462. *Studies in Molecular Rearrangement. Part VII.* The Oxotropic Rearrangement of* cis-*Propenylcarbinols. The Stereochemical Course of Anionotropy.*

By E. A. Braude and J. A. Coles.

Three-carbon anionotropy in *cis*-ethylenic systems has been investigated for the first time, with particular reference to the stereochemical course of the reaction.

Phenyl-*cis*-propenylcarbinol (I*a*), like its *trans*-isomer (I*b*), rearranges under acidic conditions to give mainly, or exclusively, methyl-*trans*-styrylcarbinol (II*b*). *cis*-Methylstyrylcarbinol (II*a*) has been synthesized for comparison by partial hydrogenation of 4-phenylbut-3-yn-2-ol (III). Its infra-red and ultra-violet light absorption differ significantly from those of the *trans*-isomer and provide evidence for steric inhibition of hyperconjugation.

cis-Propenylvinylcarbinol (IV*a*), unlike its *trans*-isomer (IV*b*), rearranges to give mainly or exclusively *cis*-butadienylmethylcarbinol (V*a*), which is unreactive towards maleic anhydride. *cis-trans*-Dipropenylcarbinol (X*a*) rearranges to give a mixture of stereoisomeric hepta-3 : 5-dien-2-ols (XI). A possible explanation for the unexpected formation of the *cis*-rearranged isomers from (IV*a*) and (X*a*) is suggested, which involves a novel type of intramolecular interaction, termed "π-hydrogen bonding," between the *cis*-methyl and the vinyl group.

The results lend further support to the mechanism of anionotropy involving bimolecular γ-attack by a neutral molecule, and provide compelling evidence against the intervention of free carbonium ions.

Three-carbon anionotropy has been extensively investigated in recent years in this and other laboratories, but relatively little attention has hitherto been paid to the stereochemical aspects of such reactions. The systems most extensively studied involve migration of a hydroxyl group (three-carbon oxotropy) and for these the available stereochemical information may be summarised as follows : (*a*) rearrangement of optically active allyl alcohols in aqueous media is accompanied by extensive or complete racemisation (Kenyon, Partridge, and Phillips, *J.*, 1937, 207; Airs, Balfe, and Kenyon, *J.*, 1942, 18), the rate of which is equal to that of rearrangement (Braude and Jones, *J.*, 1944, 436; Kenyon and Poplett, *J.*, 1945, 273); (*b*) in the rearrangement of *trans*-propenylcarbinols, the new double bond formed is also mainly, or exclusively, *trans*. The evidence concerning (*b*) is circumstantial rather than conclusive and is mainly based on the following observations : (i) the phenylpropenylcarbinol (I*b*) obtained from crotonaldehyde and phenylmagnesium bromide has a *trans*-configuration (Braude and Coles, *J.*, 1951, 2078) and rearranges to a methylstyrylcarbinol (II*b*) which is identical with that obtained from cinnamaldehyde and methylmagnesium bromide (Braude, Jones, and Stern, *J.*, 1946, 396) and is now shown to have a *trans*-configuration; (ii) the propenylvinylcarbinol (IV*b*) obtained from crotonaldehyde (Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 88) has been shown to have the *trans*-configuration (Braude and Coles, *loc. cit.*) and rearranges to a butadienylmethylcarbinol (V*b*) which readily forms a maleic anhydride adduct in good yield (Heilbron *et al.*, *loc. cit.*) and may therefore be assumed to have a *trans*-configuration (D. Craig, *J. Amer. Chem. Soc.*, 1943, **65**, 1006; 1950, **72**, 1678; Petrov, *J. Gen. Chem. U.S.S.R.*, 1948, **18**, 1125; L. E. Craig and Larrabee, *J. Amer. Chem. Soc.*, 1951, **73**, 1192). Clearly, however, these results do not prove that only the rearranged *trans*-isomers are initially formed unless the corresponding rearranged *cis*-isomers are stable under the reaction conditions. It is relevant also that the formation of mixtures of rearranged *cis*- and *trans*-isomers has been considered (Braude and Jones, 1946, 122; Braude, Jones, and Stern, *loc. cit.*; Braude and Stern, *J.*, 1947, 1096) as one possible explanation of certain discrepancies in the ultra-violet light absorption of the products of some oxotropic rearrangements before and after their isolation from the reaction medium.

The present paper is concerned with a closer study of the stereochemical course of three-carbon oxotropy and of the influence of geometrical configuration in the starting compounds. The rearrangements of a number of 1 : 3-substituted allyl alcohols probably having the *cis*-configuration, since they were prepared by partial catalytic hydrogenation of the corresponding 1 : 3-substituted propargyl alcohols, have been described (cf. Nazarov and Fisher, *Bull Acad. Sci.*

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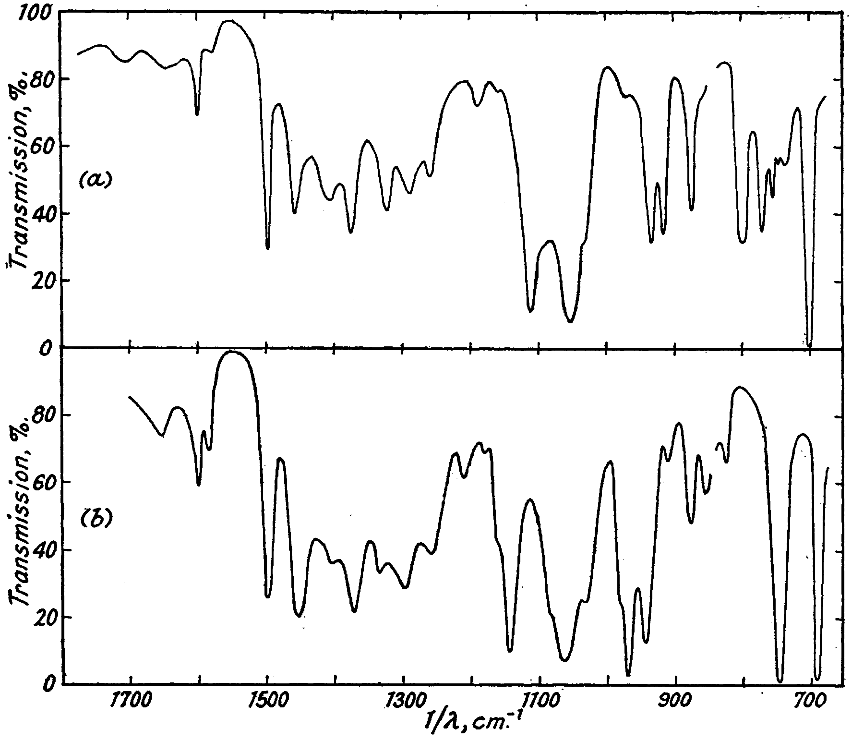
* Part VI, *J.*, 1951, 1755.

U.R.S.S., Cl. Sci. Chim., 1945, 631; 1948, 311, 427; 1949, 386; *J. Gen. Chem. U.S.S.R.*, 1950, **20**, 1107, 1114), but neither the stereochemical homogeneity of the starting materials, nor the stereochemical configuration of the products, was established. The synthesis of three stereochemically pure *cis*-propenylcarbinols described in the preceding paper provided us with an opportunity to compare, for the first time, the rearrangement of authentic geometrical isomers of known configuration.

*Oxotropic Rearrangement of Phenyl-*cis- *and* -trans-*propenylcarbinols.*—Phenyl-*cis*-propenylcarbinol (*cis*-1-phenylbut-2-enol) (I*a*), like its *trans*-isomer (I*b*), undergoes rearrangement in the presence of dilute acids in aqueous dioxan and is converted into methyl-*trans*-styrylcarbinol (*trans*-4-phenylbut-3-en-2-ol) (II*b*). The identity of the rearrangement products of (I*a* and *b*) was established by their ultra-violet and infra-red light absorption and by the formation of the same *p*-nitrobenzoate. The structure and configuration of methyl-*trans*-styrylcarbinol follows from its alternative syntheses (Klages, *Ber.*, 1902, **35**, 2650; Wright, *J. Org. Chem.*, 1936, **1**, 457; Kenyon, Partridge, and Phillips, *loc. cit.*; Braude, Jones, and Stern, *loc. cit.*) and from a comparison of its physical properties with those of the *cis*-isomer described below. Quantitative spectrometric measurements, which will be reported in detail later, show that the rearrangement of *cis*-phenylpropenylcarbinol is about half as fast as that of the *trans*-isomer and that the product in each case contains less than 5% of methyl-*cis*-styrylcarbinol.

FIG. 1.

Infra-red light absorption in 20% *carbon tetrachloride* (1800—840 *cm.*$^{-1}$) *and* 10% cyclo*hexane* (840—670 *cm.*$^{-1}$). *Cell thickness*, 0·013 *cm.* (*a*) *Methyl-*cis- *and* (b) -trans-*styrylcarbinol.*



Ph·CH(OH)·CH=CHMe	Ph·CH=CH·CHMe·OH	Ph·C≡C·CHMe·OH
(I; *a* = *cis*; *b* = *trans*.)	(II; *a* = *cis*; *b* = *trans*.)	(III.)

To confirm the configuration of (II*b*) and test the possibility that its formation as above might proceed partly or wholly through (II*a*), the latter was synthesized by condensing phenylethynylmagnesium bromide with acetaldehyde and partially hydrogenating the resulting 4-phenylbut-3-yn-2-ol (III) in the presence of a palladium–calcium carbonate catalyst. *cis*-Methylstyrylcarbinol (II*a*), unlike the *trans*-isomer, is a liquid at room temperature and there are interesting differences in their light absorption properties. The infra-red results which were kindly determined by Mr. Philpotts and Mr. Thain (cf. *Nature*, 1950, **166**, 1028) are shown in Fig. 1. As with the stereoisomeric phenylpropenylcarbinols (Braude and Coles, *loc. cit.*), the *trans*-isomer exhibits bands near 970 and 760 cm.$^{-1}$ which are much more intense than those of the *cis*-isomer. The assignment of the 760-cm.$^{-1}$ band is uncertain, while the 970-cm.$^{-1}$ band also appears in other *trans*-ethylenic carbinols and is ascribed to superposed deformation frequencies of the $-C-O-H$ and $R-CH=CH-R$ groupings; it is noteworthy that this frequency is very little affected by conjugation with a phenyl group.

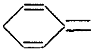
The ultra-violet data are shown in Fig. 2. Both methylstyrylcarbinols exhibit an intense band near 2500 A. associated with the styryl chromophore, but whereas the maximum of the *trans*-isomer (2510 A., ε 19,500) is displaced towards longer wave-lengths and intensified with respect to that of styrene itself ($\lambda_{max.}$ 2420 A., ε 10,000), the location and intensity of the maximum of the *cis*-isomer (2400 A., ε 12,000) are very similar to those of styrene. It has previously been shown (Braude and Timmons, *J.*, 1950, 2000) that the bathochromic and hyperchromic displacements of the *K*-band in the *trans*-isomer is due to the hyperconjugative effect of the CHMe·OH substituent, *e.g.*, to contributions from + =CH–CH=CHMe OH⁻. Now, hyperconjugation like other types of conjugation imparts some double-bond character to conventional single bonds and therefore requires a coplanar or nearly coplanar arrangement of the groups concerned. In methyl-*trans*-styrylcarbinol, there is no hindrance to free rotation of the CHMe·OH group, but in the *cis*-isomer (Fig. 3) considerable steric interference occurs with the *o*-hydrogen atoms of the phenyl group (Fig. 3 has been drawn with covalent radii which represent a *minimum* measure of interference; cf., *J.*, 1949, 1890). Consequently, hyperconjugation will be inhibited, with the result that the absorption closely resembles that of styrene itself. A similar case of steric inhibition of hyperconjugation has been observed in the more highly substituted dimethyl-α-methyl-*trans*-styrylcarbinol (Braude and Timmons, *loc. cit.*).

FIG. 2.

Ultra-violet light absorption of methyl-cis- (· — · — · —) *and* -trans-*styrylcarbinol* (————) *in ethanol.*

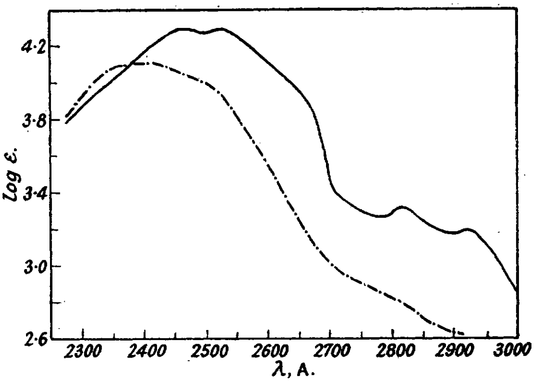
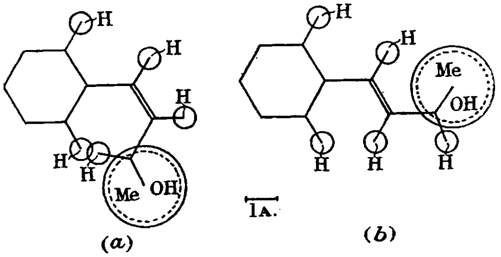


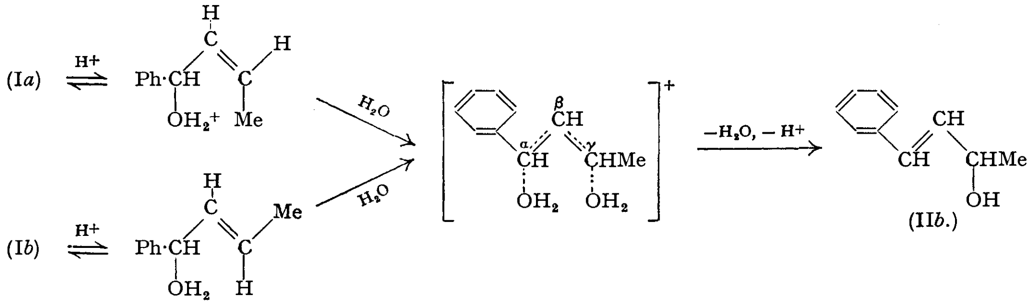
FIG. 3.

Planar projections (covalent bond radii) of methyl-cis-*styrylcarbinol (a) and* trans-*methylstyrylcarbinol (b).*



Methyl-*cis*-styrylcarbinol shows no tendency to isomerise to the *trans*-isomer under ordinary conditions or in presence of dilute acids in aqueous dioxan. It may therefore be concluded that methyl-*trans*-styrylcarbinol is the *direct* product of the oxotropic rearrangement of both *cis*- and *trans*-phenylpropenylcarbinol. This result is not unexpected. It has been shown that, under the conditions used, the reaction proceeds predominantly by way of a bimolecular attack of a solvent water molecule at the γ-carbon atom of the oxonium ion, formed by the reversible addition of a proton to the hydroxyl group of the carbinol (Braude, Jones, and Stern, *loc. cit.*; Braude, *Ann. Reports*, 1949, **46**, 125; *Quart. Reviews*, 1950, **4**, 404). Initially, rotation about the C_α–C_β bond will be quite free, but during the formation of the transition state the phenyl group would be expected to take up a position on the far rather than on the near side of the γ-carbon atom, since the latter arrangement would result in serious over-crowding which is shown by scale models and borne out by the physical properties of methyl-*cis*-styrylcarbinol (see below). Thus, whichever the orientation of the double bond in the unrearranged carbinol, the new double bond which is formed between the C_α- and C_β-carbon atoms would be expected to assume the *trans*-configuration, in agreement with the experimental results in this case.

Oxotropic Rearrangement of cis- *and* trans-*Propenylvinylcarbinols.*—The acid-catalysed



rearrangement of *trans*-propenylvinylcarbinol (*trans*-hexa-1 : 4-dien-3-ol) (IV*b*) was first studied by Heilbron, Jones, McCombie, and Weedon (*loc. cit.*) who found that under mild conditions the only product is butadienylmethylcarbinol (hexa-3 : 5-dien-2-ol) (V) although the latter undergoes further rearrangement into sorbyl alcohol (VI) under more strongly acid conditions (Nazarov and Fisher, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1948, 311, 427). A more detailed study of the corresponding reactions of higher homologues has shown (Braude and Timmons, *J.*, 1950, 2007) that in the oxotropic rearrangement of unsymmetrical dialkenylcarbinols, the hydroxyl group always migrates preferentially to the more highly substituted γ-carbon atom and that the three-carbon oxotropic change is followed by a slower, reversible, five-carbon oxotropic change which results in a mixture of the two conjugated isomers. As the ratio of the rates of the two reactions is of the order of 10^3, only the first product is isolated under suitable conditions. The butadienylmethylcarbinol obtained by Heilbron *et al.* (*loc. cit.*) formed an α-naphthylurethane, m. p. 84°; it gave a maleic anhydride adduct readily and in good yield and therefore consisted mainly, or entirely, of the *trans*-isomer (V*b*). *cis*-Propenylvinylcarbinol (Braude and Coles, *loc. cit.*) similarly rearranges in the presence of dilute mineral acid to a butadienylmethylcarbinol, the skeletal structure of which was proved by catalytic hydrogenation to hexan-2-ol and oxidation of the latter to *n*-butyl methyl ketone, identified as the 2 : 4-dinitrophenylhydrazone. The rearrangement is about half as fast as that of the *trans*-

$Me{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$ (IV; *a* = *cis*; *b* = *trans*.) $Me{\cdot}CH(OH){\cdot}CH{=}CH{\cdot}CH{=}CH_2$ (V; a = *cis*; b = *trans*.) $Me{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CH_2{\cdot}OH$ (VI.)

$Me{\cdot}CH{=}CH{\cdot}CH{=}CH_2$ (VII.)

isomer, and, as in the latter case, no detectable amount of the alternative rearrangement product, sorbyl alcohol (VI), is formed under these conditions. However, unlike the *trans*-butadienylmethylcarbinol obtained from *trans*-propenylvinylcarbinol, the butadienylmethylcarbinol produced by rearrangement of *cis*-propenylvinylcarbinol gave an α-naphthylurethane, m. p. 74—75°, and did not form a maleic anhydride adduct and must therefore be *cis*-butadienylmethylcarbinol (V*a*). The stereochemical relations of the geometrical isomers are reflected in a regularity of the melting points of the α-naphthylurethanes (Table I).

TABLE I.

M. p.s of α-naphthylurethanes.

	cis-Isomer.	*trans*-Isomer.	Difference.
Propenylvinylcarbinols (IV)	86—88°	94—95°	7—8°
Butadienylmethylcarbinols (V)	74—75	85—86	11

The two stereoisomeric butadienylmethylcarbinols also exhibit an interesting difference in ultra-violet light absorption. Both have a maximum at the same wavelength as piperylene (VII), but that of the *trans*-isomer is somewhat intensified, whereas that of the *cis*-isomer is somewhat reduced in intensity. By contrast, *cis*- and *trans*-piperylene have maxima of identical intensity in ethanol solution (Table II).*

TABLE II.

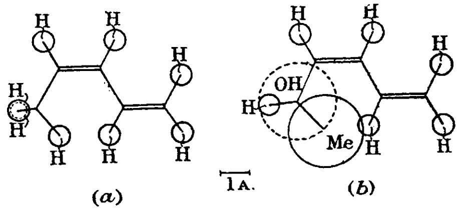
	$\lambda_{max.}$, A.	$\varepsilon_{max.}$ (in ethanol).
cis-Piperylene (VII*a*)	2230	22,600
trans-Piperylene (VII*b*)	2235	23,000 [1]
cis-Butadienylmethylcarbinol (V*a*)	2240	20,000
trans-Butadienylmethylcarbinol (V*b*)	2230	28,000 [2]

[1] Booker, Evans, and Gillam, *J.*, 1940, 1453. [2] Heilbron, *et al.*, *loc. cit.*

Our interpretation of these data is briefly as follows. The enhanced intensity in the *trans*-carbinol (V*b*) compared with piperylene is caused by the larger hyperconjugative effect of the –C–OH compared with the –C–H grouping; similar differences are found for other ethylenic carbinols (Braude and Timmons, *J.*, 1950, 2000, 2007). The reduced intensity in the *cis*-carbinol (V*a*) is ascribed to steric interference between the CHMe·OH and the CH$=$CH$_2$ groupings (see Fig. 4*b*) which prevents complete coplanarity of the hyperconjugated system; this effect is very similar to, but smaller than, that observed for methyl-*cis*-styrylcarbinol (see above).† In piperylene, on the other hand, no steric opposition to coplanarity is indicated in the *cis*-form (see Fig. 4*a*) and the absorption of the two geometrical isomers is therefore identical.

FIG. 4.

Planar projections (covalent bond radii) of cis-*piperylene (a) and* cis-*butadienylmethylcarbinol (b).*



The formation of the two different stereoisomeric butadienylmethylcarbinols by the rearrangement of *cis*- and *trans*-propenylvinylcarbinols is quite unexpected, for two reasons. First, whatever the relative stability of the *cis*- and *trans*-butadienylmethylcarbinols, *the same*

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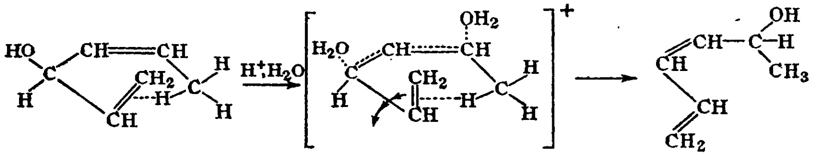
* In heptane, the value of $\varepsilon_{max.}$ is about 10% higher for *trans*- than for *cis*-piperylene (Jacobs and Platt, *J. Chem. Physics*, 1948, **76**, 1142). In this less solvating solvent, the vibrational structure of the bands is more pronounced and the shapes of the band-envelopes for the two isomers differ considerably. In such circumstances, the integrated band areas rather than $\varepsilon_{max.}$ must be used as a measure of the probability of the electronic transition and are, in fact, identical within experimental error. In the vapour phase, the value of $\varepsilon_{max.}$ for *trans*-piperylene is reported to be almost doubled (Jacobs and Platt, *loc. cit.*). The reason for this is not clear.

† There is a significant difference between the two cases. The main contribution to hyperconjugation comes from the C–OH bond and for this hyperconjugation to be fully effective, the C–OH bond must be parallel to the π-electron orbitals of the styryl system, *i.e.*, *at right angles* to the plane of the styryl system. This requirement follows both from valency-bond theory, since the other three groups attached to the terminal carbon atom will tend to be coplanar in the extreme hyperconjugated structure $X^- {=}CH{-}CH{=}CR_2\,OH^+$, and from molecular-orbital theory by the principle of maximum overlap. In the optimum arrangement, the C–H and C–Me bonds of the CHMe·OH group will therefore be symmetrically disposed at angles of about 18° with respect to the plane of the styryl system. Now with *cis*-methylstyrylcarbinol, steric interference is indicated for either of the two rotational positions of the CHMe·OH group, representing the optimum arrangement. With *cis*-butadienylmethylcarbinol, on the other hand, steric interference is indicated in only one (*e.g.*, that shown in Fig. 4*b*) of the two rotational positions representing the optimum arrangement of the CHMe·OH group. Thus steric inhibition of hyperconjugation will be less severe in the latter case. These matters will be dealt with more fully in a forthcoming publication in another series (cf. *J.*, 1949, 1890).

product would be expected from both cis- *and* trans-*propenylvinylcarbinols since rotation about the* C_α–C_β *bond should be essentially free,* so that the configuration of the rearranged carbinol should be independent of the configuration of the starting carbinol. Secondly, it would be expected that the rearranged *trans*-carbinol should be formed preferentially, as in the case of methylstyrylcarbinol, since in the rearranged *cis*-carbinol effective conjugation is somewhat inhibited by steric hindrance to coplanarity. However, one of these assumptions is evidently incorrect, and some factor is clearly operative which results in the formation of the thermodynamically less stable structure from *cis*-propenylvinylcarbinol. The conclusion appears inevitable that rotation about the C_α–C_β bond is essentially free in *trans*-propenylvinylcarbinol, but not free in *cis*-propenylvinylcarbinol and that *some interaction occurs between the* cis-*methyl substituent and the vinyl group, which holds the latter in a* cis-*orientation both before and during the rearrangement.* In explanation, we advance the tentative hypothesis that this effect has its origin in the hyperconjugation of the propenyl group which confers a fractional positive charge on the hydrogen atoms of the *cis*-methyl substituent and that an intramolecular interaction takes place between the hyperconjugated hydrogen atoms and the π-electrons of vinyl group to form a pseudo-cyclic structure, as shown below (IV*a*). Such an interaction, which may be termed "π-hydrogen bonding," can be visualised as intermediate in character between ordinary hydrogen bonding, in which a potential proton interacts with a basic group, such as NR_2 or OR, carrying unshared electron pairs, and π-bonding, in which a cation or potential cation, such as H^+, Ag^+ or Br^+, interacts with the unsaturation electrons of a multiple bond (Dewar, *J.*, 1946, 406; for further examples, see Hildebrand, Benesi, and Mower, *J. Amer. Chem. Soc.*, 1950, **72**, 1017; Mulliken, *ibid.*, p. 600; Andrews and Keefer, *ibid.*, pp. 5034, 5170; Brown *et al.*, *ibid.*, p. 5347). The present conception is novel, however, in that the π-bonded proton is derived from a hyperconjugated C–H bond, instead of from a more highly polar N–H, O–H, or Hal–H bond.



π-Hydrogen bonding must be visualised as a weak type of bonding, representing a stabilisation of not more than 1—2 kcals./mole. This is clearly shown by the fact that *cis*-phenylpropenylcarbinol, in which π-hydrogen bonding would similarly be expected to take place between the *cis*-methyl and the phenyl group, rearranges to the *trans*-styryl isomer. In this case, any stabilisation of the *cis*-orientation in the unrearranged carbinol is clearly outweighed by steric opposition to the formation of the *cis*-rearranged isomer, which may amount to not less than 4 kcals./mole and becomes the controlling factor in the transition state, as was discussed above (p. 2088). Again, *iso*butenylvinylcarbinol (VIII), which contains both a *cis*- and a *trans*-methyl substituent, appears to rearrange to *trans*-butadienyldimethylcarbinol (IX*b*) since the product

$Me_2C{=}CH{\cdot}CH(OH){\cdot}CH{=}CH_2$ (VIII.) $\qquad$ $Me_2C(OH){\cdot}CH{=}CH{\cdot}CH{=}CH_2$ (IX.)

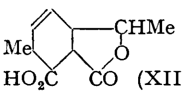
gives a maleic anhydride adduct in moderate yield and has normal light-absorption properties (Braude and Timmons, *locc. cit.*). In this case also, the corresponding *cis*-rearranged isomer will be considerably more sterically hindered than *cis*-butadienylmethylcarbinol; in addition π-hydrogen bonding will be weaker in (VIII) than in (IV*a*), since reactivity data show that the extent of hyperconjugation *per methyl substituent* is considerably smaller in an *iso*butenyl than in a propenyl group (Braude and Jones, *J.*, 1946, 122, 128).

The observation that the oxotropy of two stereoisomeric ethylenic carbinols can give rise to two different stereoisomeric products has another important consequence, which is quite independent of the above explanation. Although recent work from this laboratory has provided strong evidence for a mechanism of oxotropy which involves bimolecular attack by a neutral reagent at the γ-carbon atom of the oxonium ion (cf. Braude, *Ann. Reports*, 1949, **46**, 125; Braude and Forbes, *J.*, 1951, 1755), yet it has not been possible hitherto to exclude with certainty an alternative view, which involves unimolecular ionisation of the oxonium ion into a free mesomeric carbonium ion. Indeed, the exponents of the latter type of mechanism (cf. Catchpole, Hughes, and Ingold, *J.*, 1948, 8) still consider that the carbonium ion may be formed by direct ionisation of the carbinol, whereas we have for some time regarded the preceding formation of the oxonium ion and the essential requirement of hydrogen-ion catalysis in aqueous media as definitely proven. *The present results, moreover, provide compelling evidence against the intervention of the free, mesomeric carbonium ion,* for the following reason. The postulate of a free carbonium-ion intermediate is equivalent to the assumption of a reversible heterolysis of the existing C–O bond *before* the new C–O bond is formed, and to a reversible migration of the fully developed positive charge from one end to the other of the pentadiene chain. Under such conditions, the stereochemical configuration about each of the carbon bonds will be quite labile and the hypothetical ions derived from two stereoisomeric carbinols such as (IV*a*) and (IV*b*) would be able to adopt the same configuration or mixture of configurations, and therefore give rise to sterically identical products.

Oxotropic Rearrangement of cis-trans-*Dipropenylcarbinol.*—*cis-trans*-Dipropenylcarbinol (-hepta-2 : 5-dien-4-ol) (X*a*), like its lower homologue, undergoes oxotropic rearrangement in the presence of dilute acids to give the conjugated isomer hepta-3 : 5-dien-2-ol (XI). The skeletal structure of the product was proved by its ultra-violet light absorption ($\lambda_{max.}$ 2270 A., ε 23,000), typical of a diene system containing two alkyl substituents, and by catalytic hydrogenation to heptan-2-ol, followed by oxidation to *n*-amyl methyl ketone, identified as the 2 : 4-dinitrophenylhydrazone. Although (X) is skeletally symmetrical and can give rise to only one type of conjugated isomer, an element of dissymmetry is introduced in the present instance through the different geometrical configurations of the propenyl groups and the rearrangement can involve the migration of either of the ethylenic bonds. As judged by the results obtained in the oxotropy of the propenylvinylcarbinols, the new double bond formed would be expected to have a different geometrical configuration in the two cases. Since, moreover, the rates of rearrangement of *cis*- and *trans*-propenylvinylcarbinol are of the same order, it would be expected that the rearrangement of *cis-trans*-dipropenylcarbinol will give rise to a mixture of stereoisomeric hepta-3 : 5-dien-2-ols. This is in accord with the extinction coefficient of the product, which is intermediate between the values for a *cis*- and a *trans*-dienol (Table II) and with the fact that the product reacted with maleic anhydride to give a low yield of adduct which was isolated as the lactonic acid (XII) analogous to those obtained from homologous dienols (Heilbron *et al.*, *loc. cit.*; Braude and Timmons, *loc. cit.*). Although the possibility of some geometrical isomerisation under the influence of the reagents cannot definitely be excluded, it thus appears that the rearrangement of *cis-trans*-dipropenylcarbinol yields a mixture of the *cis-trans*- and *trans-trans*-isomers (XI).

Me·CH=CH·CH(OH)·CH=CHMe (X.)

Me·CH(OH)·CH=CH·CH=CHMe (XI.)


(XII.)

EXPERIMENTAL.

M. p.s were determined on a Kofler block and are corrected.

*Rearrangement of Phenyl-*cis-*propenylcarbinol* (I*a*).—A solution of phenyl-*cis*-propenylcarbinol (Braude and Coles, *loc. cit.*, p. 2082; 9 g.) in 60% aqueous acetone (100 ml.) 0·01M. in respect of hydrochloric acid was kept for 20 hours at room temperature. After neutralisation with sodium carbonate, the acetone was distilled off and the residue extracted with ether. Fractionation of the ethereal extract from a trace of potassium carbonate gave methyl-*trans*-styrylcarbinol (6 g.), b. p. 97°/0·1 mm., n_D^{19} 1·5654 (Braude, Jones, and Stern, *J.*, 1946, 396, give b. p. 104°/1 mm., n_D^{21} 1·5665), the ultra-violet and infra-red light absorptions of which were indistinguishable from those (Figs. 1*a* and 1*b*) of an authentic specimen obtained by the rearrangement of phenyl-*trans*-propenylcarbinol. It formed a *p*-nitrobenzoate, m. p. 57—58° (Kenyon, Partridge, and Phillips, *J.*, 1937, 207, give m. p. 58—59°), undepressed on admixture with an authentic specimen.

4-*Phenylbut*-3-*yn*-2-*ol* (III) *and Methyl-*cis-*styrylcarbinol* (II*a*).—Phenylacetylene (34 g.) (Nef, *Annalen*, 1899, **308**, 267), b. p. 95°/166 mm., n_D^{24} 1·5468, in ether (30 ml.) was gradually added to a solution of ethylmagnesium bromide (from Mg, 9 g.) in ether (300 ml.) (cf. Wilson and Hyslop, *J.*, 1924, 1556). After 4 hours' refluxing, the solution was cooled to 0° and freshly distilled acetaldehyde (16 g.) in ether (30 ml.) was added. Stirring was continued overnight and the products were then worked up in the usual manner to give 4-*phenylbut*-3-*yn*-2-*ol* (30 g., 61%), b. p. 101°/0·3 mm., n_D^{21} 1·5672 (Found: C, 82·5; H, 7·1. $C_{10}H_{10}O$ requires C, 82·2; H, 6·9%).

4-Phenylbut-3-yn-2-ol (4·85 g., 0·033 mol.) in methanol (25 ml.) was hydrogenated in the presence of 0·3% palladium–calcium carbonate (0·4 g.) until 800 ml. (0·033 mol.) at 20°/766 mm. had been absorbed. Removal of the catalyst and fractionation gave methyl-*cis*-styrylcarbinol (3·6 g.), b. p. 77°/0·1 mm., n_D^{21} 1·5510 (Found: C, 80·95; H, 8·1. $C_{10}H_{12}O$ requires C, 80·9; H, 8·1%). Light absorption: see Figs. 1*a* and 1*b*. The ultra-violet light absorption of a solution of the carbinol in 60% aqueous dioxan 0·1M. in respect of hydrochloric acid remained unchanged after 18 hours at room temperature.

Rearrangement of cis-*Propenylvinylcarbinol* (IV*a*).—(*a*) A solution of *cis*-propenylvinylcarbinol prepared by the condensation of *cis*-propenyl-lithium with acraldehyde (Braude and Coles, *loc. cit.*, p. 2083) (4 g.) in 60% aqueous acetone (100 ml.) 0·05M. in respect of hydrochloric acid was kept at room temperature for 20 hours. After neutralisation with sodium carbonate (0·3 g.), the acetone was distilled off through an 8″ Fenske column, and the residue extracted with ether. Fractionation of the ethereal extract gave cis-*butadienylmethylcarbinol* (cis-*hexa*-3 : 5-*dien*-2-*ol*) (2 g.), b. p. 113°/99 mm., 57—58°/14 mm., n_D^{21} 1·4800 (Found: C, 73·6; H, 10·0. $C_6H_{10}O$ requires C, 73·4; H, 10·25%). Light absorption in ethanol: Max. at 2240 A., ε 20,000. The carbinol formed an α-naphthylurethane, m. p. 74—75° (Found: C, 76·6; H, 6·4. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4%), but gave no adduct on being kept with maleic anhydride in benzene for a week.

Hydrogenation of *cis*-butadienylmethylcarbinol (0·6 g.) in methanol (20 ml.) in the presence of platinic oxide resulted in the uptake of 320 ml. at 20°/763 mm. (Calc., 300 ml.). After removal of the catalyst and solvent, the residue was taken up in ether (10 ml.) and oxidised by shaking it with potassium dichromate (0·7 g.) in M-sulphuric acid. The product was extracted with ether and converted into the 2 : 4-dinitrophenylhydrazone. Chromatography of the latter on alumina from benzene solution yielded only the *n*-butyl methyl ketone derivative, which after crystallisation from aqueous methanol had m. p. 108°, undepressed on admixture with an authentic specimen.

(*b*) A mixture (2 g.; b. p. 44—47°/12 mm., n_D^{20} 1·4500) of *cis*-propenylvinylcarbinol and ethylpropenylcarbinol, obtained by partial hydrogenation of ethynylpropynylcarbinol (Braude and Coles, *loc. cit.*) was treated with aqueous acetone and hydrochloric acid as under (*a*). The product before fractionation had $\lambda_{max.}$ 2240, ε 10,200 which corresponds to a mixture consisting of *cis*-butadienylmethylcarbinol 50% and unchanged ethylpropenylcarbinol 50%. This mixture was fractionated through a 3″ Fenski column to give the following main fractions: (i) b. p. 56—57°/15 mm., n_D^{24} 1·4615 (0·5 g.); (ii) b. p. 57—58°, n_D^{24} 1·4652 (0·4 g.); (iii) b. p. 58—59°, n_D^{24} 1·4696 (0·4 g.); and (iv) b. p. 59—60°, n_D^{24} 1·4738 (0·3 g.). The last fraction consisted of almost pure *cis*-butadienylmethylcarbinol; it had $\lambda_{max.}$ 2240 A., ε 19,500, and gave an α-naphthylurethane, m. p. 75—76°, undepressed on admixture with specimen obtained as under (*a*), but depressed to 67—69° on admixture with the α-naphthylurethane of ethylpropenylcarbinol (Braude and Coles, *loc. cit.*, p. 2084).

Rearrangement of cis-trans-*Dipropenylcarbinol* (X).—A solution of *cis-trans*-dipropenylcarbinol (Braude and Coles, *loc. cit.*, p. 2084) (6 g.) in 60% aqueous acetone (100 ml.) 0·01M. in respect of hydrochloric acid was kept for 1 hour at room temperature. After neutralisation with potassium carbonate (70 mg.) the acetone was distilled off through an 8″ Fenske column, the aqueous residue was extracted with ether, and the ethereal extract was dried (Na_2SO_4–K_2CO_3) and fractionated to give *hepta*-3 : 5-*dien*-2-*ol* (4·5 g.), b. p. 78°/20 mm., n_D^{21} 1·4897 (Found: C, 74·7; H, 10·8. $C_7H_{12}O$ requires C, 75·0; H, 10·8%). Light absorption in ethanol: $\lambda_{max.}$ 2270 A., ε 20,700. A solution of the carbinol (0·5 g.) and maleic anhydride (0·5 g.) in dry benzene (2 ml.), after being kept for 2 weeks, deposited 3-1′-*hydroxyethyl*-6-*methyl*cyclo*hexene*-4 : 5-*dicarboxylic acid* 4-*lactone* (XII) (0·2 g.) which crystallised from aqueous ethanol in prisms, m. p. 182—183° (Found: C, 62·7; H, 6·8. $C_{11}H_{14}O_4$ requires C, 62·85; H, 6·7%).

Hydrogenation of hepta-3 : 5-dien-2-ol (1·95 g.) in methanol (30 ml.) in the presence of platinic oxide resulted in the uptake of 820 ml. at 18°/768 mm. (Calc., 825 ml.) to give *n*-heptan-2-ol (1·6 g.). A small portion was converted into the α-naphthylurethane which was crystallised from light petroleum (b. p. 100—120°) and had m. p. 122—123°. The remainder (1·5 g.) was dissolved in ether (10 ml.) and oxidised with potassium dichromate (1·3 g.) in M-sulphuric acid (30 ml.), to give *n*-amyl methyl ketone, identified as the 2 : 4-dinitrophenylhydrazone (2·1 g.) which after chromatography on alumina from benzene solution and crystallisation from methanol had m. p. 96—97°, undepressed on admixture with an authentic specimen.

cis-*Piperylene*.—A sample of highly purified *cis*-piperylene, b. p. 43·2°/733 mm., n_D^{20} 1·4360, was kindly furnished by Dr. D. Craig, to whom we express our thanks.

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