Claisen rearrangement of allyl aryl ethers

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The Claisen rearrangement of allyl aryl ethers was studied. On the basis of original results as well as the revaluation of the published results concerning the *ortho-* and *para*-Claisen rearrangement it has been proved that the *ortho-* and *para*-Claisen rearrangement is a reaction of the zero order. Only in a special case, provided the solvent is present in a great excess, the *ortho-* and *para*-Claisen rearrangement obeys the temporal law of the first-order reactions.

Изучалась перегруппировка Клайзена аллиларилэфиров. На основании собственных работ и переоценки опубликованных данных по исследованию кинетики *орто-* и *пара*-перегруппировки Клайзена было доказано, что *орто-* и *пара*-перегруппировки Клайзена являются реакциями нулевого порядка. Только в особом случае, в присутствии большого избытка растворителя, протекают *орто-* и *пара*-перегруппировки Клайзена как реакции первого порядка.

The *ortho*-Claisen rearrangement proceeds through the pseudocyclic transition state [1—4] which represents the initial stage of intramolecular electrophilic substitution. Subsequently this species is transformed into cyclohexadienone [5—9] and in the last stage of rearrangement it isomerizes to give a more stable enol isomer.
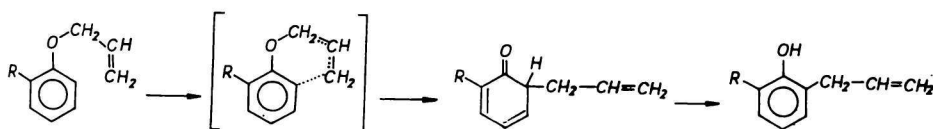
The *para*-Claisen rearrangement of allyl aryl ethers is an intramolecular process [10—13] which proceeds *via* two pseudocyclic transition states [9, 14—16] without any inversion of allyl group [7, 13—15, 17—19]. The formation of cyclic dienone involved in the rearrangement of allyl aryl ethers is the slowest step and is reversible [13, 20—22]. The enolization of the dienone arising in the *ortho-* and *para*-Claisen rearrangement is very fast [23] while the hydrogen atom migrates as a proton probably not directly to the oxygen of the oxo group [24].

The basic paper on reaction kinetics of the *ortho*-Claisen rearrangement was published by *Kincaid* and *Tarbell* [25] who ascertained that the rearrangement of unimolar solution of *p*-tolyl allyl ether in diphenyl ether was a first-order reaction. This statement was confirmed by other investigations [26—29] performed with low concentrations of allyl aryl ethers.

The rate of the Claisen rearrangement of allyl aryl ethers depends on pressure [30, 31], the character of substituents in the aromatic ring [26, 27—29], and the kind of the solvent used [26, 28, 31, 44, 45]. It is the highest in the medium of the substances containing hydroxyl group by which it is influenced in the order: carbitol < octanol < benzyl alcohol < ethylene glycol < phenol. The lowest reaction rates were measured in the medium of diphenyl ether, diphenylmethane, and decaline [26].

The *para*-Claisen rearrangement of 2,6-dimethylphenyl allyl ether in the excess of solvent was studied by *Tarbell* and *Kincaid* [32] as well as by *H. Schmid* and *K. Schmid* [10] who proved that it was a first-order reaction.

When investigated the *ortho*-Claisen rearrangement of *p*-tolyl allyl ether in the absence of solvent Kincaid and Tarbell came to the conclusion that this reaction was not a first-order one. However, they were not more concerned with this problem. H. Schmid and K. Schmid who studied the *para*-Claisen rearrangement of 2,6-dimethylphenyl allyl ether as well as *Rhoads* and *Crecelius* [12] who studied the rearrangement of γ-methylallyl 2,6-dimethylphenyl ether and γ-ethylallyl 2,6-dimethylphenyl ether came to equal conclusion.

In this paper we are concerned with the problem of reaction kinetics of the Claisen rearrangement in the absence or in the presence of a small amount of solvent. This problem has not been solved up to now but the results of the kinetic study of the rearrangement in unimolar solutions of allyl aryl ethers have been generalized which leads to the view that the Claisen rearrangement is unambiguously a first-order reaction.

Experimental

Chemicals

Allyl phenyl ether was prepared by the reaction of potassium phenolate (232 g) in dimethylformamide (250 g) with allyl chloride (153 g) at 45°C. The reaction took 14 hrs, the yield being 71.1%. Melting point 84—85°C/2.53 kPa, hydroxyl number 0, double bonds 44.3 g CH_3COOH/100 g (theory 44.75 g CH_3COOH/100 g), D_4^{20} 0.9766 g cm^{-3}, n_D^{20} 1.521.

Toluene "pure" was heated for 12 hrs in the presence of Raney nickel (2% by weight) up to the boiling point and subsequently distilled. Boiling point 110°C/99.3 kPa, D_4^{20} 0.867 g cm^{-3}.

The *o*-allylphenol was prepared according to [33]. Boiling point 104—105°C/2.53 kPa, D_4^{20} 1.0104 g cm^{-3}.

o-Claisen rearrangement

Allyl phenyl ether (3 ml) was measured into glass ampoules of the volume of 6.5 ml which had been blown with nitrogen. After repeated blowing through the ampoules were sealed. The kinetic measurements were carried out in a thermostat the temperature of which was held constant with accuracy of ± 1°C. After certain periods of time the ampoules were removed from the thermostat, cooled to room temperature, opened, and their content was analyzed.

The product of the *ortho*-Claisen rearrangement of allyl phenyl ether in the absence of solvent was analyzed using a double-beam UR-10 (Zeiss, Jena) infrared spectrophotometer. After thermostating at 20°C, 0.3 ml of sample was pipetted into carbon disulfide (10 ml) and the concentration of allyl phenyl ether was determined from the peak at the wavenumber $\lambda = 689$ cm^{-1}. The analysis of each sample was performed three times with parallel experiment.

The concentration of o-allylphenol in the product of the rearrangement of allyl phenyl ether in toluene was determined by the acetylation method using thymolphthalein as an indicator [34].

Results and discussion

We were concerned with the Claisen rearrangement of allyl aryl ethers by studying the hydroformylation of allyl phenyl ether and 2,4-dichlorophenyl allyl ether [35, 36] and their hydrocarboxylation with the aim of preparing γ-(2,4-dichlorophenoxy)butyric acid.

The results of the measurement of the *ortho*-Claisen rearrangement of allyl phenyl ether without any solvent at 200°C are presented in Table 1. It is evident from these results that the rate constants for the first-order reaction increase with time and exhibit the same dependence as observed by *Kincaid* and *Tarbell* [25]. The increase of the rate constants indicates that the reaction order chosen is higher than the real one. We found that the rearrangement of allyl phenyl ether in the absence of solvent is governed by the equation of the zero-order reaction

$$\frac{-dc}{dt} = k,$$

which assumes the following form after integration

$$c = -k\, t + Q.$$

c — concentration of o-allylphenol (mol l^{-1}),
k — rate constant (mol l^{-1} s^{-1}),
t — time of experiment (s),
Q — integration constant.

In order to confirm our finding, we recalculated the results of *Kincaid* and *Tarbell* [25] obtained for the rearrangement of p-tolyl allyl ether in the absence of solvent. In the

Table 1

Rearrangement of allyl phenyl ether at 200 ± 1°C

Time s	Concentration of o-allylphenol weight%	Rate constants of the reaction	
		first order $k \cdot 10^5$ s^{-1}	zero order $k \cdot 10^4$ gmol l^{-1} s^{-1}
2700	28	12.1	7.53
3600	41.8	15.2	8.49
4500	51.3	16.99	8.37
5400	64.1	18.46	8.77
6300	72.2	20.32	8.51
7200	79.2	22.23	8.23
8100	86.0	24.27	7.94
9000	98.3	45.27	8.22

$\emptyset$ $k \cdot 10^4 = 8.26$ gmol l^{-1} s^{-1}.

Table 2

Rate constants of the first-order reaction according to [10, 12, 25, 32] and the values of the rate constants determined for the zero-order reactions

Part of the table	Ref.	Reaction rate constants						
		first order $k \cdot 10^5$ s^{-1}						
		zero order $k \cdot 10^4$ gmol l^{-1} s^{-1}						
a	[25]	3.06	3.28	3.62	4.74	6.30		
		1.88	1.90	1.99	2.16	2.06		
b	[25]	9.82	9.65	10.49	10.60	14.81	16.61	17.10
		5.81	5.80	5.39	5.94	6.16	5.98	6.03
	[10]	7.75	8.73	10.54	10.92	11.85		
		4.17	4.19	4.18	3.98	3.73		
d	[32]	27.0	27.8	30.4	33.1			
		14.42	13.37	12.02	10.79			
e	[10]	5.01	5.62	6.36	7.32	8.50	11.26	
		2.71	2.89	2.91	2.91	2.75	2.71	
f	[12]	4.64	5.93	7.07	8.12	10.13		
		2.30	2.64	2.71	2.62	2.13		
g	[12]	1.7	1.94	2.14	2.38	2.68	3.10	3.82
		0.83	0.87	0.94	0.96	0.98	1.00	0.89

calculation of the rate constants of the zero-order reaction we used the value d_4^{20} 0.9726 g cm^{-3} for allyl p-tolyl ether and the value d_4^{20} 1.0120 g cm^{-3} for 2-allyl-4-methylphenol [6]. The original data which are given together with the rate constants of the zero-order reaction in Table 2 (as a and b) demonstrate that the rearrangement of p-tolyl allyl ether in the absence of solvent is also a zero-order reaction.

From the Arrhenius equation we determined the value of the energy of activation ($E = 31\ 400$ cal mol^{-1}). This value is practically in agreement with the value of the energy of activation ($E = 33\ 100$ cal mol^{-1}) calculated by *Kincaid* and *Tarbell* [25] from the rate constants of the rearrangement of p-tolyl aryl ether in excess diphenyl ether on the assumption that it is a first-order reaction.

In order to find out whether the *para*-Claisen rearrangement of allyl aryl ethers in the absence of solvent is also a zero-order reaction, we used the published results of the study of the rearrangement of 2,6-dimethylphenyl allyl ether [10, 32], γ-methylallyl 2,6-dimethylphenyl ether [10, 32], and 2,6-dimethylphenyl ether [12]. The data published were recalculated and the values of rate constants determined for the first- and zero-order reactions are presented in Table 2 (c—g). By comparing the rate constants of the first- and zero-order reactions (Table 2; c—g) it appears that the *para*-Claisen rearrangement of allyl

Table 3

ortho-Claisen rearrangement of allyl phenyl ether in toluene
Molar ratio 3 : 1, 200±1°C

Time s	Concentration of o-allylphenol weight %	Reaction rate constants	
		first order $k \cdot 10^5$ s^{-1}	zero order $k \cdot 10^4$ gmol l^{-1} s^{-1}
900	5.05	7.59	3.92
2700	14.6	8.02	3.80
3600	18.46	7.85	3.61
4500	24.46	8.77	3.83
5400	28.80	8.97	3.77
6300	34.00	9.59	3.82
7200	37.87	9.77	3.73
8100	42.84	10.46	3.76
9000	46.55	10.77	3.69

$\varnothing \, k \cdot 10^4 = 3.77$ gmol l^{-1} s^{-1}.

aryl ethers, too, proceeds as a zero-order reaction. The values of the zero-order reaction rate constants found for the rearrangement 2,6-dimethylphenyl allyl ether at 185°C (Table 2; *d*) are less reliable because of a small number of measurements. On the other hand, the results concerning the rearrangement of 2,6-dimethylphenyl allyl ether at lower temperature (Table 2; *e*) fully confirm our conclusions. The rearrangement of γ-methylallyl 2,6-dimethylphenyl ether and γ-ethylallyl 2,6-dimethylphenyl ether also obeys the law of the zero-order reaction. Some small incongruities in the calculation of the rate constants of the zero-order reaction might be due to the use of the density of γ-methylallyl 2,6-dimethylphenyl ether and 2,6-dimethyl-4-methylallylphenol [14] instead of the density of γ-ethylallyl 2,6-dimethylphenyl ether and 2,6-dimethyl-4-γ-ethylallylphenol or to the use of the reaction time calculated from the rate constants and degree rearrangement.

The rearrangement of allyl phenyl ether in the presence of 25 weight % of toluene was studied at 200°C and it was found that it showed equal character as the rearrangement in the absence of solvent (Table 3). The values of rate constants for the zero-order reaction increase with conversion while they remain constant for the zero order. Equal dependence is exhibited by the rate constants of the rearrangement of allyl phenyl ether in the presence of 50 weight % of toluene (Table 4).

The results of *H. Schmid* and *K. Schmid* [10] obtained in the study of the rearrangement of 2,6-dimethylphenyl allyl ether of the 44% concentration by weight are presented together with the recalculated values of rate constants of the zero-order reaction in Table 5. They confirm that the *para*-Claisen rearrangement is also a zero-order reaction provided higher concentrations of allyl aryl ether are used.

From the rate constants of the zero-order reaction (Table 3 and 4) and from the time dependence of the degree of the rearrangement of allyl phenyl ether it is obvious that the rate of the rearrangement decreases with increasing amount of solvent. Equal dependence is also to be observed for the *ortho-* and *para*-Claisen rearrangement which obeys the law of the first-order reactions [25, 32].

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Table 4

ortho-Claisen rearrangement of allyl phenyl ether in toluene
Molar ratio 1 : 1, 200±1°C

Time	Concentration of *o*-allylphenol weight %	Reaction rate constants	
		first order $k \cdot 10^5 \text{ s}^{-1}$	zero order $k \cdot 10^4 \text{ gmol } l^{-1} \text{ s}^-$
900	2.1	4.77	1.59
1800	4.42	5.14	1.67
2700	6.0	4.74	1.51
3600	8.84	5.41	1.67
4500	11.76	5.96	1.78
6300	14.83	5.58	1.61
7200	18.54	6.44	1.76
8100	20.51	6.52	1.73

$\varnothing \; k \cdot 10^4 = 1.67 \text{ gmol } l^-$

Table 5

para-Claisen rearrangement of 2,6-dimethylphenyl allyl ether in diphenyl ether according to *H. Schmid*
and *K. Schmid* [10] with calculated values of the rate constants of the zero-order reaction

Time	Concentration of 4-allyl-2,6-di-methylphenol weight %	Reaction rate constants	
		first order $k \cdot 10^5 \text{ s}^{-1}$	zero order $k \cdot 10^4 \text{ gmol } l^{-1} \text{ s}^{-1}$
5 184	10.12	5.04	1.24
8 286	16.72	5.77	1.29
15 366	27.94	6.56	1.16
20 723	35.42	7.89	1.08

The zero-order reactions appear if the rearrangement of the substance in pure state is produced by thermal activation and volatile products or a precipitate arise owing to which the composition of the reaction mixture does not change. If the reaction is accelerated as much as the amount of the reacting substances decreases, the reaction remains of the zero order [46].

The *ortho*- as well as *para*-Claisen rearrangement of allyl aryl ethers proceeds as a zero-order reaction not only in pure state but also in the presence of solvent approximately up to 50—60 weight %.

This fact may be explained by the mechanism of the Claisen rearrangement in which the arising product, *i.e.* allylphenol, plays an important role. It is known [26, 44, 45] that phenolic compounds raise considerably the rate of the rearrangement which is explained by the polar character of solvent or the possible formation of hydrogen bonds between solvent and allyl phenyl ether [35, 44] or acid catalysis [44].

Table 6

ortho-Claisen rearrangement of N-allyl-1-naphthylamine according to *Marcinkiewicz et al.* [43] with calculated values of the rate constants of the first- and zero-order reaction

t °C	Time s	% of rearrangement		Reaction rate constants		
				first order $k \cdot 10^5$ s		
		original experimental values	determined graphically	original values	from the values determined graphically	zero order $k \cdot 10^3$ gmol l^{-1} s^{-1}
240.2	1 800	5.4	5.21	3.08	2.97	2.89
	3 600	10.6	10.42	3.11	3.03	
	5 400	15.9	15.63	3.21	3.14	
	7 200	20.5	20.84	3.19	3.24	
258.2	600	7.0	5.21	12.1	8.92	
	1 200	11.0	10.42	9.71	9.17	
	1 800	16.0	15.63	9.69	9.43	8.68
	2 400	20.9	20.84	9.77	9.74	
	3 000	25.0	26.06	9.59	10.06	
	3 600	29.7	31.27	9.90	10.43	
280.0	600	18.7	14.25	34.51	25.62	
	1 200	32.6	28.5	32.88	27.96	
	1 800	43.9	42.75	32.12	30.98	23.75
	2 400	54.8	57.0	33.09	35.17	
	3 000	69.8	71.25	39.92	41.5	
	10 800	91.7	—	—	—	

On the other hand, the rearrangements of allyl vinyl ether [37, 38] or of the derivatives of allyl vinyl methane [39—42] which have been studied as analogous reactions of the ortho-Claisen rearrangement are intramolecular and show the character of the first-order reaction. They differ from the rearrangement of allyl phenyl ether by the fact that they do not proceed *via* cyclic dienone with subsequent enolization stage to give phenolic compounds. This difference between the reaction mechanisms manifests itself in the reaction kinetics of the rearrangements of the above-mentioned compounds. While the Claisen rearrangement of allyl aryl ethers is a zero-order reaction and obeys the law of the first-order reactions only in the presence of excess solvent, the rearrangement of allyl vinyl ether and of the derivatives of allyl vinyl methane is governed merely by the law of the first-order reactions.

The results of *Marcinkiewicz et al.* [43] who studied the ortho-Claisen rearrangement of N-allyl-1-naphthylamine in the absence of solvent as a first-order reaction are in disagreement with our findings. Assuming the mechanisms of the rearrangement of N-allyl-1-naphthylamine to be analogous to the mechanism of the ortho-Claisen rearrange-

ment of allyl aryl ethers, the rearrangement of *N*-allyl-1-naphthylamine should also proceed as a zero-order reaction. Therefore we have revalued the data published and the results obtained as well as the original values are given in Table 6. From the rate constants of the first-order reactions calculated from the experimental results obtained at 240.2°C it could be concluded that the rearrangement of *N*-allyl-1-naphthylamine was a first-order reaction. As some values of the rate constants show considerable fluctuation at higher temperatures, we represented the experimental values graphically using the least-squares method. From the values thus determined we calculated the rate constants of the first-order reaction and assuming equal densities of *N*-allyl-1-naphthylamine and 2-allylnaphthylamine we determined the rate constants of the zero-order reaction. From the results given in Table 6 it may be concluded that the rearrangement of *N*-allyl-1-naphthylamine is also a zero-order reaction which confirms the correctness of our assumption. The activation energy of the rearrangement of *N*-allyl-1-naphthylamine determined from the rate constants of the zero-order reaction is 23 ± 1 kcal mol^{-1}.

From the present knowledge and our results of the study of the Claisen rearrangement of allyl aryl ether it ensues that only such a rearrangement which proceeds through a pseudocyclic transition state giving a cyclic dienone or analogous intermediary product with subsequent enolization or similar step may be regarded as a Claisen rearrangement. Such a rearrangement is a zero-order reaction but in the presence of excess solvent obeys the temporal law of the first-order reactions.

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