dinitrophenylhydrazine reagent to the allenic acetate (II) gave, within a few seconds, vermilion needles which had the characteristic ultraviolet absorption bands expected from the 2 : 4-dinitrophenylhydrazone of a conjugated, unsaturated carbonyl compound.[2,3] The acetate (II) was apparently hydrolysed, under the acid conditions used, to 2 : 2 : 6-trimethyl*cyclo*hexylideneacetaldehyde (IV) which immediately gave the 2 : 4-dinitrophenylhydrazone.



A compound described by Henbest and Woods [4] as the 2 : 4-dinitrophenylhydrazone of (IV) but differing substantially in melting point and light absorption from our derivative had been obtained from a by-product in the formic acid isomerisation of 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexanol; the free aldehyde had not been isolated, the main product being 1-acetyl-2 : 2 : 6-trimethyl*cyclo*hexene (VI). In our hands the product obtained by this method (as used by Henbest and Woods or under varying conditions) did not yield the vermilion 2 : 4-dinitrophenylhydrazone, but very slowly afforded yellow needles, apparently (by ultraviolet absorption) the 2 : 4-dinitrophenylhydrazone of the unconjugated ketone (VII). As expected, ketone (VI), with the lone methyl and the acetyl group uniplanar, does not form a 2 : 4-dinitrophenylhydrazone [4] (confirmed by the present authors), whereas the isomer (VII) to which no similar restriction applies gives the derivative with reasonable ease. An attempt to effect the isomeration (VI) ⟶ (VII) by prolonged acid treatment in the absence of 2 : 4-dinitrophenylhydrazine proved unsuccessful,



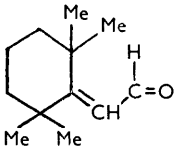
the equilibrium presumably lying predominantly towards (VI). It may be noted that substantially pure ketone (VI) results after only one distillation of the product, from the use of 98% formic acid in place of more aqueous mixtures hitherto used.

Hydrolysis of the allenic acetate (II) in the absence of dinitrophenylhydrazine might

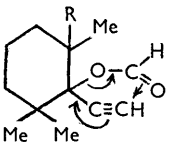
[2] Braude, *J.*, 1945, 490.
[3] Braude and Wheeler, *J.*, 1955, 321.
[4] Henbest and Woods, *J.*, 1952, 1150.

afford the aldehyde (IV), which has not yet been described. However, fairly vigorous conditions (methanolic hydrogen chloride at room temperature for three hours) yielded, not the conjugated aldehyde (IV), but the isomeric unconjugated 2 : 2 : 6-trimethyl*cyclo*hex-1-enylacetaldehyde (V) characterised by its ultraviolet and infrared absorption spectra [bands at 2700 (w) and 1715 (s) cm.$^{-1}$] and by a yellow 2 : 4-dinitrophenylhydrazone. Hydrolysis for shorter times gave different proportions of the aldehydes (IV) and (V) and unchanged acetate (II), as shown by the different intensities of the infrared bands at 1665, 1715, 1750, and 1970 cm.$^{-1}$; similar mixtures were also obtained by heating the allenic acetate (II) with aqueous acetic acid under varying conditions, thus pointing to a ready prototropic change even in weakly acid medium. In no case was the conjugated aldehyde obtained pure, for the isomers and starting material could not be separated on the scale used. However, light-absorption properties of the impure conjugated aldehyde agreed well with those of the corresponding aldehyde prepared in the tetramethyl series (see below) where a prototropic rearrangement cannot take place.

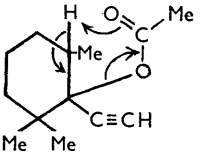
A further example of this pyrolysis was provided by the conversion of 1-ethynyl-2 : 2 : 6 : 6-tetramethyl*cyclo*hexylacetate into 2 : 2 : 6 : 6-tetramethyl*cyclo*hexylidenevinyl acetate in excellent yield (89%). Elimination of acetic acid is now impossible since no α-hydrogen atom is available. The tetramethyl allenic compound showed light absorption similar to that of the trimethyl analogue, *i.e.*, no ultraviolet maximum and strong infrared bands at 1970 and 1750 cm.$^{-1}$. It gave the red 2 : 4-dinitrophenylhydrazone of the conjugated aldehyde (VIII), and was hydrolysed quantitatively by acid to the aldehyde (VIII). A hypsochromic shift of the infrared conjugated carbonyl stretching frequency from 1665 cm.$^{-1}$ for the trimethyl to 1695 cm.$^{-1}$ for the tetramethyl compound, as well as the low-intensity ultraviolet absorption [$\lambda_{max.}$ 2480 Å; ε 5418; a mixture containing approx. 50% of trimethyl-aldehyde (IV) gave $\lambda_{max.}$ 2440 Å, ε 4931], suggested steric hindrance to the existence of a planar enone system. Inspection of models showed that even in the less sterically hindered *s-trans*-form (VIII) considerable interference occurs between a methyl group and the aldehyde-hydrogen atom. There is, however, no steric hindrance to the formation of a 2 : 4-dinitrophenylhydrazone.



(VIII)



(IX)



(X)

A plausible mechanism for the rearrangement of acetylenic acetates to allenic acetates involves a six-membered cyclic transition state (IX).[5] In the trimethyl series where R = H a rival cyclic transition state (X) competes with (IX) and results in elimination of acetic acid [6] with formation of the enyne system in (III). A necessary stereochemical condition for the formation of the cyclic form (X) is for the acetate and the 2-hydrogen atom to be located *cis* with respect to each other. It is tempting to postulate that the *cis*-isomer gives the enyne (III) while the *trans*-isomer, which cannot form (X), is converted into the allenic acetate *via* (IX). If that were so the yields of the products (II) and (III) indicate the ratio of *trans*- and *cis*-compounds present in the acetate (I). However, the acetylenic acetate (I) used as starting material was composed of sharp-melting crystals, obtained in 70% yield, and although the possibility of a mixture cannot be excluded it seems rather unlikely. From the stereochemical point of view the 6-methyl group in 2 : 2 : 6-trimethyl*cyclo*hexanone should be predominantly in the less hindered equatorial position; attack by the acetylene anion similarly will be from the less hindered side of the molecule, placing the 1-ethynyl (axial) and the 6-methyl group (equatorial) *cis* to each other. Thus the 1-hydroxyl group and the 6-hydrogen atom are also *cis* to each other,

[5] Lacey, *J.*, 1954, 827.
[6] Barton, *J.*, 1949, 2174.

and the *cis*-isomer should predominate in the product. A 70% yield of the corresponding crystalline acetate (OAc and H *cis*) would appear reasonable on this basis. Both transition states (IX) and (X) are now capable of formation and the two mechanisms are competitive.

Attempts to convert 1-ethynyl*cyclo*hexyl acetate and 1-phenylprop-2-ynyl acetate into the corresponding allenic acetates met with little success. In the former case 1-ethynyl-*cyclo*hexene was the main product, the presence of 2-hydrogen atoms unimpeded by methyl groups favouring a mechanism of type (X). 1-Phenylprop-2-ynyl acetate, on the other hand, gave a small distillate possessing the distinctive odour of cinnamaldehyde and yielding the 2 : 4-dinitrophenylhydrazone of the atter, but the bulk of the product was an intractable brown polymer.

The only previous reference to an allenic acetate is by Zakharova [7] who converted 3-chloro-3-methylbut-1-yne into a mixture of acetates by warming it with silver acetate in acetic acid at 60°. 3-Methylbuta-1 : 2-dienyl acetate was isolated in 37% yield together with smaller quantities of 1 : 1-dimethylprop-2-ynyl acetate and 1 : 2-diacetoxy-3-methylbut-2-ene. In view of the conditions used (polar medium, low temperature) in this case the allenic acetate is not likely to be produced by intramolecular rearrangement of the acetylenic acetate but is probably formed by an S_N2' mechanism by the action of acetate ion on the chloroacetylene.

Experimental

Ultraviolet spectra were determined in 95% EtOH (unless otherwise specified) by using a Unicam S.P.500 spectrophotometer, and infrared spectra in CS_2 with a Perkin-Elmer Model 21 double-beam instrument. M. p.s were determined on a Kofler block. The acetylenic acetates were purified until there was no hydroxyl band in the infrared apectra.

2 : 2 : 6-*Trimethyl*cyclo*hexylidenevinyl Acetate* (II).—Pyrolysis of 1-ethynyl-2 : 2 : 6-trimethyl-*cyclo*hexyl acetate [1] (31 g.; m. p. 59—60°) with zinc oxide (6 g.) in Silicone oil (25 g.; MS 550) gave, by working up in light petroleum (b. p. 40—60°), washing with aqueous sodium hydrogen carbonate, and fractionation through a 6" column filled with Dixon rings, two main fractions; the first, b. p. up to 90°/15 mm. (7 g., 31%), rapidly becoming pink in the air, was 1-ethynyl-2 : 2 : 6-trimethyl*cyclo*hexene (III), absorption max. at 2270 Å (ε 11,000); the second, b. p. 81—83°/0·5 mm., was 2 : 2 : 6-*trimethyl*cyclo*hexylidenevinyl acetate* (II) (11 g., 35%) (Found : C, 74·7; H, 9·3. $C_{13}H_{20}O_2$ requires C, 74·9; H, 9·6%).

The product (II) (0·4 g.) with 2 : 4-dinitrophenylhydrazine reagent [0·75 g. of the base in sulphuric acid (2·5 ml.) and methanol (40 ml.)] gave a red precipitate in a few seconds; this was filtered off after 3 hr. at room temperature, purified by chromatography on alumina and elution with benzene, then recrystallised from chloroform–methanol solution, giving 2 : 2 : 6-*trimethyl*cyclo*hexylideneacetaldehyde* 2 : 4-*dinitrophenylhydrazone* (0·58 g.), m. p. 182—183° (Found : C, 59·2; H, 6·45; N, 16·1. $C_{17}H_{22}O_4N_4$ requires C, 59·0; H, 6·4; N, 16·1%), absorption max. (in $CHCl_3$) at 3870 Å (ε 31,300) [Henbest and Woods [4] give m. p. 214—215°, λ_{max} 3800 Å (ε 31,500)].

2 : 2 : 6-*Trimethyl*cyclo*hex*-1-*enylacetaldehyde* (V).—Concentrated hydrochloric acid (3) ml. was slowly added to a solution of 2 : 2 : 6-trimethyl*cyclo*hexylidenevinyl acetate (1 g.) in methanol (15 ml.) so as to keep the solution homogeneous. Heat was evolved. After 3 hr. at room temperature, the mixture was diluted with water and worked up in ether, giving on distillation the *aldehyde*, b. p. 81—83°/3 mm., absorption max. at 2960 Å (ε 36), 2 : 4-*dinitrophenylhydrazone*, yellow plates (from methanol–chloroform), m. p. 118—119° (Found : C, 58·5; H, 6·3; N, 16·2. $C_{17}H_{22}O_4N_4$ requires C, 59·0; H, 6·4; N, 16·2%), absorption max. (in $CHCl_3$) at 3590 Å (ε 22,700).

Further hydrolysis in methanolic hydrochloric acid for 5 min. and isolation with ether gave a product with $\lambda_{max.}$ 2440 Å (ε 4931) and some of the 2 : 4-dinitrophenylhydrazone identical with that of (II) above.

Isomerisation of 1-*Ethynyl*-2 : 2 : 6-*trimethyl*cyclo*hexanol*.—The alcohol (5 g.) was isomerised in 90% formic acid (cf. Henbest and Woods [4]). Isolation with ether gave a product (3·2 g.), b. p. 84—90°/20 mm., absorption max. at 2400 Å (ε 1590). No 2 : 2 : 6-trimethyl*cyclo*hexylideneacetaldehyde 2 : 4-dinitrophenylhydrazone was obtained on adding 2 : 4-dinitrophenylhydrazine reagent, even after standing overnight at 0°, from either the distillate or the residue in the flask.

[7] Zakharova, *Zhur. obshchei Khim.*, 1945, **15**, 429.

A further isomerisation of the alcohol (5 g.), carried out in 98% formic acid (20 ml.) for 1 hr., gave, on isolation with ether, 1-acetyl-2 : 2 : 6-trimethyl*cyclo*hexene (3·4 g.), b. p. 86—90°/20 mm., absorption max. at 2430 Å (ε 1290). With 2 : 4-dinitrophenylhydrazine reagent this gave, in 2 weeks at room temperature, 2-*acetyl*-1 : 1 : 3-*trimethyl*cyclo*hex*-3-*ene* 2 : 4-*dinitrophenylhydrazone* as yellow needles, m. p. 152—154° (from methanol–chloroform) (Found : C, 58·9; H, 6·7; N, 16·15. $C_{17}H_{22}O_4N_4$ requires C, 59·0; H, 6·4; N, 16·1%), absorption max. (in $CHCl_3$) at 3710 Å (ε 25,000).

1-*Ethynyl*-2 : 2 : 6 : 6-*tetramethyl*cyclo*hexyl Acetate*.—1-Ethynyl-2 : 2 : 6 : 6-tetramethyl*cyclo*hexanol (prepared from 2 : 2 : 6 : 6-tetramethyl*cyclo*hexanone by sodium acetylide in liquid ammonia in 77% yield; b. p. 92°/15 mm. after one repetition of the procedure on the crude product) was acetylated *via* the Grignard compound (cf. Attenburrow *et al.*[1]) and recrystallised from ethanol, giving the *acetate*, as needles, m. p. 96° (Found : C, 75·3; H, 9·8. $C_{14}H_{22}O_2$ requires C, 75·5; H, 9·9%).

2 : 2 : 6 : 6-*Tetramethyl*cyclo*hexylidenevinyl Acetate*.—Pyrolysis of 1-ethynyl-2 : 2 : 6 : 6-tetramethyl*cyclo*hexyl acetate (4 g.) gave, after working up and fractionation, 2 : 2 : 6 : 6-*tetramethyl*cyclo*hexylidenevinyl acetate*, b. p. 132°/17 mm. (3·2 g., 89%) (Found : C, 75·6; H, 9·9. $C_{14}H_{22}O_2$ requires C, 75·5; H, 9·9%). This gave 2 : 2 : 6 : 6-*tetramethyl*cyclo*hexylideneacetaldehyde* 2 : 4-*dinitrophenylhydrazone*, m. p. 181° (after chromatography and recrystallisation from methanol–chloroform) (Found : C, 59·9; H, 6·7; N, 15·8. $C_{18}H_{24}O_4N_4$ requires C, 60·0; H, 6·7; N, 15·5%), absorption max. (in $CHCl_3$) at 3840 Å (ε 28,200).

2 : 2 : 6 : 6-*Tetramethyl*cyclo*hexylideneacetaldehyde* (X).—Hydrolysis of the foregoing acetate (1 g.) in methanol (15 ml.) with concentrated hydrochloric acid (3 ml.) gave, after distillation, the *aldehyde*, b. p. 105—106°/6 mm., absorption max. at 2480 Å (ε 5418). The 2 : 4-dinitrophenylhydrazone had m. p. 181° alone or mixed with the specimen described above.

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