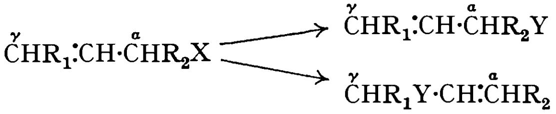
360. *The Mechanism of Replacement Reactions in Allyl Compounds: Reactions of* (+)-n-*Propylpropenylcarbinol and its Derivatives.*

By C. L. Arcus and J. Kenyon.

From a study of the replacement reactions of the hydrogen phthalic ester and of the chloride of (+)-*n*-propylpropenylcarbinol, it is concluded that that the reactions proceed *via* dissociation into the ion $\overbrace{\text{CHMe·CH·CHPr}}^{\oplus}$, leading to racemisation and isomerisation. Two general mechanisms of substitution reactions in allyl compounds are formulated from a consideration of results now, and previously, reported, and their stereochemical consequences considered.

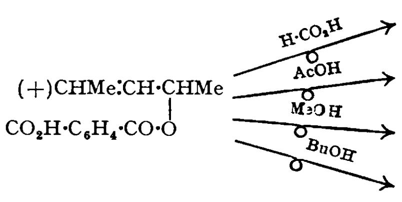
An explanation of the behaviour on saponification of the hydrogen phthalic esters of substituted allyl alcohols, which is normal in alkaline, abnormal in neutral solutions, is suggested.

Several investigations on the isomerisation occurring during replacement reactions of substituted allyl alcohols have been described (Prévost, *Compt. rend.*, 1927, **185**, 1283; Meisenheimer and Beutter, *Annalen*, 1934, **508**, 58; Burton, J., 1928, 1650; Young and Lane, *J. Amer. Chem. Soc.*, 1938, **60**, 847). The study of such reactions by the use of optically active substituted allyl alcohols was initiated by Hills, Kenyon, and Phillips (on αγ-dimethylallyl alcohol; J., 1936, 576) and was extended to those of derivatives of (—)-α-phenyl-γ-methylallyl alcohol by Kenyon, Partridge, and Phillips (J., 1937, 207).



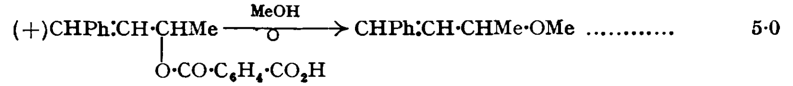
$$\overset{\gamma}{\text{C}}\text{HR}_1\text{:CH·}\overset{\alpha}{\text{C}}\text{HR}_2\text{X} \rightarrow \overset{\gamma}{\text{C}}\text{HR}_1\text{:CH·}\overset{\alpha}{\text{C}}\text{HR}_2\text{Y} \quad \text{and} \quad \overset{\gamma}{\text{C}}\text{HR}_1\text{Y·CH:}\overset{\alpha}{\text{C}}\text{HR}_2$$

The pronounced loss of optical purity is a striking feature of these reactions. Hills, Kenyon, and Phillips observed the following replacements (in course of publication):



	Optical purity, %.
CHMe:CH·CHMe·O·CHO	0·7
CHMe:CH·CHMe·OAc	0·8
CHMe:CH·CHMe·OMe	6·0
CHMe:CH·CHMe·OBu^a	8·0

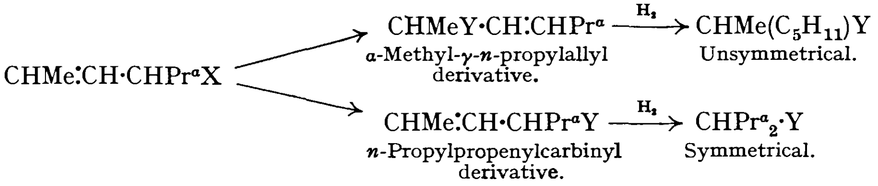
and Kenyon, Partridge, and Phillips (*loc. cit.*) the following:



$$(+)\mathrm{CHPh{:}CH{\cdot}\underset{\displaystyle O{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H}{CHMe}} \xrightarrow[\mathrm{O}]{\mathrm{MeOH}} \mathrm{CHPh{:}CH{\cdot}CHMe{\cdot}OMe} \quad \ldots\ldots\ldots\ldots \quad 5{\cdot}0$$

The difficulty in interpreting the mechanism of replacement reactions of αγ-dimethylallyl derivatives is enhanced by the fact that, owing to the symmetrical character of the molecule, α and γ entrances yield the same chemical product, and the question as to whether entrance into the γ-position results in the formation of an optically active derivative cannot be settled.

The replacement reactions of derivatives of the less symmetrical (+)-*n*-propylpropenylcarbinol have now been examined; the resolution of this alcohol and the optical rotatory powers of its derivatives have already been reported (Arcus and Kenyon, this vol., p. 312). The production of an optically active derivative by entrance of the substituent group into the γ-position may be detected in this case by catalytic reduction of the reaction product, whereupon that optical activity due to a *n*-propylpropenylcarbinyl derivative is removed (owing to the production of a symmetrical di-*n*-propylcarbinyl derivative) whilst any optical activity due to a derivative of α-methyl-γ-*n*-propylallyl alcohol will persist as the optical activity of a methyl-*n*-amylcarbinyl derivative.



In view of the possibility of encountering the derivatives of α-methyl-γ-*n*-propylallyl alcohol, a knowledge of this compound was desirable, and its preparation and properties have been described (Arcus and Kenyon, this vol., p. 698). It was not found possible efficiently to separate mixtures of the isomeric alcohols, *n*-propylpropenylcarbinol and α-methyl-γ-*n*-propylallyl alcohol, which were the products of replacement reactions of certain derivatives of the former compound. Mixtures of the *p*-xenylurethanes, the *p*-nitrobenzoates, and the hydrogen phthalic esters underwent but little separation on recrystallisation; the hydrogen phthalic esters of the corresponding reduced alcohols, di-*n*-propylcarbinol and methyl-*n*-amylcarbinol, also are not readily separable. Estimation, by physical means, of the composition of a mixture of the unsaturated alcohols is also not possible owing to the similarity of the constants of these isomerides.

	B. p.	$n_D^{18°}$.	$d_{4°}^{18°}$.
n-Propylpropenylcarbinol	64°/15 mm.	1·4381	0·839
α-Methyl-γ-*n*-propylallyl alcohol	66°/16 mm.	1·4391	0·833

These considerations led to the adoption of the following procedure for the investigation of the product of a given reaction of (+)-*n*-propylpropenylcarbinyl hydrogen phthalate or of (—)-Δ^{β}-δ-chloroheptene. The product, which is referred to as a heptenyl derivative, was isolated as a constant-boiling fraction having physical constants in agreement with those of the corresponding pure *n*-propylpropenylcarbinyl derivative; after its rotatory power had been determined, the product was reduced with hydrogen at 2 atm. in the presence of either nickel or platinum catalyst, and the rotatory power of the reduced product was determined.

The results of replacement reactions of (+)-*n*-propylpropenylcarbinyl hydrogen phthalate with acetic, formic, and benzoic acids are given in Table I.

The optical result of these reactions is seen to be complete, or almost complete, racemisation. Moreover, when the acetate was reduced, the product was optically inactive. In no case therefore is an optically active derivative of α-methyl-γ-*n*-propylallyl alcohol formed, and hence no asymmetry is transferred to the C^{γ} atom. [Had such an optically active derivative been formed, the methyl-*n*-amylcarbinyl derivative obtained on reduction would certainly possess a sufficiently high rotatory power for detection; for the alcohol has $[\alpha]_{5893}$ + 10·32° (homogeneous) (Pickard and Kenyon, J., 1911, **99**, 45; 1914, **105**, 830), and the acetate has $[\alpha]_{5893}$ + 5·02° in ethyl alcohol.]

Hence, such optical activity as is shown by a product of the replacement reaction is due to a derivative of *n*-propylpropenylcarbinol. Comparison of the rotatory power of the acetate derived from the replacement reaction in Table I with the acetate prepared by the action of acetic anhydride on (+)-*n*-propylpropenylcarbinol shows that the former has been produced with inversion of configuration and has 0·2% of the maximum recorded rotatory power. This reaction proceeded slowly (the time for one-half total change in rotation being 317 hours) and was followed polarimetrically (Table III). The benzoate obtained in the last experiment in Table I was saponified with alcoholic potash, and the resultant heptenol converted into the *p*-xenylurethane, which was found to be a mixture.

TABLE I.

Replacement Reactions of (+)-n-Propylpropenylcarbinyl Hydrogen Phthalate.

(+)Hydrogen phthalate: $[\alpha]_{5461}$ in EtOH.	Optical purity, %.	Reaction mixture.	Temp.	Product, and optical properties.
+15·8°	69	H.P.,* 5 g. $CH_3{\cdot}CO_2H$, 20 g.	32°	Acetate, α_{5461} +0·05° (*l*, 0·5) = 0·2% of maximum; hence, inversion = 0·3%
+9·77	43	H.P., 11 g. $H{\cdot}CO_2H$, 4 g.	80	*dl*-Formate
+7·8	34	H.P., 20 g. $Ph{\cdot}CO_2H$, 27 g.	125	*dl*-Benzoate

* H.P. = Hydrogen phthalate.

(—)-Δ^{β}-δ-Chloroheptene was prepared by adding (+)-*n*-propylpropenylcarbinol mixed with pyridine to cooled phosphorus trichloride; since the last reagent, in the presence of pyridine, is believed to react invariably with inversion (Frankland, J., 1913, **103**, 713; Hughes, Ingold *et al.*, J., 1937, 1252), the chloride obtained will possess a configuration opposite to that of the carbinol.

The results of replacement reactions with water, methyl alcohol, and the acetate ion are given in Table II. Reduction of the first two products afforded optically inactive substances (λ_{5461}).

The optical results of the replacement reactions of the chloro-compound are similar to those of the hydrogen phthalic ester. (1) There is much, or complete, racemisation. (2) In no case is the reduced product optically active, whence no optically active derivative of α-methyl-γ-*n*-propylallyl alcohol is produced and no asymmetry is transferred to the C^{γ} atom. (3) Again, the whole of the optical activity is due to derivatives of *n*-propylpropenylcarbinol. The fact that the chloride is produced from the alcohol with inversion of configuration, together with a comparison of the sign and magnitude of the rotatory powers of the alcohol and the methyl ether produced in the first two reactions in Table II with those of the (+)alcohol and the methyl ether prepared from the (+)alcohol (by a method which

TABLE II.

Replacement Reactions of (—)-Δ^{β}-δ-Chloroheptene.

Rotation of original alcohol.	Optical purity, %.	Rotation of chloride.	Reaction mixture.	Temp.	Product, and optical properties.
$\alpha_{5461}^{20^\circ}$ +4·10° (*l*, 0·5)	95	$\alpha_{5461}^{22^\circ}$ −1·68° (*l*, 0·5)	Chloride, 4·2 g. Na_2CO_3, 2·3 g. H_2O, 45 g.	65°	Carbinol, $\alpha_{5461}^{23^\circ}$ +0·04° (*l*, 0·24) = 2% opt. pure; hence inversion = 2%
$\alpha_{5461}^{16\cdot5^\circ}$ −5·44 (*l*, 2·0)	30	$\alpha_{5461}^{16^\circ}$ +0·59 (*l*, 0·5)	Chloride, 6·3 g. K_2CO_3, 6·3 g. MeOH, 12·6 g.	80	Methyl ether, $\alpha_{5461}^{12^\circ}$ +0·09° (*l*, 0·5) = 0·38% opt. pure; hence inversion = 1·3%
$\alpha_{5461}^{16\cdot5^\circ}$ −5·44° (*l*, 2·0)	30	$\alpha_{5461}^{21^\circ}$ +0·48 (*l*, 0·5)	Chloride, 6·1 g. NaOAc, 5·5 g. HOAc, 14·4 g.	65	*dl*-Acetate

does not disturb the bonds of the asymmetric carbon atom), leads to the following conclusions. In the first reaction the carbinol is produced from the chloride with inversion of configuration and has 2% of the maximum rotatory power; in the second reaction the chloride undergoes alcoholysis to the methyl ether with inversion of configuration, and the ether has 1·3% of its maximum rotatory power.

An undetermined part of this great loss of optical activity occurs during the conversion of the alcohol into the chloride. The rotatory power of the latter is, however, of the same order as that of the alcohol from which it is derived, whereas the products of replacement reactions of the chloride possess rotatory powers of an order lower than that of the chloride. It is therefore likely that the bulk of the racemisation occurs during the reactions of the chloride, and not during its preparation.

The first experiment in Table II was repeated with the dl-*chloride*, a portion of the resultant heptenol being converted into the hydrogen phthalate, and a second portion reduced to the saturated alcohol, which was converted into its hydrogen phthalic ester. Both these hydrogen phthalates were mixtures. Under the conditions employed for the third reaction in Table II, it was found that the chloride does not react to an appreciable extent with the solvent, acetic acid.

From a study of the molecular rearrangement of (—)phenylmethylcarbinyl *dl-p*-toluenesulphinate (Arcus, Balfe, and Kenyon, this vol., p. 485), it was concluded that a free carbonium kation ($\overset{\oplus}{\mathrm{C}}\mathrm{HMePh}$) was liberated during this rearrangement, and that this kation possesses an effectively planar configuration; the dissociation into this kation is facilitated by a medium of high dielectric constant, and by solvation, in particular by hydroxylic solvents. The latter condition was present in all the above experiments, the solvents being water, methyl alcohol, and carboxylic acids. In view of the racemisation and isomerisation occurring during the replacement reactions of the hydrogen phthalic ester and the chloride of (+)-*n*-propylpropenylcarbinol, it may therefore be postulated that the carbonium kation $\overbrace{\mathrm{CHMe{\cdot}CH{\cdot}CHPr^{a}}}^{\oplus}$, which is effectively planar, is an intermediate in these reactions. Such an ion will lead to the formation of racemic products, and afford the possibility of entry by the substituent group at either the C^{α} or the C^{γ} atom, yielding a mixture of heptenyl derivatives.

Similar carbonium kations have been postulated by Prévost (*loc. cit.*) as intermediates in a number of reactions of compounds $\mathrm{CHR{:}CH{\cdot}CH_2X}$ and $\mathrm{CHRX{\cdot}CH{:}CH_2}$ during which isomerisation leading to a mixed product occurs. Young and Lane (*loc. cit.*) conclude from a study of the reaction of hydrogen bromide under defined conditions with crotyl alcohol, $\mathrm{CHMe{:}CH{\cdot}CH_2{\cdot}OH}$, and methylvinylcarbinol, $\mathrm{CHMe(OH){\cdot}CH{:}CH_2}$, that the major part of the reaction of each alcohol occurs *via* the common resonating ion $\overbrace{\mathrm{CHMe{\cdot}CH{\cdot}CH_2}}^{\oplus}$, yielding mixtures of the bromides $\mathrm{CHMe{:}CH{\cdot}CH_2Br}$ and $\mathrm{CHMeBr{\cdot}CH{:}CH_2}$. The difference (up to 12%) in composition of the mixtures of bromides from the two alcohols is attributed to subsidiary bimolecular substitutions whereby each alcohol yields the corresponding bromide.

The reactions recorded in Tables I and II are accompanied by up to 2% inversion of configuration at the C^{α} atom. This may arise from a subsidiary mechanism of substitution in which the substituent group becomes attached to the asymmetric carbon atom before the dissociation of the displaced group, leading to a Walden inversion (Kenyon and Phillips, *Trans. Faraday Soc.*, 1930, **26**, 451). Alternatively, during the above dissociation into a carbonium kation, the receding anion may shield that side of the carbon atom to which it was attached from the attacking molecules or ions, causing a small preponderance of the inverted configuration (Hughes, Ingold, *et al.*, J., 1937, 1252). It may be noted that the stereochemical consequences assigned by those authors to the two mechanisms of substitution denoted S_N1 and S_N2 do not, in such cases, furnish unequivocal information about the mechanism of a reaction from its stereochemical result; a replacement reaction accompanied by extensive racemisation may occur either by S_N1 or by a preponderating S_N1 mechanism with subsidiary S_N2.

A replacement reaction in an allyl compound has been studied kinetically by Meisenheimer and Beutter (*loc. cit.*). For the reaction of cinnamyl chloride with potassium acetate they found that (*a*) in acetic anhydride solution the reaction is approximately of the second order with regard to [$\mathrm{CHPh{:}CH\cdot CH_2Cl}$] and [KOAc], and cinnamyl acetate only is produced; (*b*) in acetic acid solution the reaction is intermediate between first and second order and the product is a mixture of cinnamyl acetate and phenylvinylcarbinyl acetate. A mechanism involving a termolecular reaction (one molecule being that of activated solvent) was proposed. The facts receive an alternative explanation if the reaction is regarded as proceeding by two courses. The first, involving slow preliminary ionisation followed by combination with acetate ion:

$$\mathrm{CHPh{:}CH\cdot CH_2Cl} \rightleftharpoons \overbrace{\mathrm{CHPh\cdot CH\cdot CH_2}}^{\oplus} + \mathrm{Cl}^{\ominus};\ \overbrace{\mathrm{CHPh\cdot CH\cdot CH_2}}^{\oplus} + \mathrm{AcO}^{\ominus} \begin{array}{l} \nearrow \mathrm{CHPh{:}CH\cdot CH_2(OAc)} \\ \searrow \mathrm{CHPh(OAc)\cdot CH{:}CH_2} \end{array}$$

will be kinetically of the first order, and the kation $\overbrace{\mathrm{CHPh\cdot CH\cdot CH_2}}^{\oplus}$ will permit the formation of a mixed product of cinnamyl and phenylvinylcarbinyl acetates.

The second course requires attack by the acetate ion on a molecule of cinnamyl chloride, is bimolecular, and should yield cinnamyl acetate only:

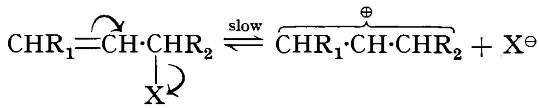
$$\mathrm{AcO}^{\ominus}\ .\ .\ .\ \mathrm{CH_2(CH{:}CHPh)Cl} \longrightarrow \mathrm{AcO\cdot CH_2(CH{:}CHPh)} + \mathrm{Cl}^{\ominus}$$

(These mechanisms are essentially those developed generally by Hughes and Ingold, J., 1935, 244, and designated S_N1 and S_N2.)

In the non-hydroxylic medium, acetic anhydride, the solvation necessary for ionisation does not appear to occur, and the reaction follows the second course. In acetic acid the first mechanism becomes effective, the kinetics approach towards the first order, and a mixture of acetates is produced.

It thus appears that the replacement reactions of substituted allyl compounds may be represented generally by a combination of two such mechanisms:

(*a*)



$$\mathrm{CHR_1{=}CH\cdot CHR_2(X)} \overset{\text{slow}}{\rightleftharpoons} \overbrace{\mathrm{CHR_1\cdot CH\cdot CHR_2}}^{\oplus} + \mathrm{X}^{\ominus}$$

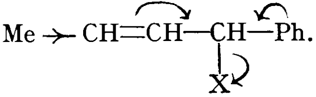
$$\overbrace{\mathrm{CHR_1\cdot CH\cdot CHR_2}}^{\oplus} + \mathrm{Y}^{\ominus} \begin{array}{l} \nearrow \mathrm{CHR_1{:}CH\cdot CHR_2Y} \\ \searrow \mathrm{CHR_1Y\cdot CH{:}CHR_2} \end{array}$$

(*b*) $\mathrm{Y}^{\ominus}\ .\ .\ .\ \mathrm{CHR_2(CH{:}CHR_1){-}X} \xrightarrow[\circ]{} \mathrm{Y{-}CHR_2(CH{:}CHR_1)} + \mathrm{X}^{\ominus}$

the first (unimolecular) leading to an equilibrium mixture of allyl isomers, and stereochemically, to much racemisation; the second (bimolecular) resulting in one product and a high degree of inversion of configuration about the C^{α} atom. The relative importance of these two mechanisms will be determined by the nature of the medium and reagent and the groups R_1 and R_2.

The liberation of the anion $X^{\ominus}$ in the above reactions is facilitated by the tautomeric (+ *T*) effect of the allyl group. Further, in those compounds in which R_1 is an alkyl group (*e.g.*, αγ-dimethylallyl alcohol, α-phenyl-γ-methylallyl alcohol, and *n*-propylpropenylcarbinol), the latter contributes a favourable inductive effect: $\mathrm{Me} \rightarrowtail \mathrm{CH{=}CH{-}CHR_2{-}X}$.

Compounds in which R_2 is the phenyl group are less stable than the isomers in which this group occupies the position R_1, the former passing into the latter (Burton, *loc. cit.*; Kenyon, Partridge, and Phillips, *loc. cit.*). The last authors, from a study of the facile rearrangement of α-phenyl-γ-methylallyl derivatives into those of γ-phenyl-α-methylallyl alcohol, concluded that the migrating anions are not kinetically free, since there is a high retention of asymmetry; also, the rearrangement is not markedly promoted by increasing dielectric constant of the medium, and the change was found to proceed at ordinary temperatures in the solid state in a single crystal of the hydrogen phthalic ester. The great ease with which this rearrangement proceeds appears to be due to the addition of the tautomeric (+ *T*) effect of the phenyl group to the electromeric effects already mentioned:



$\mathrm{Me} \rightarrowtail \mathrm{CH{=}CH{-}\underset{\underset{X}{|}}{C}H{-}Ph}$.

The α-phenylallyl esters (in which a γ-alkyl group is absent) also rearrange into their cinnamyl isomers (Burton, *loc. cit.*), but less readily than do the corresponding α-phenyl-γ-methylallyl compounds (Duveen, *Compt. rend.*, 1938, **206**, 1185).

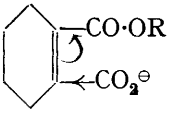
Since an alkyl radical cannot supply the tautomeric (+ *T*) effect of the phenyl nucleus, rearrangements similar to the above should proceed much less readily amongst the purely aliphatic allyl compounds. This accords with the following observations: on heating *dl*-α-phenyl-γ-methylallyl hydrogen phthalate (with an equal weight of pyridine), and the *dl*-*p*-nitrobenzoate (alone), on the steam-bath for 1 and 2½ hours, respectively, these esters were very largely converted into the *dl*-γ-phenyl-α-methylallyl isomerides (Kenyon, Partridge, and Phillips, *loc. cit.*). After similar treatment, the hydrogen phthalic esters and *p*-nitrobenzoates of the isomeric *n*-propylpropenylcarbinol and α-methyl-γ-*n*-propylallyl alcohol were recovered unchanged.

Change Undergone by (+)-n-*Propylpropenylcarbinyl* dl-p-*Toluenesulphinate*.—On adding *p*-toluenesulphinyl chloride to a cooled solution of (—)-*n*-propylpropenylcarbinol in pyridine, the (+)-*p*-toluenesulphinic ester is obtained by a method which does not involve rupture of a bond of the asymmetric carbon atom. On standing, the homogeneous ester undergoes a spontaneous change into a non-saponifiable substance with accompanying racemisation. This substance is presumed to be a sulphone, but repeated attempts failed to isolate a pure material. Specimens of the *dl*- and of the (+)-esters were maintained at 32°, the fall in saponification value was followed by periodic determinations with alcoholic potassium hydroxide, and the rotation of the (+)-ester was also observed. The apparent ester content and the rotatory power fall concurrently after a period of induction.

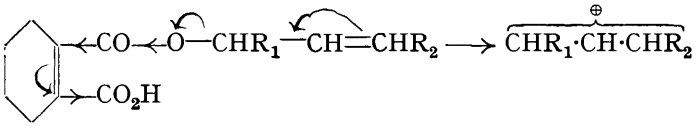
Racemisation occurring during Saponification of the Hydrogen Phthalic Esters of Substituted Allyl Alcohols.—It was found by Hills, Kenyon, and Phillips (*loc. cit.*) that, by saponification of optically pure (+)-αγ-dimethylallyl hydrogen phthalate with 5N-sodium hydroxide, the optically pure alcohol was obtained; but that saponification in aqueous sodium acetate and carbonate gave the racemic alcohol. Further, when saponified with aqueous sodium carbonate, (+)-γ-phenyl-α-methylallyl hydrogen phthalate yielded the *dl*-alcohol, but saponification with 5N-sodium hydroxide, or with 2·5N-aqueous-alcoholic sodium hydroxide gave the (+)alcohol in a state approaching optical purity; less concentrated solutions of sodium hydroxide caused increasing racemisation (Kenyon, Partridge, and Phillips, J., 1936, 85). (+)-*n*-Propylpropenylcarbinyl hydrogen phthalate on saponification with 5N-sodium hydroxide gave the (+)alcohol, which was reconverted into its hydrogen phthalic ester having 93% of its original rotatory power. On saponification in aqueous sodium acetate, the (+)hydrogen phthalic ester gave an optically inactive heptenol; its *p*-xenylurethane proved to be a mixture.

At some stage during the saponification with sodium acetate it appears likely that the carbonium kation $\overset{\oplus}{\overbrace{\mathrm{CHR_1{\cdot}CH{\cdot}CHR_2}}}$ has been liberated, leading to racemisation and permitting isomerisation; it appears also that this ion was not liberated during saponification with sodium hydroxide. That the ion might arise by dissociation of the liberated alcohol is intrinsically unlikely, and Kenyon, Partridge, and Phillips (*loc. cit.*, 1937) have observed that the easily isomerised α-phenyl-γ-methylallyl alcohol is stable in the presence of strong and weak alkali. An explanation is suggested according to which the hydrogen phthalic ester is regarded as an *o*-substituted benzoic ester which follows different courses of saponification according as the *o*-substituent is the carboxyl ion or the undissociated carboxyl group.

In strongly alkaline solution the hydrogen phthalic ester will exist as the ion, and the carboxylic anion will increase the electron availability at the position ortho to it, leading to inductive effects opposing the release of R as a carbonium kation: saponification in this case will proceed in the normal manner, in which the O—R bond is not broken (Ingold and Ingold, J., 1932, 756; Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508).



When the saponification is conducted in solution with sodium acetate or carbonate, the hydrogen phthalic ester will be present partly as the sodium salt and partly as the undissociated ester–acid. In the latter, the substituent ortho to the esterified carboxyl group is now an undissociated carboxyl group, which attracts electrons, causing a deficiency at the position ortho to it, and thereby promoting the separation of R as the kation R$^{\oplus}$. Since R is an allyl radical, it can readily undergo electron displacements permitting dissociation:



By the reaction of this carbonium kation with water or with hydroxyl ion, a racemised equilibrium mixture of the isomeric allyl alcohols results.

A comparison of the ease of separation of the carbonium kation from (*a*) the ionised and (*b*) the un-ionised hydrogen phthalic ester may be made; if R is a hydrogen atom, then the ease of separation is in proportion to (*a*) the second and (*b*) the first dissociation constant of phthalic acid. These constants are $3{\cdot}1 \times 10^{-6}$ and $1{\cdot}26 \times 10^{-3}$, respectively, whence it appears that the un-ionised hydrogen phthalic ester will liberate the carbonium kation some 500 times more readily than will the ionised hydrogen phthalic ester.

EXPERIMENTAL.

The *dl*- and (+)-*n*-propylpropenylcarbinols were prepared by methods previously described (Arcus and Kenyon, *loc. cit.*).

dl-n-*Propylpropenylcarbinyl* p-*nitrobenzoate*, prepared by adding *p*-nitrobenzoyl chloride (6·2 g.) to a mixture of the *dl*-alcohol (3·8 g.) and pyridine (2·7 g.) and heating them at 80° for 1 hour, separated from aqueous alcohol in plates, m. p. 40—41° (Found: C, 63·6; H, 6·4. $C_{14}H_{17}O_4N$ requires C, 63·8; H, 6·5%).

The p-*xenylurethane* of *dl*-*n*-propylpropenylcarbinol, prepared by heating the *dl*-alcohol (1·2 g.) with *p*-xenylcarbimide (2·0 g.) at 80° for 1 hour and extracting the mixture with hot light petroleum, separated from this solvent in needles, m. p. 103·5° (Found: C, 77·3; H, 7·5. $C_{20}H_{23}O_2N$ requires C, 77·7; H, 7·5%).

dl-n-*Propylpropenylcarbinyl formate*, prepared by heating the *dl*-alcohol (4 g.) with formic–acetic anhydride (6 g.) for one hour at 80°, had b. p. 53—54°/11 mm., $n_D^{14^\circ}$ 1·4285, $d_{4^\circ}^{20^\circ}$ 0·873 (Found: C, 68·4; H, 10·2. $C_8H_{14}O_2$ requires C, 67·6; H, 10·0%).

dl-n-*Propylpropenylcarbinyl* p-*toluenesulphinate* was prepared by the slow addition of *p*-toluenesulphinyl chloride (19·2 g., prepared according to Phillips, J., 1925, **127**, 2552) to an ice-cooled mixture of the *dl*-alcohol (12·4 g.) and pyridine (9·7 g.); an equal volume of dry ether was then added. Subsequently, more ether was added, and the extract washed with dilute hydrochloric acid, then with sodium carbonate, and dried (calcium chloride). On removal of the ether, a yellow oil remained; it decomposed without distilling when heated to 150° at $< 0{\cdot}1$ mm. Traces of unreacted carbinol were therefore removed by heating to 90° at $< 0{\cdot}1$ mm.; the product then had $n_D^{20^\circ}$ 1·5273 (Found: S, 13·0. $C_{14}H_{20}O_2S$ requires S, 12·7%).

(+)-*n*-Propylpropenylcarbinyl *p*-toluenesulphinate was similarly prepared from the (−)alcohol having $\alpha_{5461}^{17^\circ}$ − 5·44°, (*l*, 2·0); it had $n_D^{17^\circ}$ 1·5271, $\alpha_{5893}^{17^\circ}$ + 1·85°, $\alpha_{5780}^{17^\circ}$ + 2·07°, $\alpha_{5461}^{17^\circ}$ + 2·27° (*l*, 0·5).

dl-Δ^{β}-δ-*Chloroheptene* was prepared by the slow addition of a mixture of *dl*-*n*-propylpropenylcarbinol (11·4 g.) and pyridine (1·6 g.) to phosphorus trichloride (5·2 g.) at 0°; after standing at room temperature for 1·5 hours, the upper layer was decanted and redistilled; it had b. p. 49°/21 mm., $n_D^{21^\circ}$ 1·4430, $d_{4^\circ}^{18^\circ}$ 0·879 (Found: Cl, 26·4. $C_7H_{13}Cl$ requires Cl, 26·7%).

(−)-Δ^{β}-δ-Chloroheptene, similarly prepared from the (+)alcohol having $\alpha_{5461}^{20^\circ}$ + 4·10° (*l*, 0·5), had b. p. 44°/14 mm., $n_D^{21^\circ}$ 1·4430, $\alpha_{6438}^{22^\circ}$ − 1·21°, $\alpha_{5893}^{22^\circ}$ − 1·48°, $\alpha_{5461}^{22^\circ}$ − 1·68°, $\alpha_{4358}^{22^\circ}$ − 3·20° (*l*, 0·5).

It was desired to reduce catalytically the last compound in order to ascertain its degree of optical purity, but the C—Cl bond is rapidly attacked. To dry ether containing the reduced platinum catalyst of Adams, Voorhees, and Shriner ("Organic Syntheses," **8**, 92), *dl*-Δ^{β}-δ-chloroheptene (6·7 g.) was added, and hydrogen supplied at 2 atm. The initial rapid absorption ceased, but recommenced on addition of sodium carbonate, whence it appears that the reaction is inhibited by the production of hydrogen chloride. After the theoretical quantity of hydrogen required for saturation had been absorbed, the solution yielded a mixture of chloroheptene and chloroheptane, b. p. 101°/183 mm., $n_D^{19^\circ}$ 1·4363, $d_4^{12\cdot5^\circ}$ 0·883 (Found: C, 63·4; H, 10·3. Calc. for $C_7H_{13}Cl$: C, 63·4; H, 9·9. Calc. for $C_7H_{15}Cl$: C, 62·4; H, 11·25%).

Saponification of (+)-n-*Propylpropenylcarbinyl Hydrogen Phthalate.*—(i) *In* 5N-*sodium hydroxide.* This has been described by Arcus and Kenyon (*loc. cit.*). (ii) *In aqueous sodium acetate.* A current of steam was passed through a solution of the (+)hydrogen phthalic ester ($[\alpha]_{5461}^{18^\circ}$ + 20·0° in ethyl alcohol; 13 g.) and sodium acetate (9 g.) in water (50 c.c.). The distillate was saturated with potassium carbonate, and extracted with ether. The latter yielded a heptenol (4 g.), b. p. 63°/15 mm., $n_D^{18^\circ}$ 1·4379, optically inactive to light of λ 5461. It furnished a *p*-xenylurethane which was a mixture, m. p. 70—80°, from which, after 6 crystallisations from methylene chloride–light petroleum, the *p*-xenylurethane of *dl*-*n*-propylpropenylcarbinol, m. p. 102—104°, alone or mixed with an authentic specimen, was obtained.

Stability of the Hydrogen Phthalates and p-*Nitrobenzoates of* n-*Propylpropenylcarbinol and* α-*Methyl*-γ-n-*propylallyl Alcohol.*—*dl*-*n*-Propylpropenylcarbinyl hydrogen phthalate (3 g.) and pyridine (3 g.) were heated together at 80° for 80 minutes. Ether was added, and the solution washed with dilute hydrochloric acid and dried (calcium chloride). On evaporation and addition of light petroleum, the hydrogen phthalic ester separated as needles, m. p. 72·5°, alone or mixed with the original material. Similar treatment of *dl*-α-methyl-γ-*n*-propylallyl hydrogen phthalate gave the pure ester, m. p. 67·5°, alone or when mixed with the original material.

0·2 G. of each of the isomeric *p*-nitrobenzoates was maintained at 80° for 1 hour; the melts were allowed to supercool, and each was inoculated with a trace of its isomeride. After solidification, the *n*-propylpropenylcarbinyl ester had m. p. 41°, and the α-methyl-γ-*n*-propylallyl ester m. p. 29°, *i.e.*, each was unaltered.

Change undergone by (+)-n-*Propylpropenylcarbinyl* p-*Toluenesulphinate.*—The *dl*-ester, $n_D^{18^\circ}$ 1·5271, was kept in a thermostat at 32°; portions were removed at intervals, and the saponification value determined by means of alcoholic potassium hydroxide.

t	0 *	7·5 hrs.	24 hrs.	72 hrs.	97 hrs.	120 hrs.	33 days
Apparent ester content, %	83	81	70	24	25	24	25

* This observation relates to the ester as prepared.

A similar experiment was performed with the (+)sulphinate, placed in a 0·5-dm. tube in the thermostat, and periodically removed, allowed to cool, and the rotation measured.

t (hrs.)	0	2·2	19·7	45
$\alpha_{5461}^{20^\circ}$	+2·25°	+2·27°	+2·43°	−0·04°
Ester content, %, by saponification	84	—	—	21

Repeated attempts to isolate a pure product of this change were unsuccessful.

Replacement Reactions of (+)-n-*Propylpropenylcarbinyl Hydrogen Phthalate.*—(i) *With formic acid.* A mixture of the (+)hydrogen phthalate ($[\alpha]_{5461}$ + 9·77° in ethyl alcohol; 11 g.) and anhydrous formic acid (4 g.) was heated on the steam-bath for 1 hour. From the ethereal extract, after washing with sodium carbonate and drying (calcium chloride), heptenyl formate (2·5 g.) was obtained, b. p. 54°/12 mm., $n_D^{17^\circ}$ 1·4266, optically inactive to light of λ_{5461} (*l*, 0·25). The sodium carbonate solution afforded phthalic acid (4·9 g.), m. p. 200—205° (decomp.).

(ii) *With acetic acid.* A solution of the (+)hydrogen phthalate ($[\alpha]_{5461}^{18^\circ}$ + 15·8° in ethyl alcohol; 5·0 g.) in acetic acid (m. p. 17°, 20 g.) was kept at 32°, periodically removed, cooled, and the rotatory power determined. The results are given in Table III (temp., approx. 18°; *l*, 2·0).

TABLE III.

t, hrs.	0	17	46	65	90	112	160	184	233	258
α_{5461}	+2·06°	+1·91°	+1·83°	+1·74°	+1·55°	+1·28°	+1·10°	+0·95°	+0·66°	+0·51°
t, hrs.	376	449	497	544	597	664	736	833	1001	1169
α_{5461}	−0·16°	−0·50°	−0·75°	−0·93°	−1·09°	−1·24°	−1·38°	−1·56°	−1·70°	−1·69°

Ether was added, and the extract filtered from the remaining phthalic acid, which crystallised from hot water, m. p. 200—204° (decomp.) (0·5 g.). The ethereal extract, washed with sodium carbonate, and dried (calcium chloride), yielded heptenyl acetate, b. p. 73°/17 mm., $n_{\mathrm{D}}^{21^\circ}$ 1·4264, $\alpha_{5461}^{20^\circ}$ + 0·05°, $\alpha_{5893}^{20^\circ}$ + 0·03° (*l*, 0·5); it (0·5 g.) was reduced in ethyl-alcoholic solution (7 c.c.) by hydrogen at 2 atm. in the presence of Raney nickel catalyst. The filtered solution, which showed no unsaturation, was inactive to light of λ_{5461}.

(iii) *With benzoic acid.* A mixture of *n*-propylpropenylcarbinyl hydrogen phthalate ($[\alpha]_{5461}$ + 7·8° in ethyl alcohol; 20 g.) and benzoic acid (27 g.) was kept at 120—130° for one hour. The cooled mixture was triturated with ether. The filtered ethereal extract, washed with sodium carbonate, and dried (sodium sulphate), yielded *dl*-heptenyl benzoate (2·3 g.), b. p. 149°/13 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·5048, optically inactive to light of λ 5461 (*l*, 0·25). This material was saponified with alcoholic potassium hydroxide on the steam-bath for one hour; the ethereal extract, washed with water and dried, gave a heptenol, b. p. 61°/13 mm. (0·7 g.). This latter with *p*-xenylcarbimide yielded a mixture from which after six crystallisations the *p*-xenylurethane of *n*-propylpropenylcarbinol, m. p. 100° alone and mixed with an authentic specimen, was obtained.

Replacement Reactions of (—)-Δ^{β}-δ-*Chloroheptene*.—(i) *By hydroxyl.* (—)-Δ^{β}-δ-Chloroheptene [$\alpha_{5461}^{22^\circ}$ — 1·68° (*l*, 0·5), prepared from (+)-*n*-propylpropenylcarbinol having $\alpha_{5461}^{20^\circ}$ + 4·10° (*l*, 0·5); 4·2 g.] was kept at 65° for 4 hours, with shaking, in a solution of sodium carbonate (2·3 g.) in water (45 g.). The suspension was saturated with potassium carbonate and extracted with ether, which yielded a (+)heptenol (1·2 g.), b. p. 63°/16 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·4372, $\alpha_{5461}^{23^\circ}$ + 0·04° (*l*, 0·236). On reduction of this material in ethereal solution (10 c.c.) with hydrogen at 2 atm. in the presence of platinum catalyst, the theoretical volume was rapidly absorbed, yielding a heptanol, b. p. 62°/15 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4207, optically inactive to light of λ_{5461} (*l*, 0·236).

dl-Δ^{β}-δ-Chloroheptene was hydrolysed by this method, giving a heptenol, b. p. 68°/17 mm., $n_{\mathrm{D}}^{20^\circ}$ 1·4388, which was converted into its hydrogen phthalic ester, a mixture which was not separated after repeated crystallisation from carbon disulphide and light petroleum. Reduction of the heptenol gave a heptanol, b. p. 64°/16 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4212, which was converted into its hydrogen phthalic ester, a mixture not separable by recrystallisation from ether–light petroleum.

(ii) *By methoxyl.* (+)-Δ^{β}-δ-Chloroheptene [$\alpha_{5461}^{16^\circ}$ + 0·59° (*l*, 0·5), prepared from (—)-*n*-propylpropenylcarbinol having $\alpha_{5461}^{17^\circ}$ — 5·44° (*l*, 2·0); 6·3 g.)], dissolved in anhydrous methyl alcohol (13 g.), was heated with potassium carbonate (6·3 g.) on the steam-bath for one hour. The ethereal extract, washed with water and dried (calcium chloride), yielded (+)methyl heptenyl ether (3·5 g.), b. p. 133—135°/760 mm., $n_{\mathrm{D}}^{12^\circ}$ 1·4221, $\alpha_{5461}^{12^\circ}$ + 0·09° (*l*, 0·5). This was reduced in ethereal solution (35 c.c.) with hydrogen at 2 atm. in the presence of platinum catalyst; the theoretical volume was absorbed in 2 hours, producing *dl*-methyl heptyl ether, b. p. 136°/760 mm., $n_{\mathrm{D}}^{15^\circ}$ 1·4056, optically inactive to light of λ_{5461} (*l*, 0·25).

(iii) *By acetate ion.* *dl*-Δ^{β}-δ-Chloroheptene (9·4 g.) did not react when heated in acetic acid (m. p. 17°, 22 g.) solution at 65° for 40 minutes, and was recovered having b. p. 46°/19 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·4452.

(+)-Δ^{β}-δ-Chloroheptene [$\alpha_{5461}^{21^\circ}$ + 0·48° (*l*, 0·5), prepared from (—)-*n*-propylpropenylcarbinol having $\alpha_{5461}^{17^\circ}$ — 5·44° (*l*, 2·0); 6·1 g.] and anhydrous sodium acetate (5·5 g.), dissolved in acetic acid (14·4 g.), were heated at 65° for one hour. The ethereal extract, washed with sodium carbonate and dried (calcium chloride), yielded *dl*-heptenyl acetate, b. p. 68°/16 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·4270, optically inactive to light of λ_{5461} (*l*, 0·5).

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