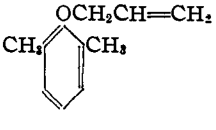
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

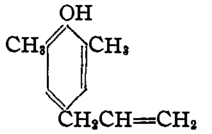
The Claisen Rearrangement. II. A Kinetic Study of the Rearrangement of Allyl 2,6-Dimethylphenyl Ether in Diphenyl Ether Solution

BY D. STANLEY TARBELL AND JOHN F. KINCAID

A recent study[1] of the kinetics of the rearrangement of allyl *p*-tolyl ether in diphenyl ether solution indicated that the reaction is first order and proceeds by some mechanism which does not require catalysis by acids or bases. The case studied involves migration of the allyl group to the free ortho position and might be expected to be a unimolecular reaction. If both ortho positions of an allyl phenyl ether are blocked, however, the allyl group enters the para position on rearrangement, and the reaction might be expected to involve a bimolecular mechanism. We wish to report a study of the rate of rearrangement of a compound of this type, allyl 2,6-dimethylphenyl ether (I).



I



II

The rate of conversion of this compound to 2,6-dimethyl-4-allylphenol (II) in one molar solution in diphenyl ether has been studied at three temperatures, 185.8, 171.6, and 156.9°. At the two higher temperatures the rate of reaction of the pure liquid has been measured, and at 171.6° the effect of dimethylaniline and acetic acid has been studied, as well as the rate in solutions more concentrated and more dilute than one molar.

The structure of the rearrangement product II was proved by the fact that it was identical with the product obtained from direct C-alkylation of 2,6-dimethylphenol with allyl bromide. With allyl bromide and sodium ethylate in alcohol, 2,6-dimethylphenol yielded a mixture of approximately 85% of the ether I and 15% of the C-alkylation product II. In a trial run with allyl bromide and sodium in benzene, the product consisted of 55% of the ether and 45% of the C-alkylation product.

It was found that the phenylurethan of the rearrangement product II could be prepared readily using a trace of dry hydrogen chloride as catalyst; aluminum chloride and bases are also known to catalyze the formation of phenylurethans from phenols.[2]

The isolation of the rearrangement products described in the experimental part was carried out in order to determine whether side reactions occurred during the reaction. The results of the fractionation showed that 95% of the product was pure 2,6-dimethyl-4-allylphenol when the rearrangement of the pure liquid was carried out at 171.6° in the absence of air. Five per cent. of a non-volatile product was formed which was probably a polymer. Since polymerization reactions should be slower in solution than in the pure liquid, it is concluded that the rearrangement in solution is greater than 95% quantitative.

The first order rate constants obtainable from these data by the usual equation, given in Tables I to III, show that the kinetics of the rearrangement are strictly first order. If the slow step in the reaction mechanism were bimolecular, the first order constants for 80% reaction would be only about one-half as great as the initial values, whereas inspection of the table reveals that the constants for the two most dilute solutions do not change greatly with the percentage reaction, while those for the most concentrated solution actually increase with percentage reaction. This increase is very marked for the pure liquid, the rate constant for 77% reaction being 11.85×10^{-5} sec.$^{-1}$ compared to 7.75×10^{-5} sec.$^{-1}$ for 16% reaction. It should be mentioned that these rate constants are not an accurate measure of the specific rate of the rearrangement in the two cases since they were computed from an equation integrated with the condition that k remain constant as the reaction proceeds. Actually the rate of the rearrangement is about three times the initial rate after 80% reaction in the pure liquid. This behavior is similar to that previously noted for allyl *p*-tolyl ether.[1] Although the reaction takes place considerably faster in the pure liquid than it does in solution, the initial values of the rate constants are almost the same. This constancy of the initial values is further proof that the reaction is first order.

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(1) Kincaid and Tarbell, THIS JOURNAL, **61**, 3085 (1939).

(2) Leuckart, *Ber.*, **18**, 875 (1885); Claisen, *Ann.*, **418**, 82 (1918).

TABLE I[a]

FIRST ORDER RATE CONSTANTS AT 171.6°

4.30% I and 95.70% diphenyl ether					
2,050	4,450	6,950	12,910	20,360	
13.89	25.26	36.98	55.98	73.44	mean
7.28	6.55	6.65	6.35	6.52	6.67
14.13% I and 85.87% diphenyl ether					
1,970	4,420[b]	4,470	13,480[b]	13,810	
13.21	27.13	27.90	63.76	64.37	mean
7.21	7.16	7.31	7.53	7.47	7.34
17.75% I and 82.25% diphenyl ether					
2,290	4,000	6,900	13,880	21,580	
14.99	25.33	40.15	66.62	83.13	
7.09	7.29	7.44	7.90	8.25	
100% I					
2,200	4,900	8,380	10,000	12,460	
15.68	34.83	58.65	66.44	77.14	
7.75	8.73	10.54	10.92	11.85	
11.23% I, 9.93% dimethylaniline and 78.84% diphenyl ether					
1,790	3,720	6,630	12,820	19,300	
14.35	26.50	42.61	65.76	80.72	mean
8.68	8.30	8.37	8.36	8.53	8.45
13.11% I, 1.07% acetic acid and 85.82% diphenyl ether					
2,740[c]	8,000	12,600	22,320		
22.66	51.73	69.31	88.18		mean
9.38	9.11	9.37	9.56		9.36
11.65% I, 2.05% acetic acid and 86.30% diphenyl ether					
1,940	3,270	5,630	9,380		
18.33	28.70	44.16	63.27		mean
10.42	10.36	10.35	10.68		10.45

[a] The first row gives the time in sec., the second gives the percentage reaction, and the third gives the rate constants in reciprocal seconds times 10^5.

[b] Solution of new materials, 12.46%.

[c] 19.78% I, 0.99% acetic acid and 79.23% diphenyl ether.

TABLE II[a]

FIRST ORDER RATE CONSTANTS AT 185.8°

14.13% I and 85.87% diphenyl ether					
700	1,300	2,290	5,560		
15.51	24.89	39.06	69.84		mean
24.1	22.0	21.6	21.6		22.3
100% I					
700	1,720	2,920	4,180	6,340	
17.24	38.04	58.80	74.98	94.61	
27.0	27.8	30.4	33.1	...	

[a] The first row gives the time in sec., the second gives the percentage reaction, and the third gives the rate constants in reciprocal seconds times 10^5.

The effect of dimethylaniline on the rate was studied in order to determine whether the slow step in the mechanism involved the transfer of a proton. If this were the case, then dimethylaniline should considerably accelerate the rate since it is a far better proton acceptor than diphenyl ether. From Table I it is seen that the addition of 10% of dimethylaniline increases the rate by about 15%. This relatively small increase is interpreted as indicating that a prototropic change is not the slow step in the reaction, although it does not preclude the possibility that such a change is involved somewhere in the mechanism. This 15% increase is, however, to be compared with only a 3% increase for a similar experiment carried out with allyl *p*-tolyl ether.[1]

TABLE III[a]

FIRST ORDER RATE CONSTANTS AT 156.9°

14.13% I and 85.87% diphenyl ether					
5,920	8,440	11,680	22,780	43,420	
12.00	16.78	21.35	43.36	65.80	mean
2.16	2.18	2.06	2.50	2.47	2.27

[a] The first row gives the time in sec., the second gives the percentage reaction, and the third gives the rate constants in reciprocal seconds times 10^5.

The two series of runs in the presence of acetic acid indicate that the reaction is speeded up to some extent by the presence of acids. Thus the rate constant for a 1% solution of acetic acid is 28%, and that for a 2% solution is 42%, greater than that for the reaction in the absence of acids. This effect, although not very great, appears to be definitely beyond any possible experimental error. On the other hand, it appears definite that the reaction as it takes place in the pure liquid or in solution in pure diphenyl ether is not a catalyzed reaction since a much greater increase in the rate would be expected if the reaction could occur *only* in the presence of acids.

The mean rate constants for the 14% solutions at the three temperatures were used to compute the activation energy for the reaction from the Arrhenius equation

$$k = A \exp\,(-\Delta E/RT) \qquad (1)$$

we obtain $A = 0.583 \times 10^{11}$ sec.$^{-1}$, and $\Delta E =$ 30.3 kcal. per mole. The entropy of activation for the reaction, $\Delta S^{\ddagger}$, may be obtained from the constant A by means of the equation[3] for the absolute rate of any reaction

$$k = (\mathrm{k}t/h)\,\kappa \exp\,(\Delta S^{\ddagger}/R) \exp\,(-\Delta E^{\ddagger}/RT)$$

Here k is Boltzmann's constant, h is Planck's constant, κ is the transmission coefficient, and $\Delta S^{\ddagger}$ and $\Delta E^{\ddagger}$ are the entropy and energy of activation, respectively. By making the usual assumption that κ equals unity, we find that $\Delta S^{\ddagger}$

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(3) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

= −10.1 E. U. at 171.6°. This value is to be compared to $\Delta S^{\ddagger}$ = −9.5 E. U. for the rearrangement of allyl *p*-tolyl ether.[4] The fact that the entropies of activation for the rearrangement to the ortho and para positions differ by only 0.6 E. U. suggests strongly that the slow step is the same in each case.

Two mechanisms were discussed[1] as possibilities for the rearrangement to the ortho position. The first, the cyclic mechanism, is one in which the γ carbon atom on the allyl group starts to form a bond with the atom in the ring simultaneously with the breaking of the carbon–oxygen bond. The second mechanism proposed, the dissociation mechanism, is one in which the slow step is the breaking of the carbon–oxygen bond, the allyl group being split off as a radical or positive ion. The chemical evidence favors the cyclic mechanism for the rearrangement to the ortho position. This mechanism requires inversion of the allyl group during rearrangement, and this has been observed repeatedly.[5] That the allyl group is never free during the rearrangement to the ortho position is indicated by the work of Hurd and Schmerling,[6] who showed that mixed products are not formed when a mixture of cinnamyl phenyl ether and allyl β-naphthyl ether is rearranged. On the other hand, the chemical evidence favors the dissociation mechanism for the rearrangement to the para position. Thus it has been shown[7] that inversion does not usually occur during the migration of the allyl group to the para position. The chemical evidence for the incorrectness of the cyclic mechanism for the rearrangement to the para position is supported by the use of Fisher-Hirschfelder atomic models. They show that, even in the most favorable orientation, there is still an internuclear distance of more than 4 Å. between the para and γ carbon atoms. Not only is this too great to be favorable for bond formation but the angle is not suitable, being about 120° away from the stable configuration in the plane of the ring.

Thus the chemical evidence appears to indicate that the mechanisms of the migrations to the ortho and para positions are different, while the kinetic studies lead to the conclusion that they are the same. It must, however, be remembered that rate measurements, by themselves, can give information *only* about the slow step in the reaction.

Experimental

The technique of carrying out the measurements and analyzing the reaction mixture already has been described.[1]

Allyl 2,6-Dimethylphenyl Ether (I).—Eastman Kodak Co. 2,6-dimethylaniline was purified through the crystalline formyl derivative[8] and 2,6-dimethylphenol prepared from the purified amine by the method of Bamberger.[9] To a solution of 19.5 g. of sodium in 350 cc. of alcohol, 103.5 g. of recrystallized 2,6-dimethylphenol (m. p. 47–48°) was added, followed by dropwise addition of 121 g. of allyl bromide, while heating the solution on the steam-bath. The reaction mixture, which formed a solid precipitate immediately, was heated on the steam-bath for three hours, and poured into 1.5 liters of water. The product was isolated by extraction with 400 cc. of low boiling petroleum ether in two portions; the extract was washed twice with 100-cc. portions of 20% sodium hydroxide solution, dried, the solvent removed, and the product distilled in nitrogen through a modified Widmer column. The main fraction of 63.9 g. had the boiling point of 67–68° at 2 mm., bath temperature 100–105°; d^{25}_{4} 0.9422, n^{25}_{D} 1.5048. *Anal.*[10] Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.69. Found: C, 81.53; H, 8.70. Analysis by the usual method showed that this sample contained 0.4% of 2,6-dimethyl-4-allylphenol (II).

2,6-Dimethyl-4-allylphenol (II).—The sodium hydroxide wash solution of the preceding paragraph yielded on acidification and extraction 34 g. of oil, which was separated by fractionation into two fractions: 10.8 g. of 2,6-dimethylphenol, b. p. 103–115° at 22 mm., and 10 g. of the C-alkylation product, 2,6-dimethyl-4-allylphenol, b. p. 131–138° at 21 mm. The phenylurethan prepared as described below, melted at 139–140.5° after two crystallizations from ligroin, and gave no depression when mixed with the phenylurethan of II produced by rearrangement.

When 8.45 g. of 2,6-dimethylphenol was alkylated with the equivalent amount of sodium and allyl bromide in benzene solution, 2.8 g. of the O-alkylation product I was obtained, and 2.1 g. of the C-alkylation product II.

Isolation of the Products of the Rearrangement.—Forty-three grams of the ether (I) was heated for seven hours at 171.6° in sealed tubes.

The product II (41.3 g.) was distilled in a nitrogen atmosphere through a modified Widmer at a distillation rate of about six drops per minute. At 2 mm. pressure, the boiling point of fractions 2, 3 and 4 varied between 90.5 and 91.4°.

These fractions were analyzed in duplicate for active hydrogen by the usual method, and the molecular weights per active hydrogen are shown in Table IV. The fact

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[4] The value previously found for $\Delta S^{\ddagger}$ for the rearrangement of allyl *p*-tolyl ether[1] was −8.1 E. U. However, for purposes of comparison with the present case this must be corrected by $-R \ln 2$ (−1.4 E. U.) due to the fact that there are two ortho positions in the ring available for substitution.

[5] Claisen and Tietze, *Ber.*, **58**, 275 (1925).

[6] Hurd and Schmerling, This Journal, **59**, 107 (1937).

[7] Mumm and Müller, *Ber.*, **70**, 2214 (1937); Mumm, Hornhardt and Diederichsen, *ibid.*, **72**, 100 (1939); Mumm and Diederichsen, *ibid.*, **72**, 1523 (1939); Späth and Kuffner, *ibid.*, **72**, 1580 (1939).

[8] Busch, *ibid.*, **32**, 1008 (1899).

[9] Bamberger, *ibid.*, **36**, 2036 (1903).

[10] Analyses by Dr. L. Weisler.

TABLE IV

Fraction	% Total material	Mol. wt.[a]
1	2.8	
2	55.2	162.8
3	25.5	164.3
4	5.8	162.9
5	9.0	
Total	98.3	

[a] Mol. wt. of 2,6-dimethyl-4-allyl phenol, 162.2.

that these fractions have the expected molecular weight per active hydrogen indicates that they are composed of pure rearrangement product. That fraction 1 was composed almost entirely of the unrearranged ether (I) and its rearrangement product (II) was shown by analyses of samples taken before and after this fraction had been heated for five hours more at the same temperature. The molecular weight per active hydrogen was 296 before and 169.5 after further heating. If fraction 1 is considered to be a mixture of I and its rearrangement product only, these figures are equivalent to a percentage composition of 55% II and 96% II before and after the second heating. These data make it appear probable that no appreciable amount of material formed by side reactions was present in the low boiling fraction.

Fraction 6, the residue left in the still pot, was distilled from a 5-cc. Claisen flask at reduced pressure; 40% of the material distilled at the expected boiling point, but the remainder of this fraction, 5.4% of the original 41.3 g., did not distil. It was evidently polymeric. The portion which distilled had a molecular weight per active hydrogen which agreed with that for (II) to within 0.2%.

The material not accounted for in Table IV, 1.7%, was held up in the still, and by washing out the apparatus with ether a small amount of material was recovered which boiled at the correct place for the rearrangement product. The amount available was insufficient for analysis.

Therefore the only product except the rearrangement product and unreacted ether which could be found was 5.4% of polymeric material in fraction 5. Since polymerization reactions would be expected to be somewhat less rapid in solution than in the pure liquid, it seems certain that the reaction in solution is greater than 95% quantitative. The pure 2,6-dimethyl-4-allylphenol (fractions 2, 3 and 4) has the following properties: b. p. 90.5–91.4° at 2 mm.; d^{25}_{4} 0.9870; n^{25}_{D} 1.5370.

The **phenylurethan** was prepared from 1 cc. of the phenol and 0.6 cc. of phenyl isocyanate by passing dry hydrogen chloride over the surface of the solution and heating the mixture on the steam-bath for ten minutes. The product, which crystallized on cooling, was recrystallized twice from ligroin, m. p. 141–142.5°, and gave no depression when mixed with samples from the 2,6-dimethyl-4-allylphenol prepared by direct C-alkylation of 2,6-dimethylphenol.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.84; H, 6.81. Found: C, 76.79; H, 6.78.

Summary

1. Allyl 2,6-dimethylphenyl ether and 2,6-dimethyl-4-allylphenol have been prepared and characterized.

2. The rate of rearrangement of allyl 2,6-dimethylphenyl ether has been measured at 156.9, 171.6 and 185.8°, in the pure liquid at the two upper temperatures, and in diphenyl ether solution at all three temperatures. Measurements covering a four-fold range in concentration in solution showed the reaction to be first order, and the initial values of the rate constants for the pure liquid are the same as those in solution.

3. The reaction rate is not appreciably affected by 10% of dimethylaniline, but 1% and 2% of acetic acid lead to increases in the rate constant of 28% and 42%, respectively.

4. The energy of activation for the reaction is 30.3 kcal. per mole, and the entropy of activation is -10.1 E. U. From a comparison of this value of $\Delta S^{\ddagger}$ with that for the rearrangement to the ortho position, it is concluded that the slow step is the same in each case.

5. The rearrangement has been shown to be at least 95% quantitative in solution.

6. Appreciable amounts of the C-alkylation product are observed in the reaction of allyl bromide and 2,6-dimethylphenol even when the reaction is carried out in alcohol solution in the presence of sodium ethylate.

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