leaflets from alcohol, m. p. 76°. The compound is odorless; yield from 12 g. of the phenol, 11 g.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.58; H, 7.36. Found: C, 84.26; H, 7.16.

The methyl ether of p-hydroxydiphenyl, first prepared by Werner,[7] was obtained in nearly quantitative yield, using methyl iodide as the halide, m. p. 90°. The very minute water-white granular crystals have no odor.

4-Diphenyl-propyl Ether.—Propyl bromide was condensed with p-hydroxydiphenyl as in the preparation of the ortho ether. The product when purified and crystallized from alcohol gave white leaflets, m. p. 76–77°. It is difficultly soluble in petroleum ether; yield from 10 g. of the phenol, 9 g., odorless.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.85; H, 7.60. Found: C, 84.62, 84.71; H, 7.55, 7.60.

4-Diphenyl-isopropyl Ether.—Isopropyl bromide was used as the halide. The reaction in acetone took place more slowly than in the case of the ortho ether. Dull white needles were obtained from slow evaporation of an alcoholic solution, and hexagonal leaflets from more concentrated solutions; m. p. 73°, odorless; yield from 10 g. of the phenol, 4 g.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.85; H, 7.60. Found: C, 84.51; H, 7.66.

4-Diphenyl-allyl Ether.—Large transparent leaflets from alcohol; m. p. 86–87°, odorless; yield from 12 g. of the phenol, 14 g. The melted crystals show a slight darkening when heated to 290°, but there is no further

decomposition when maintained at or above this temperature for one hour.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.67; H, 6.72. Found: C, 85.43; H, 6.79.

4-Diphenyl-n-butyl Ether.—Butyl bromide was used as the halide. The filtrate on acidification gave negligible quantities of unchanged p-hydroxydiphenyl; large white leaflets from alcohol; m. p. 74–75°, odorless; yield from 10 g. of the phenol, 13 g.

Anal. Calcd. for $C_{16}H_{18}O$: C, 85.67; H, 6.72. Found: C, 85.43; H, 6.79.

4-Diphenyl-benzyl Ether.—Using benzyl chloride as halide, the odorless ether was obtained in nearly quantitative yield; from 12 g. of the phenol, 18 g. of the ether was prepared; heavy white plates from alcohol, m. p. 136°.

Anal Calcd. for $C_{19}H_{16}O$: C, 87.45; H, 6.20. Found: C, 87.35, 87.65; H, 6.25; 6.20.

We were not successful in preparing the s-butyl, t-butyl or n-amyl ether by this method using acetone as solvent, nor by trials with copper as catalyst, nor with benzene as solvent. However, preliminary trials with reagents heated in sealed tubes have been attended with some success and will be reported on later.

Summary

Several new alkyl ethers of o- and p-hydroxydiphenyls have been prepared by a simplified method. The ortho ethers possess a fragrant odor, but the para ethers are odorless.

(7) Werner, *Ann.*, **322**, 167 (1902).

The Claisen Rearrangement. I. A Kinetic Study of the Rearrangement of Allyl p-Tolyl Ether in Diphenyl Ether Solution

BY JOHN F. KINCAID AND D. S. TARBELL

The rearrangement of allyl aryl ethers, illustrated by the conversion of allyl phenyl ether (I) to o-allylphenol (II), has been investigated extensively since its discovery by Claisen,[1] and
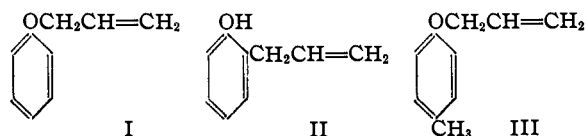
numerous features of the reaction mechanism have been established. The object of our work is to make a kinetic study of the rearrangement of allyl ethers of various types to obtain further information about the Claisen rearrangement. We wish to report a study of the kinetics of the rearrangement of allyl p-tolyl ether (III) in di-

phenyl ether solution at 214.7, 200.6, and 185.8°. At the second temperature the effect of acids, bases, and oxygen on the rate was studied, and the rate of the rearrangement of the pure liquid allyl p-tolyl ether was measured at the two lower temperatures.

Experimental

Preparation of Materials

Allyl p-tolyl ether was prepared by the method of Hurd and Yarnall,[2] using Eastman redistilled p-cresol, allyl bromide, and sodium hydroxide in aqueous acetone solution. The reaction mixture was worked up by the procedure referred to, and in addition the ether was washed several times with sodium hydroxide solution to remove unreacted cresol. The product was distilled through a modified Widmer vacuum-jacketed column at 4 mm. and

(1) Claisen, *Ber.*, **45**, 3157 (1912).

(2) Hurd and Yarnall, THIS JOURNAL, **59**, 1686 (1937).

bath temperature of 110–115°, b. p. 65 ± 1°, due to pressure fluctuations, d^{25}_4 0.9494. A blank determination showed that this sample contained 0.5% of its rearrangement product or an equivalent amount of acetylatable material. Some of the rate runs were made with a sample of ether prepared in a similar manner containing 1.8% of rearrangement product, but proper corrections were applied in both cases.

Diphenyl ether (Dow technical grade) was stirred overnight with sodium wire while being heated on the steam-bath and the precipitate filtered off; treatment with another batch of sodium gave no appreciable reaction. The material was then stirred with mercury to remove sulfur compounds, but this appeared to be unnecessary, as no darkening of the metal occurred. After removing the mercury by filtration, the diphenyl ether was washed with dilute hydrochloric acid, sodium hydroxide solution, water, dried with calcium chloride, followed by solid potassium hydroxide, and distilled in a nitrogen atmosphere, some samples being distilled at atmospheric pressure, and some in vacuum. A blank determination on this ether showed no acetylatable material present within the experimental error.

The fact that different samples of allyl p-tolyl ether and diphenyl ether gave identical values for the rate constant was shown by values of k of 8.03 × 10⁻⁵ for a new solution, compared to 8.13 × 10⁻⁵ for the stock solution with which most of the runs at 200° were made.

Dimethylaniline was distilled with acetic anhydride, washed free of acid with sodium carbonate solution and water, dried over potassium hydroxide and distilled, b. p. 192–192.5°. A blank determination showed no acetylatable material present.

Method of Analysis.—The reaction was followed by a modification of the Verley and Bölsing[3] method for determining phenols, which consists in the quantitative acetylation of the phenol by a mixture of acetic anhydride and pyridine, followed by the determination by titration of the unused acetic anhydride. An amount of the reaction mixture containing from 0.2 to 0.4 g. of the rearrangement product was weighed into a 50-cc. iodine flask, 2 cc. of an approximately 2 molar solution of acetic anhydride in pyridine was pipetted in, and the mixture heated for an hour on the steam-bath. In order to obtain consistent results, it was found necessary to put a liquid seal of mercury around the stopper, and the stopper was held in place by rubber bands. After cooling, the contents of the flask were transferred to a beaker containing 100 cc. of water, using carbon tetrachloride to rinse the flask, and the acetic acid titrated with 0.2 N alkali with vigorous stirring. Since it was impossible to use indicators in the presence of the organic liquids, the titrations were carried out with a Beckmann pH meter to a pH of 8.6. Analyses of known mixtures showed the average deviation to be about 1%, and the error in analysis was very rarely as great as 2.5%. Runs in which the mixture was heated longer than an hour showed that no appreciable percentage of the ether rearranged on heating for an hour at 100°.

Experimental Procedure.—Preliminary experiments showed that considerable material was lost by evaporation when the rearrangement reaction was carried out in glass-

stoppered flasks at 200°, so that the rate constants for longer runs were as much as 25% low. Consequently, the data given below were obtained by a procedure in which each sample was placed in a glass tube, the tube cooled in an ice-bath, and sealed off after being evacuated by an oil pump. In a trial experiment in which a tube containing a one molar solution was pumped out with an oil pump for thirty minutes at room temperature, the constant was only 4% lower than that obtained by the usual technique. Therefore the loss by evaporation during the evacuation of the tubes under the conditions used was negligible. Runs were carried out by completely immersing the sample in a well-stirred oil thermostat, kept constant to 0.1° by a mercury thermoregulator and relay. Constancy of the thermostat temperature was checked by a thermometer reading to 0.1°, and the temperature at each setting of the thermostat was determined by a one-junction copper–constantan thermocouple which was calibrated against the melting point of tin. The temperatures are estimated to have an absolute accuracy of ±0.3°, and to have a relative accuracy of ±0.1°.

The time necessary for the sample to come to the bath temperature after its immersion, estimated from blank experiments, was found to be about two hundred seconds,[4] and this was subtracted from all the observed times of reaction. This figure, although not known very accurately, is important only for the shorter runs.

Isolation of the Product of the Rearrangement.—Forty grams of allyl p-tolyl ether was heated in sealed tubes without solvent for thirteen hours at 200°, and analysis in the usual way showed that 97.7% (average of two analyses) of the theoretical amount of the rearrangement product was present. The product (40.3 g.) was distilled in a nitrogen atmosphere through the modified Widmer column at a pressure of two to three mm. and distillation temperature ranging from 68.7 to 73.7°. Each fraction was analyzed in duplicate for phenolic hydroxyl and the molecular weights calculated are given in the table.

RESULTS OF FRACTIONATION

Fraction	Wt., g.	Mol. wt.[a]
1	1.3	151.3
2	16.5	149.2
3	13.1	150.8
4	3.4	148.1
5 (Residue)	2.4	

[a] Molecular weight of 2-allyl-4-methylphenol, 148.2.

Fraction 5 was transferred to a 5-cc. Claisen flask and redistilled, getting 0.8 g., b. p. 76–87° at 2 mm., molecular weight 162.6, and 1.55 g. of undistillable material. The 3.6 g. of material not accounted for was held up in the Widmer column, and evidently was mainly the normal rearrangement product, since fraction 4 had the correct molecular weight. The possibility that the undistillable part of fraction 5 was formed during the distillation rather than during the rearrangement was eliminated by redistilling fractions 1, 2, 3, and 4 under the same conditions, when no non-volatile residue was found.

Effect of Oxygen on the Rearrangement.—Four tubes were prepared to contain varying amounts of air and oxy-

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(3) Verley and Bölsing, *Ber.*, **34**, 3354 (1901).

(4) MacDougall, Lauer and Spielman [THIS JOURNAL, **55**, 4089 (1933)] used a correction of three minutes in a similar case.

gen, and the rate measured at 200.2°. Tube 1 contained 1 atm. of pure oxygen, tube 2 was evacuated and sealed by the usual method, tube 3 was alternately frozen and melted two times under vacuum to remove all dissolved gases, and tube 4 had air bubbled through it for thirty hours before being evacuated and sealed as usual. The rate constants after being corrected to 200.6° for the four samples were 7.87, 7.48, 7.41, and 7.89, each multiplied by 10^{-5}. The allyl p-tolyl ether employed in these experiments had been freshly distilled to remove any traces of peroxide. While these results indicate that the rate of the rearrangement is not appreciably affected by the presence of oxygen, the occurrence of some side reaction under these conditions is indicated by the yellow color of the reaction mixture. Runs carried out with the usual technique were colorless even after the heating had been continued until the rearrangement was virtually complete.

Experimental Results

TABLE I
FIRST ORDER RATE CONSTANTS AT 200.6°

Time, sec.	$k \times 10^5$, sec.$^{-1}$	% reaction
4.77% Allyl p-tolyl ether and 95.23% diphenyl ether		
2260	7.65	15.88
4600	7.34	28.66
8320	7.30	45.52
12460	7.43	60.21
21580	7.89	81.77
Mean 7.52		
13.30% Allyl p-tolyl ether and 86.70% diphenyl ether		
1960	7.96	14.45
3580	8.03^a	24.93
5260	8.29	35.36
12040	8.54	64.22
14980	8.89	73.61
22240	8.55	85.08
Mean 8.38		

^{a} Solution of new materials, 14.22%.

Time, sec.	$k \times 10^5$, sec.$^{-1}$	% reaction
22.81% Allyl p-tolyl ether and 77.19% diphenyl ether		
1180	9.04	10.11
3340	8.66	25.14
6940	8.67	45.20
11980	9.51	68.00
19300	9.76	84.80
Mean 9.13		
100% Allyl p-tolyl ether		
1315	9.82	12.12
1570	9.65	13.81
2950	10.49	26.61
3280	10.60	29.37
7120	14.81	65.16
8380	16.61	75.13
8680	17.10	77.34
12.00% Allyl p-tolyl ether, 9.81% dimethylaniline and 78.19% diphenyl ether		
2140	8.87	17.29
4900	8.58	34.31
11860	8.34	62.81
19180	8.81	81.54
Mean 8.65		

Time, sec.	$k \times 10^5$, sec.$^{-1}$	% reaction
13.43% Allyl p-tolyl ether, 0.81% acetic acid and 85.76% diphenyl ether		
1600	10.0	14.79
2320	9.41	19.62
5200	9.28	38.28
10600	9.62	63.93
19780	9.88	85.82
Mean 9.64		

TABLE II
FIRST ORDER RATE CONSTANTS AT 185.8°

Time, sec.	$k \times 10^5$, sec.$^{-1}$	% reaction
14.22% Allyl p-tolyl ether and 85.78% diphenyl ether		
5200	2.68	13.02
11080	2.56	24.64
18280	2.56	37.32
31540	2.72	57.56
43000	2.87	70.88
Mean 2.69		
100% Allyl p-tolyl ether		
4600	3.06	13.11
8080	3.28	23.24
10720	3.62	32.13
17800	4.74	57.01
26860	6.30	81.62

TABLE III
FIRST ORDER RATE CONSTANTS AT 214.7°

Time, sec.	$k \times 10^5$, sec.$^{-1}$	% reaction
14.22% Allyl p-tolyl ether and 85.18% diphenyl ether		
580	24.9	13.46
1360	22.9	26.55
2260	22.6	39.97
4060	22.5	59.92
6940	22.7	79.34
Mean 23.1		

The results of runs performed at the three temperatures are tabulated in Tables I to III. The first order rate constants k were calculated from the usual equation

$$k = (1/t)\, 2.303 \log x_0/x \qquad (1)$$

in which x_0 is the initial percentage of reactant and x is the percentage of reactant remaining at time t (in seconds). The results show that the reaction is strictly unimolecular over the range of temperature and concentration studied; at 200.6° the concentrations measured cover a nearly five-fold range, from 4.77 to 22.81% (approximately 0.3 to 1.5 molar), in addition to the measurements on the pure liquid. The first order "constants" for the pure liquid (Tables I and II) show a marked increase as the reaction proceeds, but the initial rate in the pure liquid extrapolates to the same value as in solution. It should be emphasized that the use of equation (1) in this case leads to rate constants for the longer runs which

are much too low since a constant value for k is assumed in the integration leading to equation (1). Actually the rate of the rearrangement of the ether in the presence of 80% of 2-allyl 4-methylphenol is more than four times as great as it is at the beginning of the reaction, although the rate constants for 80% reaction given in Tables I and II are only about double the initial values.

The effect of dimethylaniline on the rate is of interest because Claisen[5] stated that better yields were obtained in some cases of the rearrangement when a basic solvent was used, and dimethylaniline is frequently employed as solvent when the reaction is carried out on a preparative scale. As the data in Table I show, 10% of dimethylaniline has no appreciable effect on the rate of the rearrangement.
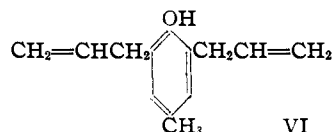
It seemed likely that the upward drift of the rate constants in the pure liquid was due to the catalytic effect of the phenol formed acting as an acid. To test the possibility that the reaction was acid catalyzed, a run was made using as solvent a 0.81% solution of acetic acid in diphenyl ether, but the rate was not affected appreciably (Table I). The possibility of error due to isomerization[6] of the 2-allyl 4-methylphenol (IV) formed by rearrangement to a coumarane derivative V by the acid present was eliminated by trial runs

OH
CH₂CH=CH₂
CH₃
IV

O—CH—CH₃
CH₂
CH₃   V
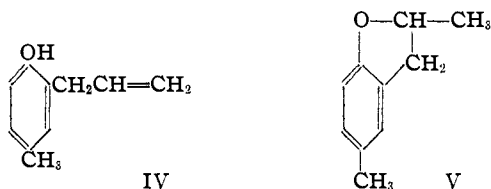
with known amounts of the phenol. An attempt to measure the effect of a stronger acid, chloroacetic, failed, because runs with known samples showed the analytical method was not reliable in the presence of chloroacetic acid; the results indicated qualitatively that there was no striking increase in the rate, however.

The rate of rearrangement is not affected by the presence of air or oxygen, as is clear from runs described in the experimental part.

To find whether side reactions take place during the rearrangement, the isolation of the products of the reaction described in the experimental part was carried out. The results show that less than 1% of 2,6-diallyl-4-methylphenol (VI) was

(5) Claisen, *Ann.*, **418**, 69 (1918).

(6) Claisen and Tietze, *Ber.*, **59**, 2344 (1926); Bartz, Miller and Adams. THIS JOURNAL, **57**, 371 (1935).

OH
CH₂=CHCH₂   CH₂CH=CH₂
CH₃   VI

formed, which Hurd and Yarnall[2] isolated in a few per cent. yield from the rearrangement of allyl p-tolyl ether carried out at higher temperature. We obtained 4% of non-volatile rearrangement product, possibly analogous to the dimer[7] isolated from the rearrangement of allyl phenyl ether. The rest of the material isolated, amounting to 87%, was pure rearrangement product, and the material not accounted for which was held up in the still was probably mainly the same thing. Since polymerization should be less important during rearrangement in solution than in the pure liquid, it seems safe to conclude that in solution the reaction is at least 95% quantitative.

Discussion

The energy of activation, ΔE, for the reaction was computed from the mean values of the rate constants for the 14% (1 molar) solutions at the three temperatures. The constants of the Arrhenius equation, $k = A \exp(-\Delta E/RT)$, were found to be 1.60×10^{11} sec.$^{-1}$ and 33.1 kcal./mole for A and ΔE, respectively. These quantities may be interpreted with the aid of the equation due to Eyring[8] for the absolute rate of any reaction

$$k = (kT/h) \, \kappa \, \exp(\Delta S^{\ddagger}/R) \exp(-\Delta E^{\ddagger}/RT) \quad (2)$$

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. Following the usual practice of assuming that κ equals unity, we find that $\Delta S^{\ddagger}$ equals -8.1 e. u./mole at 200°, $i.$ $e.$, the activated complex is poorer in entropy by 8.1 units than the normal reactant molecule.

Two structures for the activated complex seem possible. The γ carbon atom on the allyl group might be expected to start to form a bond with the carbon atom ortho to the oxygen simultaneously with the breaking of the carbon–oxygen bond. A second 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, although any mechanism in which the allyl group is ever free seems inconsistent

(7) Hurd and Schmerling, *ibid.*, **59**, 107 (1937).

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

with the findings of Hurd and Schmerling,[7] who rearranged a mixture of allyl ethers without finding mixed products. The ring closure mechanism would be expected to involve a considerably larger entropy decrease than is observed here, while in the absence of strong solvation effects the second mechanism should involve an entropy *increase* on the formation of the activated complex. Since it seems impossible to prove the exact mechanism from the data available at present, further discussion will be deferred until later papers of this series.

Summary

1. The rate of the rearrangement of allyl *p*-tolyl ether in diphenyl ether solution has been measured at 214.7, 200.6, and 185.8°, the reaction being followed by determination of the phenol formed by quantitative acetylation with pyridine and acetic anhydride.

2. Over this temperature range and for a five-fold change in concentration the reaction is unimolecular, and the initial rate of the rearrangement in the pure liquid is the same as in solution.

3. The rate is not appreciably affected by the addition of 10% of dimethylaniline, 1% of acetic acid, or by the presence of air or oxygen.

4. The energy of activation is 33.1 kcal./mole, the data for the one normal solutions being represented by the expression $k = 1.60 \times 10^{11} \exp(-33.1/RT)$.

5. The rearrangement has been shown to be at least 95% quantitative at 200° in solution.

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Sulfonation Reactions with Sulfuryl Chloride

By M. S. Kharasch and Alice Tanner Read[1]

Introduction

In a recent paper[2] chlorination reactions with sulfuryl chloride were discussed, and it was shown that many types of organic molecules can be chlorinated with this reagent by the use of a peroxide catalyst. If the mechanism which was postulated for that reaction is correct, namely, a chain reaction involving the formation of chlorine atoms and SO_2Cl free radicals, then sulfonation as well as chlorination should take place, by the direct action of the SO_2Cl radical on the hydrocarbon, *i. e.*, sulfuryl chloride should, under the proper conditions, be a sulfonating as well as a chlorinating agent. Although no sulfonation products are isolated from the peroxide-catalyzed reaction, even when the sulfuryl chloride is added slowly (a procedure which minimizes any inhibitory effect of sulfuryl chloride itself), other catalysts have been found which, in the light, give both sulfonated and chlorinated products, the proportion of each being dependent upon the type of catalyst and the conditions used. With the exception of peroxides, which yield only the chlorinated hydrocarbons both in the dark and in the light, none of the catalysts investigated were very active in complete darkness. If the reaction were allowed to continue for some time, a small yield of chlorinated product could be obtained, but in no case did we obtain in the absence of light more than a trace of sulfonated product.

Discussion

Since a free-radical mechanism has been demonstrated in the addition of mercaptans to unsaturated molecules in the presence of oxygen,[3] the mercaptan type of compound seemed a likely catalyst for reactions with sulfuryl chloride. A number of such compounds were tried in preliminary test-tube experiments and found to be effective in starting the reaction. The most promising of these were studied on a larger scale with cyclohexane, which was selected as a suitable hydrocarbon because all the hydrogen atoms in this molecule are equivalent, and the products, cyclohexyl chloride and cyclohexylsulfonyl chloride, are easily separated and identified. In all the reactions in which the mercaptan type of catalyst was used, sulfonation as well as chlorination took place. In order to ascertain the op-