463. *Studies in Molecular Rearrangement. Part VIII.* The Five-carbon Oxotropic Rearrangement of 1-Phenylhexa-2 : 4-dien-1-ol.*

By H. C. Barany, E. A. Braude, and J. A. Coles.

The reaction of sorbaldehyde with phenylmagnesium bromide gives 1-phenylhexa-2 : 4-dien-1-ol (VI) which undergoes five-carbon oxotropy under acidic conditions to 6-phenylhexa-3 : 5-dien-2-ol (VII). The latter has been dehydrated to 1-phenylhexa-1 : 3 : 5-triene (IX).

Kinetic measurements for the rearrangement are reported and discussed. It is shown that the partly rearranged isomer, 1-phenylhexa-1 : 4-dien-3-ol (VIII), is not an intermediate, and the reaction is considered to proceed mainly by way of a bimolecular attack by a water molecule at the $C_{(5)}$-atom of the oxonium ion (X). The mobility of the system (VI) $\longrightarrow$ (VII) is compared with that of the corresponding three-carbon rearrangement of 1-phenylbut-2-en-1-ol (XI) to 4-phenylbut-3-en-2-ol (XII).

Whereas three-carbon anionotropy has been known for many years and has been extensively investigated (for a summary, cf. Braude, *Quart. Reviews*, 1950, **4**, 404), five-carbon anionotropic systems have been little studied until quite recently. The first example of an open-chain oxotropic system was provided by Heilbron, Jones, and McCombie (*J.*, 1944, 134), who condensed sorbaldehyde with sodium acetylide and showed that the resulting carbinol (I; $\mathrm{X = C{:}CH}$, $\mathrm{R = Me}$) readily underwent rearrangement to the fully conjugated isomer (II; $\mathrm{X = C{:}CH}$, $\mathrm{R = Me}$), in the presence of dilute acids. A number of similar examples have since been described (Heilbron *et al.*, *J.*, 1949, 287, 742, 2023) and it has been shown that butadienylcarbinols carrying only alkyl substituents (*e.g.* I; $\mathrm{X = H}$, $\mathrm{R = Me}$) undergo reversible five-carbon oxotropy, leading to a mixture of the two isomers (Nazarov and Fisher, *Bull. Acad. Sci., U.R.S.S., Cl. Sci. Chim.*, 1945, 631; 1948, 311, 427; Braude and Timmons, *J.*, 1950, 2007).

(I.) $\mathrm{HO{\cdot}CHX{\cdot}CH{:}CH{\cdot}CH{:}CHR}$ $\mathrm{CHX{:}CH{\cdot}CH{:}CH{\cdot}CHR{\cdot}OH}$ (II.)

The Synthesis, Rearrangement, and Dehydration of 1-*Phenylhexa*-2 : 4-*dien*-1-*ol*.—The present work originally had the twofold object of (*a*) providing an example of five-carbon oxotropy in a system terminated by a phenyl group, and (*b*) carrying out a quantitative comparison of mobility in three- and five-carbon oxotropic systems. In the meantime, however, Woods and Sanders (*J. Amer. Chem. Soc.*, 1947, **69**, 2926) have described the isomerisation of 1-phenylpenta-2 : 4-dien-1-ol (III) to 5-phenylpenta-2 : 4-dien-1-ol (IV), and the rearrangement of the corresponding tertiary homologue, 2-phenylhexa-3 : 5-dien-2-ol, has recently been investigated by Nazarov and Fisher (*Bull. Acad. Sci., U.R.S.S.*, 1949, 386). We chose for study 1-phenylhexa-2 : 4-dien-1-ol (VI) which was readily prepared by the reaction of sorbaldehyde with phenylmagnesium bromide; its constitution was confirmed by its ultra-violet light absorption properties and by catalytic hydrogenation which resulted in the uptake of 2 molecular equivalents of hydrogen giving 1-phenylhexan-1-ol. In the presence of dilute hydrochloric acid in aqueous acetone or dioxan solution, 1-phenylhexa-2 : 4-dien-1-ol underwent rearrangement to the fully conjugated, isomeric 6-phenylhexa-3 : 5-dien-2-ol (VII), which exhibited ultra-violet light absorption characteristic of the phenylbutadiene system (see figure). Quantitative measurements (see below) show that rearrangement is substantially complete. In contrast to the other two homologous systems previously investigated, both isomers were obtained as solids at room temperature.

(III.) $\mathrm{HO{\cdot}CHPh{\cdot}CH{:}CH{\cdot}CH{:}CH_2}$ $\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH}$ (IV.)

(V.) $\mathrm{CHPh{:}CH{\cdot}CH(OH){\cdot}CH{:}CH_2}$

(VI.) $\mathrm{HO{\cdot}CHPh{\cdot}CH{:}CH{\cdot}CH{:}CHMe}$ $\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}CHMe{\cdot}OH}$ (VII.)

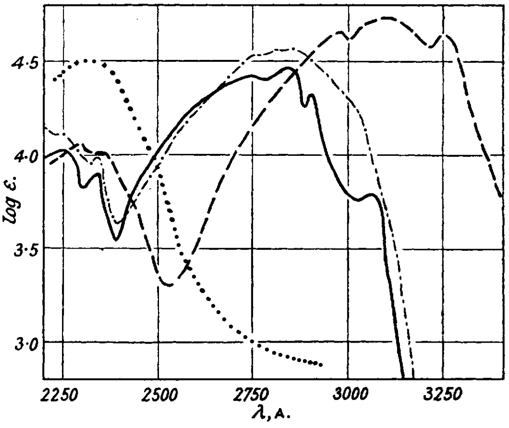
(VIII.) $\mathrm{CHPh{:}CH{\cdot}CH(OH){\cdot}CH{:}CHMe}$ $\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2}$ (IX.)

The isomerisation of (III) to (IV) and (VI) to (VII) could conceivably proceed by two

---

* Part VII, preceding paper.

successive 3-carbon oxotropic rearrangements, *via* the intermediates (V) and (VIII), respectively. This possibility was first considered by Salkind and Kulikov (*J. Gen. Chem., U.S.S.R.*, 1945, **15**, 643) who obtained what they concluded to be a mixture of (III), (IV), and (V), with the latter predominating, by partial hydrogenation of 1-phenylpent-2-en-4-yn-1-ol in ethyl acetate. No rearrangement would normally be expected under these conditions, and it must be presumed that any isomerisation which did occur was due to acetic acid impurities in the solvent. However, the evidence for the constitution of the dienol mixture obtained by Salkind and Kulikov is in any case by no means conclusive, and the formation of (V) was not observed by Woods and Sanders (*loc. cit.*). Similarly, no trace of 1-phenylhexa-1 : 5-dien-3-ol (VIII) was isolated in the present work from the rearrangement of 1-phenylhexa-2 : 4-dien-1-ol (VI). This, of course, does not necessarily exclude the possible formation of (VIII) as an intermediate, but the fact that no appreciable concentration of (VIII) is ever present during the rearrangement of (VI) to (VII) was readily established by following the reaction spectrometrically. The carbinol (VIII) contains the styrene chromophore and can safely be predicted to exhibit intense light-absorption maximum near 2510 A. ($\varepsilon \sim 20{,}000$) similar to that of cinnamyl alcohol and its homologues (Braude, Jones, and Stern, *J.*, 1946, 396; Braude and Timmons, *loc. cit.*), whereas the carbinols (VI) and (VII) exhibit only relatively low-intensity absorption ($\varepsilon \sim 2000$) in this region (see figure).



Ultra-violet light absorption of 1-*phenylbutadiene* (——), 1-*phenylhexa*-2 : 4-*dien*-1-*ol* (·······), 1-*phenylhexa*-1 : 3-*dien*-5-*ol* (— · — · —) *and* 1-*phenylhexatriene* (– – – – –) *in ethanol solution.*

Quantitative measurements (see Experimental) show that the intensity of absorption at 2510 A. throughout the rearrangement remains equal, within experimental error, to that expected for the appropriate mixture of (VI) and (VII) alone, and that the possible concentration of (VIII) at any time must be less than 1% of the concentration of (VII). Further evidence, which also excludes the incursion of (VIII) as an " unstable " intermediate, is provided by kinetic measurements which are discussed below.

On distillation from potassium hydrogen sulphate under carefully controlled conditions, 1-phenylhexa-2 : 4-dien-1-ol underwent simultaneous rearrangement and dehydration to 1-phenylhexa-1 : 3 : 5-triene (IX), which has not previously been described. It was obtained as a low-melting solid and exhibited the expected light-absorption properties (see figure) with a high-intensity maximum near 3110 A. showing some vibrational structure.

The Kinetics and Mechanism of the Rearrangement of 1-*Phenylhexa*-2 : 4-*dien*-1-*ol*.—The kinetics of the rearrangement of (VI) to (VII) under standard conditions employed in earlier studies on three-carbon oxotropy have been determined by the spectrometric technique, use being made of the change in absorption intensity at 2810 A. where (VII) exhibits a maximum. The reaction is strictly of the first order in dilute hydrochloric acid in aqueous dioxan solution (see Experimental). Rate constants were determined for two solvent compositions at 5° intervals in the temperature range 30—50°; they gave linear Arrhenius plots. As usual, the rates of rearrangement are higher, and the Arrhenius energies of activation lower, in 40% than in 60% aqueous dioxan. The results are summarised in Tables I and II, together with those for the rearrangement of phenylpropenylcarbinol (XI) to methylstyrylcarbinol (XII) for comparison.

The five-carbon rearrangement is about ten times more rapid than the corresponding three-carbon rearrangement, and has a somewhat lower energy of activation.

TABLE I.

First-order rate constants (10^4 k, *min.*$^{-1}$) *for the rearrangement* (VI) ⟶ (VII) *in a* 0·001M-*solution of hydrochloric acid in aqueous dioxan.*

Temp.	30°	35°	40°	45°	50°
40% dioxan	673	1080	1620	2250	3590
60% dioxan	175	308	495	812	1250

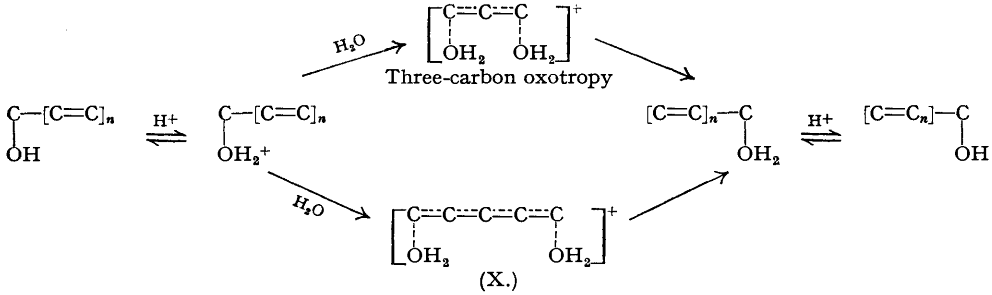
TABLE II.

Relative rate constants, energies of activation, and probability factors for three- and five-carbon oxotropic rearrangements in the system Ph·CH(OH)·[CH:CH]$_n$·Me.*

	40% dioxan.			60% dioxan.		
n.	k_{30}/c_A.	E_{Arr}.	log *A*.	k_{30}/c_A.	E_{Arr}.	log *A*.
1	7·2	18·2	12·2	1·84	19·5	12·6
2	67·3	16·1	11·7	17·5	19·0	13·1

* k_{30}/c_A is the first-order rate constant (min.$^{-1}$) at 30°, divided by the hydrochloric acid concentration. E_{Arr} and A are defined by the equation log $k/c_A = Ae^{-E_{\text{Arr}}/RT}$, where E_{Arr} is expressed in kcal./mol. and A in sec.$^{-1}$.

Two aspects of these results call for comment; first, their bearing on the mechanism of five-carbon oxotropy, and second, the difference in mobility in the three- and the five-carbon oxotropic system. With regard to the first, there is no reason to expect, and there is no evidence to indicate, any difference in mechanism between acid-catalysed three-carbon and five-carbon oxotropy. The mechanism of three-carbon oxotropy has been exhaustively discussed (cf. Braude, *J.*, 1948, 794; *Ann. Reports*, 1949, **46**, 125), and it has been shown that in all the cases so far examined, the first step is a fast, reversible addition of a proton to the hydroxyl group to give the oxonium ion. In aqueous dioxan media, the reaction then proceeds mainly by way of a rate-determining bimolecular attack by a water molecule at the $C_{(3)}$-atom together with a small contribution, which increases with decreasing water content of the medium, from an intramolecular migration of a water molecule. The corresponding mode of reaction in five-carbon oxotropy will be bimolecular attack at the $C_{(5)}$-atom, as represented below.



(X.)

Five-carbon oxotropy

The alternative possibility, that the five-carbon rearrangement takes place by two consecutive three-carbon rearrangements, is intrinsically unlikely on the basis of this mechanism, since the carbon-atom in the terminal, 5-position of the butadiene system in (VI) will be more highly polarised and more highly polarisable than in the intermediate 3-position, and will therefore be more highly susceptible to attack by a water molecule. It has already been shown that the partly rearranged isomer (VIII) is not an isolable intermediate, and evidence against its incursion as a non-isolable intermediate is afforded by the fact that the rearrangement of (VI) to (VII) accurately obeys the first-order rate law. It can be predicted from earlier studies on substituent effects (cf. Braude, *loc. cit.*) that if the two consecutive three-carbon rearrangements were involved, their rates could differ by a factor of less than 10, and it can easily be shown that a composite reaction of this type will not normally give rise to overall first-order kinetics.

The mechanism of five-carbon oxotropy has previously been discussed by Salkind and Kulikov (*loc. cit.*) and also by Dewar (" The Electronic Theory of Organic Chemistry," Oxford, 1949, p. 88). Salkind and Kulikov invoke a mechanism of the type first proposed by Burton and Ingold (*J.*, 1928, 904) involving ionisation of the carbinol into a carbonium ion and a hydroxyl ion, which does not, *inter alia*, account for the acid-catalysed nature of the reaction and does not merit further consideration. Dewar refers to the subject in the following words : " The mechanism is clearly similar to normal anionotropy of allyl compounds ; the alcohol first forms a salt which then ionises to the mesomeric carbonium ion. This ion can combine with hydroxyl ion in a number of ways, but terminal addition is naturally favoured. . . . This mechanism has been supported by various kinetic measurements and certainly no other could account for migrations of hydroxyl from one end to the other of an extensive conjugated chain." It is necessary to comment, first, that as far as we are aware the present kinetic measurements are the first to be published on polycarbon oxotropy, and that the statement appears to refer mistakenly to previous investigations from this laboratory on three-carbon oxotropy ; secondly, that any mechanism which invokes the participation of hydroxyl ions in a reaction which takes place relatively fast in acid solution and immeasurably slowly in neutral or alkaline solution must be viewed with mistrust ; and thirdly, that the last part of the quoted statement is manifestly incorrect.

We now turn to the comparison of mobility in the five-carbon system (VI) ⟶ (VII) and the corresponding three-carbon system (XI) ⟶ (XII), which has previously been studied

(XI.) $\mathrm{OH{\cdot}CHPh{\cdot}CH{:}CHMe}$ $\qquad$ $\mathrm{CHPh{:}CH{\cdot}CHMe{\cdot}OH}$ (XII.)

(Braude, Jones, and Stern, *J.*, 1946, 396; Braude and Stern, *J.*, 1947, 1096; 1948, 1982). Although the accuracy of the k values is of the order of $\pm 2\%$, that of E_{Arr} and $\log A$ is probably not better than $\pm 0{\cdot}3$ unit, and it is therefore justified to conclude from the data in Table II, that the enhanced mobility of the five-carbon system is largely due to a lower energy of activation, in conformity with previous results in this series (cf. Braude, 1950, *loc. cit.*). The lowering in energy of activation produced by the additional ethylenic grouping is not unexpected since there will be a higher degree of resonance stabilisation in the transition state (X) of the five-carbon than in the three-carbon system. The higher mobility may also be due partly to enhanced electron-accession at $\mathrm{C}_{(1)}$. There is some evidence that the effect of a substituent (in this case, the hyperconjugative effect of the methyl group) increases with the length of the unsaturated system to which it is attached; thus the dissociation constant of sorbic acid ($k = 1{\cdot}73 \times 10^{-5}$) is smaller than that of crotonic acid ($k = 2{\cdot}03 \times 10^{-5}$). Again the 3- and 5-positions in the open-chain system are somewhat analogous to the *o*- and *p*-positions in a benzenoid system, and it has been shown that the anionotropic mobility of propenyl-*p*-tolylcarbinol is considerably greater than that of propenyl-*o*-tolylcarbinol (Braude and Stern, *J.*, 1947, 1096). However, the significance of this comparison is limited in view of the additional steric effects which probably come into play in the *o*-substituted phenyl derivatives.

EXPERIMENTAL.

Whenever possible, operations were carried out in an atmosphere of nitrogen. M.p.s are uncorrected.

1-*Phenylhexa*-2 : 4-*dien*-1-*ol* (VI).—Freshly distilled sorbaldehyde (9·6 g.) (Kuhn and Hoffer, *Ber.*, 1930, **63**, 2168) in ether (50 ml.) was added to a stirred solution of phenylmagnesium bromide (from magnesium, 2·4 g.) in ether (150 ml.) during 1 hour at 0°. Stirring was continued for 2 hours, and an ice-cold, saturated aqueous ammonium chloride solution (250 ml.) was then added. The ethereal layer was separated, dried ($\mathrm{Na_2SO_4}$–$\mathrm{K_2CO_3}$), and fractionated from a trace of potassium carbonate, giving 1-*phenylhexa*-2 : 4-*dien*-1-*ol* (9 g., 52%), b. p. 104°/0·05 mm., which solidified when kept; it crystallised from pentane in needles, m. p. 40—42° (Found : C, 83·0; H, 8·2. $\mathrm{C_{12}H_{14}O}$ requires C, 82·9; H, 8·1%). Light absorption in ethanol : Maximum at 2310 A., ε 19,500.

Hydrogenation of 1-phenylhexa-2 : 4-dien-1-ol (3·7 g.) in ethanol (50 ml.) in the presence of platinic oxide (0·05 g.) resulted in the uptake of 950 ml. at 20°/761 mm. (Calc. 1000 ml.), and gave 1-phenylhexanol, b. p. 110—111°/1·5 mm. (Found : C, 81·2; H, 10·2. Calc. for $\mathrm{C_{12}H_{18}O}$: C, 80·9; H, 10·1%) (Ipatieff and Haensel, *J. Amer. Chem. Soc.*, 1942, **64**, 521 give b. p. 128°/5 mm.). Light absorption in ethanol : Maximum at 2420 A. ε 60.

6-*Phenylhexa*-3 : 5-*dien*-2-*ol* (VII).—A solution of 1-phenylhexa-2 : 4-dien-1-ol (2·5 g.) in a 0·02M-solution (50 ml.) of hydrochloric acid in 60% aqueous acetone was kept for 20 hours at room temperature. The solution was then diluted with water neutralised with potassium carbonate, and extracted with ether. The ethereal extract was dried ($\mathrm{Na_2SO_4}$–$\mathrm{K_2CO_3}$) and the ether removed under reduced pressure. The oily residue was taken up in light petroleum (b. p. 40—60° ; 3 ml.) ; when this solution was cooled in a solid carbon dioxide–methanol bath, 6-*phenylhexa*-3 : 5-*dien*-2-*ol* separated in needles (2 g.), which after one recrystallisation had m. p. 65° (Found: C, 82·85; H, 8·25. $C_{12}H_{14}O$ requires C, 82·9; H, 8·1%). Light absorption in ethanol: Maxima at 2270, 2330, and 2800 A., ε 14,800, 9,200, and 32,300, respectively; inflection at 2850 A., ε 31,300. 6-Phenylhexa-3 : 5-dien-2-ol decomposes on storage, giving a yellow oil with an odour reminiscent of cinnamaldehyde.

1-*Phenylhexa*-1 : 3 : 5-*triene* (IX.)—1-Phenylhexa-2 : 4-dien-1-ol (4 g.) and finely ground potassium hydrogen sulphate (1 g.) were placed in a 50-ml. distilling flask with a wide side-arm and receiver. The apparatus was evacuated to 0·01 mm. and dipped into an oil-bath preheated to 100°. The temperature of the bath was then rapidly raised to 130°; 1-*phenylhexa*-1 : 3 : 5-*triene* distilled as a viscous oil (1·5 g.), b. p. 80°/0·01 mm., which solidified in the receiver and was immediately crystallised from light petroleum (b. p. 40—60°) giving fine needles, m. p. 56° (Found: C, 91·7; H, 7·9. $C_{12}H_{12}$ requires C, 92·3; H, 7·7%). Light absorption in ethanol: Maxima 2290, 2350, 2990, 3110, and 3250 A., ε 11,400, 10,700, 46,000, 55,000, and 43,000, respectively. If the distillate is kept before crystallisation, an increasing portion changes into a polymer, which is insoluble in light petroleum and can be precipitated from methanol by water as a white solid, m. p. >100°. When pure, 1-phenylhexa-1 : 3 : 5-triene remains unchanged for several days if stored under nitrogen.

Kinetic Measurements.—The kinetic measurements on the rearrangement of 1-phenylhexa-2 : 4-dien-1-ol to 6-phenylhexa-3 : 5-dien-2-ol were made by the spectrometric method previously described (cf. Braude, Jones, and Stern, *J.*, 1946, 396; Braude and Fawcett, *J.*, 1950, 800), a modified technique being used in which the runs are carried out directly in the absorption cell of a Beckman photoelectric spectrophotometer. The absorption cell is contained in a thermostatically controlled holder which fits into the cell compartment, and the light beam is allowed to fall on the cell only during the brief absorption measurements, by means of a shutter arrangement. Details of this technique will be described elsewhere. It is necessary to ensure that no detectable photochemical decomposition occurs during the total period of exposure to the ultra-violet light beam; this is done by exposing the solution after termination of a run to continuous illumination for an equivalent period and noting any further change in the light absorption. No detectable photochemical decomposition occurred with the phenylhexadienols, and the rate of isomerisation was not affected by the intermittent ultra-violet illumination. Some typical runs are reproduced below.

Rearrangement of 1-*phenylhexa*-2 : 4-*dien*-1-*ol in a* 0·001M-*solution of hydrochloric acid in aqueous dioxan. Carbinol concentration,* 0·2 × 10^{-4} *g.-mol./l.*

(*a*) Dioxan concentration, 40% by volume; *t* = 30°.

Time, sec.	0	199	262	365	422	530	586	660	780	870	920	1100	10,000
$10^{-2}\varepsilon$ at 2510 A.	97	95	94	93	92	91	91	90	89	89	88	87	62
$10^{-2}\varepsilon$ at 2810 A.	22	70	83	103	114	131	138	148	162	173	183	192	263
$10^{4}k$, min.$^{-1}$ ...	—	663	672	670	683	680	672	665	668	678	673	667	—

Mean $10^{4}k$ (min.$^{-1}$): 673 ± 5.

(*b*) Dioxan concentration, 40% by volume; *t* = 40°.

Time, sec.	0	76	104	124	153	180	208	235	267	303	3000
$10^{-2}\varepsilon$ at 2810 A.	22·5	65	77·5	87·5	100	110	120	130	140	150	250
$10^{4}k$, min.$^{-1}$ ...	—	1630	1610	1630	1630	1620	1610	1630	1630	1620	—

Mean $10^{4}k$ (min.$^{-1}$): 1620 ± 10.

(*c*) Dioxan concentration, 60% by volume; *t* = 40°.

Time, min.	0	4	5·5	7	9	11	13	15·5	18·5	24	200
$10^{-2}\varepsilon$ at 2810 A.	21·5	63	78	90·5	106	120	134	149	163	184	254
$10^{4}k$, min.$^{-1}$ ...	—	480	497	495	496	495	502	510	502	497	—

Mean $10^{4}k$ (min.$^{-1}$): 495 ± 5.

We thank the Department of Scientific and Industrial Research for a grant (to J. A. C.).

Imperial College of Science and Technology,
South Kensington, London, S.W.7.

[*Received, February 9th*, 1951.]