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THE RELATION BETWEEN THE CLAISEN REARRANGEMENT OF ALLYL ETHERS AND THEIR ELECTRONIC STRUCTURE

REARRANGEMENT OF N-ALLYLAMINES

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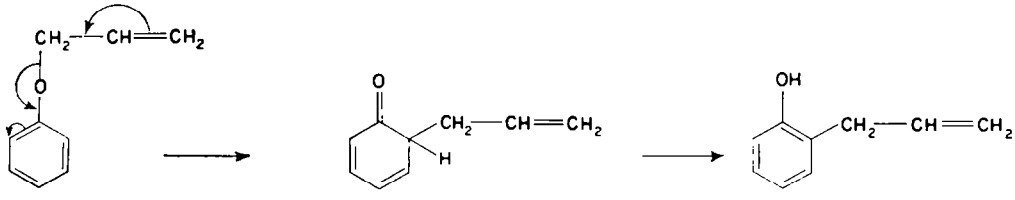
Abstract—The kinetics of a number of Claisen rearrangements have been studied and it is shown that the energy of activation of this reaction is a function of the bond orders and free valencies in the ethers undergoing rearrangement. In accordance with prediction from the derived equation, it was shown that N-allyl-1-naphthylamine rearranged smoothly and in high yield to 2-allyl-1-naphthylamine by a first order, intramolecular mechanism. This is the first recorded example of a Claisen rearrangement of an N-allyl compound. The behaviour of other ethers, whose rearrangements in the literature have been recorded as unusual or anomalous, is discussed in the light of these findings.

THE Claisen rearrangement of aromatic allyl ethers and allyl vinyl ethers has received much attention and has been extensively used in studies of the non-equivalence of bonds in aromatic compounds.[1–9] Theoretical aspects of the reaction have been in the main concerned with its mechanism. Largely due to the work of Hurd and Pollack[10], Kincaid and Tarbell,[11] Rhoads *et al.*,[12] Conroy and Firestone,[13] and Curtin and Johnson,[14] it is now clear that the rearrangement is intramolecular and of the first order



and that the mechanism is via the formation of a cyclized activated complex and an intermediate dienone.

This mechanism implies some fixation of the double bonds in the aromatic nucleus during the transition state. These earlier studies indicated that whereas in naphthalene,

[1] L. Claisen, *Ber. Dtsch. Chem. Ges.* **45**, 3157 (1912).
[2] D. S. Tarbell, *Org. Reactions* **2**, 13 (1944).
[3] L. F. Fieser and W. C. Lothrop, *J. Amer. Chem. Soc.* **57**, 1459 (1939).
[4] L. F. Fieser and W. C. Lothrop, *J. Amer. Chem. Soc.* **58**, 749 (1936).
[5] L. F. Fieser and M. N. Young, *J. Amer. Chem. Soc.* **53**, 4120 (1931).
[6] E. Ochiai and T. Nisizawa, *Ber. Dtsch. Chem. Ges.* **74**, 1402 (1941).
[7] B. Mander-Jones and W. M. Trikojus, *Proc. Roy. Soc.* N.S.W., **66**, 300 (1932).
[8] B. Mander-Jones and W. M. Trikojus, *J. Amer. Chem. Soc.* **54**, 2570 (1932).
[9] W. Baker, *J. Chem. Soc.* 1681 (1934).
[10] C. D. Hurd and M. A. Pollack, *J. Org. Chem.* **3**, 550 (1939).
[11] J. F. Kincaid and D. S. Tarbell, *J. Amer. Chem. Soc.* **61**, 3085 (1939).
[12] S. J. Rhoads, R. Raulins, and R. D. Reynolds, *J. Amer. Chem. Soc.* **75**, 2531 (1953); **76**, 3456 (1954).
[13] H. Conroy and R. A. Firestone, *J. Amer. Chem. Soc.* **75**, 2530 (1953).
[14] D. Y. Curtin and H. W. Johnson, *J. Amer. Chem. Soc.* **76**, 2276 (1954).

anthracene and phenanthrene the bonds are sufficiently stabilized to prevent the rearrangement of 2-allyl ethers occurring around the Δ^2 bond, the rearrangement of the allyl ethers of 5-hydroxyhydrindene[15] and 6-hydroxytetralin[16] is not restricted (absence of the Mills–Nixon effect) and takes place in both *ortho*-positions if they are available.

From a consideration of these facts and of the rather scanty kinetic data on the *ortho*-Claisen rearrangement, it seemed that the energy of activation of the reaction (which is a measure of the slow formation of dienone) might be used as a measure of double bond character or bond order in aromatic and aliphatic unsaturated compounds. There is kinetic data in the literature for the *ortho* rearrangement of the allyl ethers of *p*-cresol and vinyl alcohol.[17] In order to obtain sufficient data for our purposes, we have studied the kinetics of the rearrangement of several other suitably chosen aromatic ethers, using those structures for which data on bond orders was available. These were the ethers derived from 1- and 2-naphthol, 2-, 3- and 9-phenanthrol and 8-hydroxyquinoline. The details of their preparation, rearrangement and techniques used to obtain the kinetic data are described in subsequent sections below. From the data obtained (Tables 2–8), the first order rate constants (k_r) were calculated and the energy of activation for each reaction was computed from the Arrhenius equation and the entropy of activation from the Eyring equation (1), assuming the transmission coefficient to be equal to unity.[18]

$$k_r = \frac{kT}{h} \kappa \cdot e^{(\Delta S^{\ddagger}/R)} e^{(-\Delta E^{\ddagger}/RT)} \qquad (1)$$

where k = Boltzmann's constant,
h is Planck's constant,
κ is the transmission coefficient,
$\Delta S^{\ddagger}$ is the entropy of activation, and
$\Delta E^{\ddagger}$ is the energy of activation.

Since it has been shown[11] that the rate of the Claisen rearrangement is only slightly affected by the nature of the solvent, we have pooled our data with the literature data, irrespective of the presence or absence of a solvent of reaction. In Table 1, the derived activation energies are compared with the bond orders of the relevant bonds in the

TABLE 1. CORRELATION OF ENERGIES AND ENTROPIES OF ACTIVATION WITH RELEVANT BOND ORDER* IN A SERIES OF CLAISEN REARRANGEMENTS

Allyl ether of:—	$\Delta E^{\ddagger}$ (Kcal)	$\Delta S^{\ddagger}$ (e.u.)	Relevant bond order
p-Cresol	33·1	−8·1	0·667
Vinyl alcohol	30·6	−7·7	1·000
1-Naphthol	26·0	−15·9	0·725
2-Naphthol	28·5	−12·0	0·725
9-Phenanthrol	21·9	−18·1	0·775
2-Phenanthrol	29·5	−11·0	0·705
3-Phenanthrol	29·5	−11·0	0·702
8-Hydroxyquinoline	29·7	−11·4	0·701

* Bond orders were obtained by L.C.A.O. approximation.[19]

[15] W. C. Lothrop, *J. Amer. Chem. Soc.* **62**, 132 (1940).
[16] S. E. Sergievskaya and A. E. Gavrilova, *Zh. Obshch. Khim.* **11**, 1027 (1941).
[17] F. W. Schuler and G. W. Murphy, *J. Amer. Chem. Soc.* **72**, 3155 (1950).
[18] H. Eyring, *J. Chem. Phys.* **3**, 107 (1935).
[19] C. A. Coulson, *Valence*. Oxford (1954).

TABLE 2. FIRST ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF 1-ALLYLOXYNAPHTHALENE

Temperature °C	Time (min)	Yield of 2-allyl-1-naphthol (%)	k_r
158·2	20	33·7	
	40	48·5	
	60	56·5	
	80	68·0	
	100	75·1	$2{\cdot}04 \times 10^{4}$ sec^{-1}
172·2	5	22·4	
	10	34·2	
	15	46·3	
	20	55·5	
	30	66·5	$5{\cdot}5 \times 10^{-4}$ sec^{-1}
176·8	5	37·2	
	10	47·2	
	15	60·0	
	20	67·2	
	25	73·5	
	30	78·5	$7{\cdot}5 \times 10^{-4}$ sec^{-1}
186·1	5	42·9	
	10	61·5	
	15	73·0	
	20	82·0	
	25	86·6	$1{\cdot}30 \times 10^{-3}$ sec^{-1}
194·0	3	38·0	
	6	56·5	
	9	69·5	
	45	84·4	$2{\cdot}05 \times 10^{-3}$ sec^{-1}

aromatic compounds around which the rearrangements occur.[19] It is clear that the activation energy is not a function of the bond order alone.

That this is likely to be the case can be deduced by reasoning similar to that we have used previously for the interpretation of infra-red spectra of compounds containing intramolecular hydrogen bonds.[20] The energy of activation of the Claisen rearrangement may be considered as a function of three variables (i) the energy due to the stretching of the oxygen–carbon bond, (ii) the energy involved in the formation of the carbon–carbon bond and (iii) the resonance energy of the activated cyclic intermediate, which may be assumed to be proportional to the localization energy of the relevant bond in the aromatic compound and hence approximately proportional to its bond order. It may be further assumed that the energy due to the stretching of the oxygen–carbon bond is proportional to the carbon localization energy of the carbon atom in the aromatic compound that bears the oxygen atom, and that the energy due to the formation of the carbon–carbon bond is proportional to the carbon localization energy of the aromatic carbon atom involved in the rearrangement. In view of the parallelism

[20] S. Marcinkiewicz and J. Green, *J. Chem. Soc.* 849 (1959).

TABLE 3. FIRST ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF 2-ALLYLOXYNAPHTHALENE

Temperature °C	Time (min)	Yield of 1-allyl-2-naphthol (%)	k_r
158·2	20	11·0	
	40	19·5	
	60	29·4	
	80	34·2	
	100	38·0	$8{\cdot}8 \times 10^{-5}$ sec^{-1}
172·1	15	20·0	
	20	25·5	
	30	35·1	
	40	43·6	$2{\cdot}42 \times 10^{-4}$ sec^{-1}
180·0	15	33·3	
	20	39·5	
	25	46·6	
	30	53·5	
	35	61·0	
	40	66·0	$4{\cdot}45 \times 10^{-4}$ sec^{-1}
186·1	10	35·0	
	15	45·0	
	20	55·0	
	30	69·4	$6{\cdot}85 \times 10^{-4}$ sec^{-1}
194·0	5	28·0	
	10	48·5	
	15	65·1	
	60	98·7	$1{\cdot}13 \times 10^{-3}$ sec^{-1}

between free valencies and carbon localization energies, the energy of activation for the rearrangement of any allyl ether is then given by the equation:

$$\Delta E^{\ddagger} = K \,.\, p_{rs} + LF_r + L'F_s + M \qquad (2)$$

where p_{rs} stands for the mobile bond order of the bond of the aromatic or vinyl compound involved in the rearrangement, F_r is the free valence of the carbon atom that forms the new carbon–carbon bond, and F_s is the free valence of the carbon atom bearing the allyloxy group. K, L, L′ and M are constants characteristic for the rearrangement of any allyl ether. Substituting the values from Table 1 in the general equation (2), a set of 8 equations is obtained, which are approximately consistent for values of K, L, L′ and M of −45, −36, −100 and 75, respectively. That the agreement is not fortuitous is indicated from a consideration of other data in the literature, which can now be discussed.

While allyl vinyl ether and allyl α-methylvinyl ether (especially the former) require temperatures of over 250° for appreciable rearrangement to take place,[17,21] allyl α-phenylvinyl ether rearranges in a few minutes[21] at temperatures below 175°, although the bond order in styrene is *less* than that in ethene. By utilizing the known values for the bond orders in styrene in equation (2), we obtain a theoretical energy of activation

[21] C. D. Hurd and M. A. Pollack, *J. Amer. Chem. Soc.* **60**, 1905 (1938).

TABLE 4. FIRST ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF 8-ALLYLOXYQUINOLINE

Temperature °C	Time (min)	Yield of 7-allyl-8-hydroxy quinoline (%)	k_r
158·0	85	12·4	
	110	15·6	
	140	18·8	
	170	22·4	
	195	26·0	$2{\cdot}5 \times 10^{-5}$ sec^{-1}
171·9	30	17·6	
	60	26·0	
	90	35·2	
	120	43·5	
	150	50·5	$7{\cdot}5 \times 10^{-5}$ sec^{-1}
180·6	10	8·0	
	20	17·4	
	40	30·1	
	80	47·6	
	120	64·0	$1{\cdot}42 \times 10^{-4}$ sec^{-1}
186·0	10·5	12·0	
	20	20·6	
	30	32·0	
	40	38·8	$2{\cdot}05 \times 10^{-4}$ sec^{-1}
194·0	15	30·2	
	30	48·5	
	45	63·0	
	250	98·1	$3{\cdot}70 \times 10^{-4}$ sec^{-1}

for the rearrangement of allyl α-phenylvinyl ether of 16·2 kcal. This can be compared with the value of 30·6 kcal for allyl vinyl ether itself and readily accounts for the observed rate of reaction. The fact that allyl α-methylvinyl ether rearranges more readily than allyl vinyl ether[21] may be due to hyperconjugation, which would cause a decrease in the bond order of the vinyl double bond but would increase the relevant free valencies. The determination of the energies of rearrangement of these vinyl ethers would thus make it possible to determine approximately the degree of delocalization of π electrons in propene. A further example of the importance of free valencies in the Claisen rearrangement occurs in the rearrangement of allyloxy quinones. According to equation (2), the energy of activation for the rearrangement of an allyloxy-*p*-benzoquinone would be only about 5 kcal/mole, and, although the entropy of activation for such a rearrangement might be highly negative (since Table 1 indicates that the $\Delta S^{\ddagger}$ tends to decrease as $\Delta E^{\ddagger}$ decreases), it could be expected that the reaction would be nearly complete at room temperature in a few hours. Although allyloxybenzoquinones have not been prepared, Fieser[22] prepared 2-allyloxy-1,4-naphthoquinone and indeed observed that it rearranged *within a few minutes* at 135°. Calculation shows that bond orders and free valencies in this compound are probably similar to what would exist in the hypothetical allyloxybenzoquinone.

[22] L. F. Fieser, *J. Amer. Chem. Soc.* **48**, 3201 (1926).

TABLE 5. FIRST ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF 9-ALLYLOXYPHENANTHRENE

Temperature °C	Time (min)	Yield of 10-allyl-9-hydroxyphenanthrene (%)	k_r
82·1	60	8·6	
	120	15·9	
	180	22·9	
	240	29·9	$2{\cdot}42 \times 10^{-5}$ sec^{-1}
100·0	40	22·2	
	60	32·0	
	90	44·6	
	120	53·8	
	180	68·4	$1{\cdot}06 \times 10^{-4}$ sec^{-1}
110·0	15	19·6	
	30	35·1	
	45	47·5	
	60	58·1	
	75	66·6	$2{\cdot}4 \times 10^{-4}$ sec^{-1}
130·2	5	25·0	
	10	43·8	
	15	57·8	
	20	68·0	$9{\cdot}6 \times 10^{-4}$ sec^{-1}

TABLE 6. FIRST ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF 2-ALLYLOXYPHENANTHRENE

Temperature °C	Time (min)	Yield of 1-allyl-2-hydroxyphenanthrene (%)	k_r
158·0	30	5·1	
	60	9·0	
	90	13·0	
	120	16·6	
	180	23·7	$2{\cdot}45 \times 10^{-5}$ sec^{-1}
180·6	10	8·2	
	20	15·4	
	30	22·7	
	40	30·0	
	50	34·6	$1{\cdot}44 \times 10^{-4}$ sec^{-1}
194·0	10	20·0	
	20	35·4	
	30	48·5	
	40	58·0	
	50	66·9	$3{\cdot}69 \times 10^{-4}$ sec^{-1}

TABLE 7. FIRST ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF 3-ALLYLOXYPHENANTHRENE

Temperature °C	Time (min)	Yield of 4-allyl-3-hydroxyphenanthrene (%)	k_r
158·0	30	4·9	
	60	8·7	
	90	12·8	
	120	16·7	
	180	24·1	$2{\cdot}56 \times 10^{-5}$ sec^{-1}
180·6	10	7·9	
	20	14·7	
	30	22·4	
	40	29·8	
	50	34·2	$1{\cdot}39 \times 10^{-4}$ sec^{-1}
194·0	10	20·5	
	20	35·6	
	30	49·0	
	40	57·8	
	50	67·0	$3{\cdot}68 \times 10^{-4}$ sec^{-1}

TABLE 8. FIRST ORDER RATE CONSTANTS FOR THE REARRANGEMENT OF N-ALLYL-1-NAPHTHYLAMINE

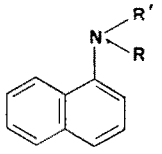
Temperature °C	Time (min)	Yield of 2-allyl-1-naphthylamine (%)	k_r
240·2	30	5·4	
	60	10·6	
	90	15·9	
	120	20·5	$3{\cdot}2 \times 10^{-5}$ sec^{-1}
258·2	10	7·0	
	20	11·0	
	30	16·0	
	40	20·9	
	50	25·0	
	60	29·7	$9{\cdot}6 \times 10^{-5}$ sec^{-1}
280·0	10	18·7	
	20	32·6	
	30	43·9	
	40	54·8	
	60	69·8	
	180	91·7	$3{\cdot}28 \times 10^{-4}$ sec^{-1}

The fact that pyrolysis of N-allylaniline gives propene and aniline instead of the expected *o*-allylaniline[23] can now be understood. The energy of the cyclic transitional state is lowest when it is coplanar with the aromatic ring. In aromatic allylamines more energy is required to bring about coplanarity than in allyl ethers, since the nitrogen atom is pyramidal. The cyclic transitional state in the rearrangement of aromatic allylamines would also lead to a more negative entropy of activation due to

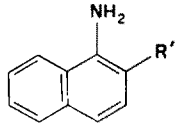
[23] F. L. Canahan and C. D. Hurd, *J. Amer. Chem. Soc.* **52**, 4586 (1930).

inhibition of the rotation of the amino hydrogen atom. Since the energy of activation for the rearrangement of allyl phenyl ether, derived by calculation from equation (2), is about 34·0 kcal and it appears that about 6 kcal is necessary to bring the nitrogen atom into the planar state,[19] the energy of activation for the hypothetical rearrangement of N-allylaniline would be about 40 kcal. The combination of high energy of activation and large negative entropy of activation would mean that the rearrangement would only take place at very high temperatures and it is therefore not surprising that at 275° only cleavage was observed,[23] since the latter reaction would occur with a positive entropy of activation.

An experimental verification would be available in the case of allylamines that correspond structurally to allyl ethers that rearrange with exceptionally low activation energies, in which case the allylamine rearrangement might be expected to occur at temperatures lower than that at which cleavage becomes important. In accordance with this hypothesis, we have prepared N-allyl-1-naphthylamine (I, R = H, R′ = $CH_2{\cdot}CH{=}CH_2$) since $\Delta E^{\ddagger}$ for the rearrangement of allyl 1-naphthyl ether is only 26·0 kcal. When this compound was heated to 280° for 3 hours, it rearranged to give 2-allyl-1-naphthylamine (II; R′ = $CH_2{\cdot}CH{=}CH_2$) in 90 per cent yield. A small



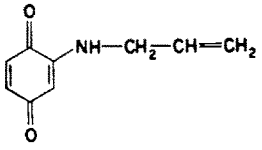
I



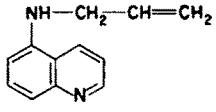
II

amount of unchanged N-allyl-1-naphthylamine remained, but cleavage, if it occurred, was so little as to be unmeasurable. This is thus the first example of a Claisen rearrangement from a nitrogen atom. The rearrangement was found to be of the first order with $\Delta E^{\ddagger} = 32{\cdot}4$ kcal (predicted 32·0 kcal) and $\Delta S^{\ddagger} = -17$ e.u.

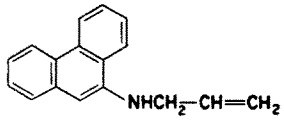
As a consequence of the theoretical treatment it should be possible to predict the pattern of rearrangement for several other interesting allylamines. Thus, 2-allylaminobenzoquinone (III) can be expected to rearrange with $\Delta E^{\ddagger} = 12$ kcal; that is, at such a rate that at room temperature it would rearrange within a few hours to give the *ortho*-substituted primary amine. 5-Allylaminoquinoline (IV) would be expected



III



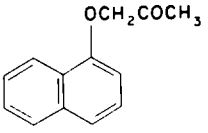
IV



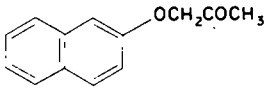
V

to rearrange with $\Delta E^{\ddagger} \approx 33$ kcal and 9-allylaminophenanthrene (V) with $\Delta E^{\ddagger} \approx 28$ kcal. It is possible that 2-allylaminopyridine (but not the 3-allylamino compound) would rearrange with $\Delta E^{\ddagger} \approx 29$ kcal. However, the calculations for this compound are complicated by the contribution of dipolar structures to the resonance hybrid, and there is thus considerable uncertainty. For similar reasons, equation (2) cannot be applied to calculations of $\Delta E^{\ddagger}$ for the rearrangement of vinylamines.

Another type of rearrangement that could take place in compounds having partly localized π electrons and high free valencies is the rearrangement of aryloxyketones. Tarbell[24] investigated the reaction of *p*-tolyloxypropanone, but found that, although a little *p*-cresol was formed by cleavage, no rearrangement took place. We have found that when 1-naphthoxypropanone (VI) and 2-naphthoxypropanone (VII) were heated



VI



VII

at 280° for 3 hours, the 2-naphthoxypropanone was largely unchanged, only a small amount of 2-naphthol being detected in the product by paper chromatography, but the 1-naphthoxypropanone decomposed almost completely, giving 1-naphthol together with some tarry material. The failure of these compounds to rearrange may be due to the very low resonance energy of the transitional state, in which the lone electron pairs on the oxygen atoms are not significantly delocalized. Nevertheless, the fact that 1-naphthyloxypropanone is much less stable to heat than the 2-naphthyloxy compound corroborates the importance of free valence in reactions.

This theoretical treatment does not make it possible to decide whether the Claisen rearrangement involves homolytic or heterolytic fission of the oxygen–carbon and nitrogen–carbon bonds, since in alternant hydrocarbons the polarization energy of a given carbon atom is independent of the nature of the polarization postulated. However, the fact that the energy of activation of the rearrangement of 8-allyloxyquinoline is consistent with equation (2) although the electronic charges at C-7 and C-8 are not equal to unity, suggests that homolytic fission of the oxygen–carbon bond occurs. If this conclusion is correct, a suitably modified form of equation (2) could be used for a study of bond orders and free valencies in various substituted allyl radicals.

That bond orders in the allyl radical itself may play a part in determining the energy of activation of the Claisen rearrangement is in fact clear from a study of available information in the literature. For example, Tarbell and Wystrach[25] studied the pyrolysis of arylmethyl ethers of 3,5-dichloro-salicylic acid. They found that while the first stage in the pyrolysis of the benzyl and β-naphthyl methyl ethers was cleavage, followed by the formation of the corresponding arylmethyl esters, the 9-phenanthrylmethyl ether mainly rearranged to 9-methyl-10-(2-hydroxy-3,5-dichlorophenyl)-phenanthrene. It is now generally held that simultaneous breaking of the carbon–oxygen bond and formation of the carbon–carbon bond occurs in the first stage of the Claisen rearrangement. This implies that in the transitional state the π electrons in the allyl radical are delocalized and contribute to the resonance of the transitional state. When the allyl radical is an arylmethyl group, the decrease of the energy of activation due to the resonance in the transitional state is opposed by the increase of the energy due to the localization energy of the two π electrons in the arylmethyl group. When the arylmethyl group is benzyl or naphthylmethyl, this localization energy is large (30 kcal for benzene, 22 kcal for the $\Delta 1$ bond in naphthalene) and consequently the energy of activation for the hypothetical Claisen rearrangement would be higher than

[24] D. S. Tarbell, *J. Org. Chem.* **7**, 251 (1942).
[25] D. S. Tarbell and V. F. Wystrach, *J. Amer. Chem. Soc.* **65**, 2149 (1943).

the energy of the cleavage reaction. When, however, the aryl methyl group is 9-phenanthrylmethyl, the energy of localization of the Δ9 bond is only 16 kcal, and the Claisen rearrangement could be expected to take place, on condition that the energy of rearrangement of the allyl ether of 3,5-dichlorosalicyclic acid is of the order of 20 kcal or less (36 kcal being probably the maximum value for the energy of activation if an ether is to rearrange at a reasonable temperature). It is again in accordance with the requirements of theory that, in fact, Claisen and Eislib[26] noted that allyl ethers of substituted salicyclic acids rearrange with elimination of carbon dioxide *at about* 100°, which indicates an energy of activation of the same order as that of 9-allyloxyphenanthrene, i.e. about 20 kcal. The energy of activation for the rearrangement of the 9-phenanthrylmethyl ether of 3,5-dichlorosalicyclic acid cannot be calculated from equation (2), since there are additional complications due to hydrogen bonding between the carboxy and allyloxy groups. Nevertheless this energy of activation could be calculated empirically if data was available on the energy of activation for the rearrangement of the allyl ether and the effect of free valencies in the allyl radical on this energy. This effect could probably be determined from a series of kinetic experiments with several suitable arylmethyl ethers of a phenol or enol and a mathematical treatment similar to that used in the present study.

Preparation of ethers, amines and rearrangement products

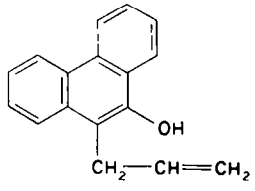
2-Allyloxynaphthalene has been described as a low-melting solid decomposing on distillation[27,28] and readily decomposing on being heated to give 1-allyl-2-naphthol.[1,27] 1-Allyloxynaphthalene also decomposed on attempted distillation[26,28,29] and its rearrangement has been described.[26] We have found that both ethers can be distilled in a short-path still under high vacuum, with only a minimal amount of rearrangement occurring. Both ethers underwent smooth rearrangement when heated under reflux in decalin for 40 minutes to give the *ortho*-substituted naphthols.

2-Allyloxy- and 3-allyloxyphenanthrene were prepared and rearranged according to Fieser and Young.[5] The compounds were found to be stable at 100° under nitrogen. In the presence of air at 100°, they turn yellow, but no rearrangement takes place. 9-Allyloxyphenanthrene was prepared by shaking the phenanthrol with allyl bromide in the presence of acetone and potassium hydroxide under nitrogen. When this ether was heated in iso-octane, under nitrogen, in a sealed tube at 156° for 3 hours it gave an oil that analysed correctly for the substituted phenanthrol (VIII). Attempts at purification through crystallization eventually gave a compound with m.p. 139° that analysed for $C_{17}H_{14}O_3$. This unexpected product liberated iodine from potassium iodide, behaved abnormally on reverse-phase paper chromatography, and had an infra-red spectrum that exhibited a very typical sharp band close to 3·0 mμ due to vibrations of an O—O—H (hydroperoxide) group.[30] These properties are consistent with it being the hydroperoxide (IX) formed through the unusually facile oxidation of 10-allyl-9-phenanthrol by atmospheric oxygen.* Fieser and Young[5] commented on the instability of 9-phenanthrol derivatives and the ease with which they can be oxidized by

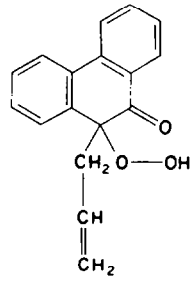
* The structure of this compound was elucidated with the help of Dr. D. McHale of these laboratories, to whom we express our thanks.

[26] L. Claisen and O. Eislib, *Monatsh.* **401**, 21 (1913).
[27] C. A. Hurd and L. Schmerling, *J. Amer. Chem. Soc.* **59**, 107 (1937).
[28] V. H. Dermer and O. C. Dermer, *J. Org. Chem.* **3**, 285 (1938).
[29] V. L. Tweedie and M. Cuscurida, *J. Amer. Chem. Soc.* **79**, 5463 (1957).
[30] O. D. Shreve, N. R. Heether, H. B. Knight and D. Swern, *Analyt. Chem.* **23**, 282 (1951).

atmospheric oxygen. In the case of retinol (8-isopropyl-2-methyl-9-phenanthrol), however, they found that oxidation stopped at 9,10-quinone stage. Fieser and Young successfully rearranged the allyl ether of retinol but gave no analysis on the oily product and identified it as the crystalline acetate. Accordingly, for analytical purposes, we converted 10-allyl-9-phenanthrol immediately after the rearrangement to an acetate, on which the required analysis was obtained. The allyl substituted phenanthrol was fortunately stable enough to be determined chromatographically in the same way as



VIII



IX

the other compounds under study. Fieser and Young also reported that the allyl ethers of 2-phenanthrol and 3-phenanthrol rearranged on the water-bath so easily that they could not be purified by vacuum distillation. We found the compounds to be stable at 100°, when heated for 4 hours, and this would be expected from our kinetic studies on these compounds. It is likely that the difficulties encountered by Fieser and Young were due to oxidation rather than rearrangement.

8-Allyloxy-quinoline was prepared according to Mander-Jones and Trikojus.[7]

N-Allyl-1-naphthylamine (I; R = H, R′ = $CH_2{\cdot}CH{:}CH_2$) has been used in pharmacological studies by several workers[31] who have not, however, described the properties of the substance. A substance described as N-allyl-1-naphthylamine was prepared by Sloviter[32] by the action of allyl chloride on 1-naphthylamine, its structure being based on an iodine number and nitrogen analysis. We were unable to repeat this experiment satisfactorily and other methods of preparation were investigated.

N-*p*-Toluenesulphonyl-1-naphthylamine with allyl bromide afforded N-allyl-N-*p*-toluenesulphonyl-1-naphthylamine (I; R = $p{\cdot}CH_3{\cdot}C_6H_4{\cdot}SO_2$; R′ = $CH_2{\cdot}CH{:}CH_2$). Attempts to effect acid or alkaline hydrolysis of the sulphonamide were unsuccessful: treatment with sodium in butanol cleaved the sulphonamide to an oil which gave a crystalline hydrochloride in poor yield. This was not N-allyl-1-naphthylamine hydrochloride, but appeared from the analytical figures to be the hydrochloride of a dihydro-derivative. Infra-red evidence supported a dihydronaphthalene structure. The required allyl-naphthylamine was eventually obtained by direct allylation of 1-naphthylamine with allyl bromide in the presence of potassium carbonate. After a preliminary distillation the bases were converted into hydrochlorides and fractionally crystallized, the separation being followed by infra-red spectra. Two isomeric monoallylated naphthylamine hydrochlorides were obtained, the major product being N-allyl-1-naphthylamine. The free base had b.p. 120°/0·5 mm, compared with b.p.

[31] U.S.P. 2,381,071 (Eastman Kodak Co.); H. Endo, *Sci. Rep. Res. Inst., Tohoku Univ.* Ser. C, 7, 351 (1957) and subsequent papers.

[32] H. A. Sloviter, *J. Amer. Chem. Soc.* 71, 3360 (1949).

110–120°/4 mm for the material described by Sloviter. Its structure was confirmed by conversion to the *p*-toluenesulphonamide, which was identical with the product isolated from the reaction of N-*p*-toluenesulphonyl-1-naphthylamine with allyl bromide. The second product contained a primary amino-group and appeared to be a C-allylnaphthylamine hydrochloride: catalytic reduction gave the corresponding C-propylnaphthylamine hydrochloride, which formed crystalline acetyl and benzoyl derivatives. These were not the same as those derived from 4-propyl-1-naphthylamine as described by Sergievskaya and Uretskaya.[33] Catalytic reduction of N-allyl-1-naphthylamine hydrochloride gave not the n-propyl derivative but 1-naphthylamine hydrochloride, characterized as acet-α-naphthalide. A somewhat analogous cleavage of an O-allyl ether has been described by Moffett and Seay,[34] who found that 2-allyloxy-3,5-bis-n-propyl-benzamide yielded the 2-hydroxy derivative on hydrogenation.

When N-allyl-1-naphthylamine was heated in a sealed tube at 260° for 4 hours, smooth rearrangement took place to give 2-allyl-1-naphthylamine (II; R′ = CH_2—$CH{=}CH_2$). Its structure was confirmed by conversion into the known *p*-nitrobenzoate of 2-allyl-1-naphthol. The derived hydrochloride showed no depression on mixed melting point with the foregoing C-allyl-1-naphthylamine hydrochloride and the infra-red spectra of the two compounds were identical. On catalytic reduction, it yielded 2-n-propyl-1-naphthylamine hydrochloride (II; R = n—C_3H_7) and hence the acetyl and benzoyl derivatives, all of which were identical with the products obtained from the C-allyl-1-naphthylamine obtained by direct allylation. It therefore appears that some C-allylation of 1-naphthylamine takes place in addition to N-allylation under the conditions used, since the temperature (boiling acetone) was far too low to have produced the C-allyl compound by a Claisen rearrangement.

EXPERIMENTAL

2-*Allyloxynaphthalene*

β-Naphthol (10·0 g), allyl bromide (8·4 g), potassium carbonate (9·6 g), and acetone (70 ml) were heated under reflux for 2 hr. The acetone was removed under red. press. and the slurry treated with aqueous N-sodium hydroxide and extracted with ether. The ether washings were washed with water, dried, and evaporated to give a light brown oil (10·2 g). A portion of the oil (5 g) in light petroleum (b.p. 40–60°) was percolated through a column of alumina (5″ × 1″, Spence type '0') and the elute evaporated to give an almost colourless oil which was distilled in a short-path still, b.p. 55–60° (bath)/10^{-3} mm (Pirani) as a colourless mobile oil (4·2 g), n_D^{21} 1·6078 (Hurd and Schmerling[35] give n_D^{25} 1·600). The picrate formed yellow needles from ethanol, m.p. 96–97° (lit,[35] m.p. 98·5–99°).

1-*Alloxynaphthalene* was similarly prepared as a colourless oil, b.p. 60° (bath)/10^{-3} mm (Pirani), n_D^{23} 1·6055 (lit,[28] n_D^{25} 1·6038). (Found: C, 84·6; H, 6·5. $C_{13}H_{12}O$ requires: C, 84·8; H, 6·6%). The picrate formed orange-yellow needles from ethanol, m.p. 99–100° (lit,[26] m.p. 100·5–101°).

1-*Allyl*-2-*naphthol*

2-Naphthylallyl ether (5·0 g) in decalin (50 ml) was heated under reflux for 40 min, cooled, diluted with ether and extracted with aqueous N-sodium hydroxide. Acidification of the extracts gave an oil which was collected and distilled, b.p. 130–134°/0·6 mm. Crystallization from light petroleum (b.p 60–80°) gave the product as colourless prisms, m.p. 56° (3·0 g) (lit,[1] m.p. 55°).

2-*Allyl*-1-*naphthol* similarly prepared had b.p. 114°/0·2 mm, needles from light petroleum (b.p. 40–60°), m.p. 35–36° (Found: C, 84·5; H, 6·6. Calc. for $C_{13}H_{12}O$: C, 84·8; H, 6·6%). Claisen and Eislib[26] describe the naphthol as an oil, b.p. 171°/12 mm.

[33] S. I. Sergievskaya and G. Ya Uretskaya, *Zh. Obshch. Khim.* **23**, 1522 (1953).
[34] R. B. Moffett and P. B. Seay, *J. Med. Pharm. Chem.* **2**, 213 (1960).

9-Alloxyphenanthrene

9-Phenanthrol (2 g), allyl bromide (4 ml), acetone (20 ml), and 20% aqueous potassium hydroxide (5 ml) were shaken together under nitrogen for 4 hr at room temp. The product was extracted into a 1:1 mixture of light petroleum and ether, washed several times with water followed by 20% potassium hydroxide solution and finally with water. The crude ether was dissolved in light petroleum and purified by passing it through a short column (10 × 1 cm) of Decalso F. The column was eluted with the same solvent (200 ml). Evaporation gave 9-allyloxyphenanthrene, crystallized from methanol, m.p. 67°. (Found: C, 87·0; H, 6·1. $C_{17}H_{14}O$ requires: C, 87·1; H, 6·0%). The ether was rearranged by heating in iso-octane, under nitrogen, in a sealed tube at 156° for 3 hr. The product was chromatographed on Decalso F and eluted with benzene. Crystallization from dil ethanol, then methanol, and finally light petroleum–benzene gave a *product*, m.p. 139°, which turned yellow in air. Its properties and infra-red spectrum were consistent with it being 10-*allyl*-10-*hydroperoxy*-9-*oxo*-9,10-*dihydrophenanthrene* (the hydroperoxide of 10-allyl-9-phenanthrol IX). (Found: C, 76·5; H, 5·0. $C_{17}H_{14}O_3$ requires: C, 76·8; H, 5·3%). In another preparation, the rearranged ether was analysed directly (Found: C, 87·0; H, 6·1. $C_{17}H_{14}O$ requires: C, 87·1; H, 6·0%), showing that no cleavage occurred and was converted immediately to the *acetate*, crystallized from light petroleum (b.p. 60–80°), m.p. 124–125°. (Found: C, 82·9; H, 5·5. $C_{19}H_{16}O_2$ requires: C, 82·6; H, 5·8%).

N-*Allyl*-N-p-*toluenesulphonyl*-1-*naphthylamine*

N-*p*-Toluenesulphonyl-1-naphthylamine[35] (17·5 g), allyl bromide (6·4 g), potassium carbonate (5·4 g) and acetone (80 ml) were refluxed for 2 hr. The *product*, isolated by addition of water, formed needles from methanol (18·0 g), m.p. 95–96° (Found: 70·8; H, 5·8; N, 4·2. $C_{20}H_{19}NO_2S$ requires: C, 71·25; H, 5·7; N, 4·2%).

N-*Allyldihydro*-1-*naphthylamine hydrochloride*

To the foregoing sulphonamide (11·2 g) and n-butanol (85 ml), heated on the steam-bath, sodium metal (7·7 g) was added in portions. After the addition was complete, the solvent was removed, and the residual oil treated with water and extracted with ether. The ether was removed and the residual oil distilled giving a main fraction of colourless oil (3·45 g), b.p. 128–138°/0·4 mm, $n_D^{20.5}$ 1·5918. The non-volatile fraction solidified on cooling and after crystallization from ethanol formed needles (2·9 g), m.p. 157–159°. The identity of this solid was not established. The oil was converted into the hydrochloride with ethanolic hydrogen chloride and the *product* crystallized from ethyl acetate–methanol to give needles, m.p. 179–180° (Found: C, 71·2; H, 7·4; N, 6·2; Cl, 15·4. $C_{13}H_{16}ClN$ requires: C, 70·5; H, 7·3; N, 6·3; Cl, 16·0%).

Reaction of 1-*naphthylamine with allyl bromide*

1-Naphthylamine (57·2 g), allyl bromide (48·4 g), potassium carbonate (56 g), and acetone (400 ml) were heated under reflux for 6 hr. The solid was filtered off and rejected and the filtrate evaporated and distilled under red. press. (i) b.p. 114–118°/0·5 mm, (32·3 g), $n_D^{21.5}$ 1·6509; (ii) b.p. 119–124°/0·5 mm, (22·5 g) $n_D^{21.5}$ 1·6460; (iii) b.p. 125–128°/0·5 mm; (10·9 g), $n_D^{21.5}$ 1·6488. The fractions were all viscous pale yellow oils and after conversion into the hydrochlorides were fractionally crystallized from ethanol or ethanol–ether, the course of the separation being followed by m.p.s and infra-red spectra. The following pure fractions were isolated: 1-naphthylamine hydrochloride (10·2 g), m.p. 270–271°; N-*allyl*-1-*naphthylamine hydrochloride*, needles from ethanol (11·7 g), m.p. 229–230° (Found: C, 70·8, H, 6·4; N, 6·4. $C_{13}H_{14}ClN$ requires: C, 71·1; H, 6·4; N, 6·4%); 2-*allyl*-1-*naphthylamine hydrochloride*, long needles from ethanol (2·2 g), m.p. 222–223°. (Found: C, 70·9; H, 6·3; N, 6·5. $C_{13}H_{14}ClN$ requires: C, 71·1; H, 6·4; N, 6·4%). The remaining crude solids (33 g) were not further investigated. N-*Allyl*-1-*naphthylamine* regenerated from the hydrochloride was an almost colourless oil, b.p. 120°/0·5 mm. (Found: C, 85·0; H, 7·0; N, 7·8. $C_{13}H_{13}N$ requires: C, 85·3; H, 7·1; N, 7·65%). When treated with *p*-toluenesulphonylchloride in pyridine on the steam-bath for 15 min, N-allyl-N-*p*-toluenesulphonyl-1-naphthylamine was obtained, m.p. 96–98° not depressed on admixture with an authentic sample.

[35] O. N. Witt and G. Schmidt, *Ber. Dtsch. Chem. Ges.* **27**, 2370 (1894).

2-Propyl-1-naphthylamine hydrochloride

2-Allyl-1-naphthylamine hydrochloride (0·3 g) in ethanol (150 ml) was shaken with hydrogen and 10% palladized charcoal till uptake of gas ceased. After removal of the catalyst, concentration yielded the *product* (0·26 g) which separated from ethanol as needles, m.p. 229–230° (Found: C, 69·9; H, 7·2; N, 6·3. $C_{13}H_{16}ClN$ requires: C, 70·4; H, 7·3; N, 6·3%). The *acetyl derivative*, needles from aqueous ethanol, had m.p. 152·5–153·5° (Found: C, 79·3; H, 7·3; N, 6·2. $C_{15}H_{17}NO$ requires: C, 79·2; H, 7·5; N, 6·2%). The *benzoyl derivative* formed needles from ethanol, m.p. 183–184° (Found, C, 83·4; H, 6·4; N, 4·8. $C_{20}H_{19}NO$ requires: C, 83·1; H, 6·6; N, 4·8%).

Reduction of N-allyl-1-naphthylamine hydrochloride

(a) The hydrochloride (0·5 g) in ethanol (80 ml) was shaken with hydrogen and 10% palladized charcoal. Initial uptake was very rapid but slowed up after ca. 1 mole of hydrogen had been absorbed. Shaking was stopped after absorption of ca. 1·2 moles, the catalyst removed and the solvent evaporated. Crystallization of the residual pale yellow solid from ethanol yielded small white needles (0·16 g), m.p. 260–265°, not depressed on admixture with α-naphthylamine hydrochloride and giving an identical infra-red spectrum.

(b) In another experiment the crude hydrochloride was converted into the base and warmed with acetic anhydride. N-Acetyl-1-naphthylamine formed needles from water, m.p. 159–160° (Found: C, 77·4; H, 6·0; N, 7·6. Calc. for $C_{12}H_{11}NO$: C, 77·7; H, 6·0; N, 7·6%).

Rearrangement of N-allyl-1-naphthylamine

N-Allyl-1-naphthylamine hydrochloride (3·0 g) was converted into the base which was heated in a sealed tube at 260° for 3 hr. The pale yellow oil was distilled in a short-path still, [76–90° (bath)/8 × 10^{-3} mm (Pirani)] as a colourless viscous oil (1·76 g), $n_D^{21·5}$ 1·6497. It was converted into the hydrochloride (1·85 g), needles from ethanol, m.p. 216–218° not depressed on admixture with 2-allyl-1-naphthylamine hydrochloride prepared as described above. The free base (0·2 g) was diazotized in 5 N sulphuric acid and the solution was heated on the steam bath for 15 min to give 2-allyl-1-naphthol, identified as the *p*-nitrobenzoate, m.p. 98–99°, and on admixture with an authentic sample.

1-Naphthoxypropanone and 2-naphthoxypropanone were prepared according to Calaway and Henze.[36] Rearrangement of these ethers was attempted without solvent, under nitrogen, in sealed tubes at 280°. After 3 hr, the 1-naphthoxy ether had almost completely decomposed and the product was mainly 1-naphthol (identified chromatographically) with some tar. The 2-naphthoxy ether gave only a small amount of 2-naphthol under these conditions.

Kinetic studies

1% solutions of the allyl ethers in iso-octane were sealed in a series of glass tubes under nitrogen and heated at temperatures necessary to give rearrangements of between about 10 and 60% (these being decided from previous pilot runs). N-allyl-1-naphthylamine was rearranged without solvent because of the high temperatures required. Tubes were removed at intervals and the contents analysed directly by ascending reversed phase paper chromatography. The kinetic data are given in Tables 2, 3, 4, 5, 6, 7 and 8.

Analytical methods

The paper chromatographic system is based on that previously described for tocopherol analysis.[37,38] Strips of Whatman No. 4 filter paper (3 × 20 cm) were impregnated with zinc carbonate and then with liquid paraffin. The mobile phase was 40% aqueous ethanol for the naphthols, naphthylamine and 8-hydroxyquinoline derivatives, and 50% aqueous ethanol for the phenanthrols. Visualization of the chromatograms was accomplished by incorporating a trace of sodium fluorescein in the zincammine solution used for paper impregnation.[38] When viewed under ultra-violet light (Hanovia "Chromatolite"), the phenols appear as dark bands against a fluorescent background. The naphthylamines fluoresce strongly in ultra-violet light and incorporation of sodium fluorescein was omitted from the preparation of papers on which these were run. For analysis, 0·04 ml of each

[36] P. K. Calaway and H. R. Henze, *J. Amer. Chem. Soc.* **61**, 1355 (1939).
[37] J. Green, S. Marcinkiewicz and P. R. Watt, *J. Sci. Fd. Agric.* **6**, 274 (1955).
[38] J. Green, *J. Sci. Fd. Agric.* **9**, 801 (1958).

solution was chromatographed (the naphthylamine ether was dissolved to give a 1% solution in iso-octane *after* rearrangement). Chromatograms were run for 1 hr, which time was sufficient for the clear separation of the allyl-substituted phenols from the allyl ethers (the latter staying on the starting line). The R_f value of each pure allyl-substituted phenol was determined by chromatography on separate strips. Quantitative determination of each rearrangement product followed the procedures previously described.[37,38] Each band was cut out, eluted with 3 ml ethanol and the phenol determined

TABLE 9. SPECTROSCOPIC DATA ON ALLYL-SUBSTITUTED REARRANGEMENT PRODUCTS

Compound	λ_{max} (mμ)	$E^{1\%}_{1cm}$
1-allyl-2-hydroxynaphthalene	335	132
2-allyl-1-hydroxynaphthalene	325	158
1-allyl-2-hydroxyphenanthrene	343	92
4-allyl-3-hydroxyphenanthrene	346	97
10-allyl-9-hydroxyphenanthrene	333	128
7-allyl-8-hydroxyquinoline	315	122
2-allyl-1-naphthylamine	330	294

spectrophotometrically. The extinction coefficient at a suitable peak was determined on each pure compound and the data is given in Table 9. In separate experiments, each compound was studied for possible losses on chromatography: these were found to be negligible (less than 3%).

The method, however, could not be used for a study of more volatile phenols: for example, the rearrangement of allyloxybenzene cannot be studied by chromatographic methods. Since 10-allyl-9-hydroxyphenanthrene was unstable in the presence of air, particular care had to be taken during its investigation. Chromatograms of the rearrangement of 9-allyloxyphenanthrene were not dried for visualization purposes but were compared directly with other simultaneously run duplicate chromatograms visualized after drying. By this means, the position of the phenanthrol was obtained rapidly and the wet papers were cut up for quantitative determination.