rate constant for neopentyl chloride formation at 240° (k_s 1.8 × 10^{-5} sec.$^{-1}$) is similar to that of the ethyl compound at the same temperature (k_s 1.17 × 10^{-5} sec.$^{-1}$).[2] The mechanism suggested by the non-rearrangement in alkyl chloride formation would lead to the prediction that all primary chloroformates would react at comparable rates. Thus if the alkyl chloroformates studied previously[2,3] reacted homogeneously, then very likely the reactions in this paper are also homogeneous.

The mechanisms suggested by the data in these and the previous papers are: (1) A one-step reaction through a cyclic transition state of ROCOCl to give RCl does exist. When favorable, it has polar character in the direction R^+OCOCl^-, but the electron deficiency of R is not sufficient to promote rearrangement in the cases studied. This mechanism is supported by the relative reactivities of the different alkyl chloroformates,[2] the large negative entropy of activation,[2] the retention of configuration[3] and the absence of rearranged alkyl chlorides.

(2) An elimination reaction through a more polar transition state, probably leading to an intermediate of substantial charge separation. The intermediate is loosely bound (as shown by the near-zero entropy of activation), it can react by alternative routes to give different olefins[3] and rearranged products, but it does not dissociate enough to give stereochemically random products.[3] The presence of an intermediate is actually suggested only by the isotope effects[3] supported further in this paper by an analogous increase in the rate of formation of 2-butenes on 1-deuteration shown in Table I for *n*-butyl chloroformate.

(3) A one-step elimination reaction not involving polar intermediates is suggested by the different reaction products from 1- and 2-butyl chloroformates, the former yielding a mixture richer in 1-butene. Since the rearranged ion-pairs from the two sources probably would be the same, the excess 1-butene may be formed by a direct route analogous to an alkyl acetate pyrolysis. This mechanism is not demonstrated, but it is by no means excluded for a portion of the reaction.

Experimental

Materials.—Neopentyl alcohol (2,2-dimethyl-1-propanol) was prepared by the lithium aluminum hydride reduction of trimethylacetic acid. The reduction of ethyl butyrate by sodium in acetic acid-*d*[6] yielded 1-butanol-1-*d*. Chloroformates were made from the alcohols by the previously described procedure.[2] Neopentyl chloroformate boiled at 43–45° (20 mm.); *n*-butyl chloroformate had b.p. 51–52° (28 mm.). Commercial *n*-hexyl chloroformate was redistilled, b.p. 43° (9 mm.). For chromatographic comparison, *t*-amyl chloride was prepared from *t*-amyl alcohol and concentrated hydrochloric acid; neopentyl chloride (contaminated with *t*-amyl chloride) was prepared from neopentyl alcohol, thionyl chloride and quinoline.[7] Butenes were commercially available and the isomeric methylbutenes were prepared by dehydration of *t*-amyl alcohol and then distillation. The preparation of 1,1-dimethylcyclopropane followed the method of Shortridge.[8]

The deuterium content of 1-butene was determined by Mr. R. Hunt of Shell Oil Co. by mass spectra. The deuterium content of the 1-butyl-1-*d* chloroformate was determined by converting it to 1-butene by the following rearrangement-free sequence. 1-Butyl-1-*d* chloroformate → 1-butanol-1-*d* (with water) → 1-butyl-1-*d* acetate (with acetyl chloride) → 1-butene-1-*d* (on pyrolysis). It contained 0.78 atom deuterium per molecule. The decomposition of 1-butyl-1-*d* chloroformate yielded butenes, separated and collected as described before,[3] and the 1-butene contained 0.71 atom deuterium per molecule. In this experiment, the smaller yields of 2-butenes did not allow analysis.

The kinetic measurements and treatments followed the previously described methods.[2] Products from neopentyl chloroformate were identified not only by comparison of retention time, but in several cases also by comparison of the infrared spectrum of the separated components in the gas phase with those of synthetic materials and with the American Petroleum Institute spectra.

The same flow system was used to show that *t*-amyl chloride, neopentyl chloride, *n*-butyl chloride, 2-butyl chloride and *cis*-2-butene were not decomposed or isomerized to as much as 1%, in agreement with the literature.[9,10]

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[6] D. G. Hill, W. H. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **74**, 5599 (1952).

[7] W. Gerrard and P. Tolcher, *J. Chem. Soc.*, 3640 (1954).

[8] R. W. Shortridge, *J. Am. Chem. Soc.*, **70**, 946 (1948).

[9] D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 2039 (1951), and earlier papers by Barton and co-workers.

[10] W. W. Anderson, J. A. Bell, J. M. Diamond and K. R. Wilson, *J. Am. Chem. Soc.*, **80**, 2384 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIF.]

The Effect of Geometry in the Allyl Group on the Rate of the Claisen Rearrangement

BY LAURENCE D. HUESTIS AND L. J. ANDREWS

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The *cis* and *trans* isomers of γ-methylallyl phenyl, γ-phenylallyl phenyl and γ-methylallyl 2,6-dimethylphenyl ethers have been prepared. The reaction rates of each pair of isomers have been determined in the neighborhood of 200° using diphenyl ether as the solvent. In general the *trans* compounds were found to be more reactive, but only slightly so, than the *cis*. Apparently the carbon of the migrating allyl group does not approach the *ortho* ring carbon atom sufficiently closely in the activation process so that the reaction rate is sterically sensitive to the geometric configuration about the β,γ-double bond. The rearrangement of *cis*-γ-methylallyl 2,6-dimethylphenyl ether, but not of its *trans* isomer, is accompanied by partial *cis–trans* isomerization of the ether. Presumably the dienone intermediate in these *para* rearrangements can revert to ether by a process in which the *trans* isomer is formed stereoselectively.

The proposal of Hurd and Pollak[1] that the *ortho*-Claisen rearrangement of phenyl allyl ethers is intramolecular in character is now quite generally accepted.[2] It seems likely that a similar cyclic mechanism is operative in the initial phase of the *para*-Claisen rearrangement, a process in

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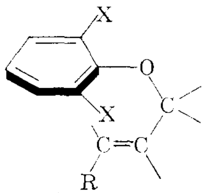
[1] C. D. Hurd and M. A. Pollak, *J. Org. Chem.*, **3**, 550 (1939).

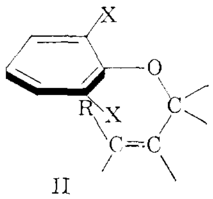
[2] For a recent discussion of the confirming evidence see Chapter 5 by D. J. Cram in the book edited by M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 295–303.

which the allyl group appears to become temporarily affiliated with the *o*-carbon atom of the phenyl group to which migration occurs.[3] The results of recent work[4,5] convincingly support the idea that as the γ-carbon of the migrating allyl group approaches the *o*-position of the benzene ring, that group falls into a plane approximately parallel to that of the ring; the conformations about the oxygen–α-carbon and α-carbon–β-carbon bonds presumably are such that the β-carbon lies outside of rather than directly above the ring.

The activated complexes for two geometrically isomeric γ-substituted phenyl allyl ethers then very likely resemble the structures which are depicted, after the fashion of Rhoads and Crecelius,[6] in formulas I and II rather than to alternate conformational arrangements. It may then be anticipated that the activation process for the *cis* isomer II should, because of physical interference between the γ-substituent (R) with *ortho* ring substituents (X or H) as well as with the ring itself, be to some degree sterically less favored than that for the *trans* isomer.



I



II

This matter now has been explored in terms of a comparative study of the rates of Claisen rearrangement of the *cis* and *trans* isomers of γ-methylallyl and γ-phenylallyl phenyl ethers and of γ-methylallyl 2,6-dimethylphenyl ether. Although a number of kinetic studies of the *ortho* and *para* rearrangements have been reported,[7] this and the coincident study of White and Norcross[8] are the only ones in which the influence of geometric configuration in the allyl group on reaction rate has so far been considered.

Experimental

trans-**Crotyl alcohol** (b.p. 120–122.5°, $n^{25}D$ 1.4263) was prepared by reduction of crotonaldehyde with lithium aluminum hydride.[9]

cis-**Crotyl Alcohol.**—Two different procedures were used to prepare this substance. In the first, 2-butyn-1-ol (b.p. 141.2–142.3°, $n^{25}D$ 1.4520) obtained as described previously[10] was subjected to partial hydrogenation over Pd–$BaSO_4$ catalyst.[9] The product had b.p. 122.0–123.7° and $n^{25}D$ 1.4323.

In the alternate method tetrolic acid was first prepared from 3-methyl-4,4-dibromo-2-pyrazolin-5-one.[11] A solution of 23.6 g. (0.28 mole) of tetrolic acid in 200 ml. of tetrahydrofuran was hydrogenated over Pd–$BaSO_4$ catalyst at atmospheric pressure until 0.28 mole of hydrogen was absorbed. Care was taken to avoid exposure of the reaction product to light. After removal of the catalyst by filtration, the solution of isocrotonic acid was added directly with stirring to a slurry of 6.45 g. (0.175 mole) of lithium aluminum hydride in 250 ml. of tetrahydrofuran over a 25-minute period. Ether then was added (110 ml.), and the excess reducing agent was decomposed with water. The organic phase was separated, and the aqueous phase was extracted with two 100-ml. portions of ether. The combined ether and tetrahydrofuran phases were dried over anhydrous potassium carbonate and concentrated by distillation. Fractionation of the concentrate provided 3.8 g. (19% yield based on tetrolic acid) of *cis*-crotyl alcohol, b.p. 118–123°. The infrared spectrum of this product was identical with that of *cis*-crotyl alcohol obtained by the alternate procedure. Both samples showed a characteristic broad *cis* double bond peak at 690 cm.$^{-1}$ and lacked the strong *trans* isomer absorption peak[9] at 965 cm.$^{-1}$. The *cis*-alcohol provided a 3,5-dinitrobenzoate derivative, recrystallized from ligroin, which had m.p. 49.5–50.5° (lit.[9] m.p. 51°).

cis- **and** *trans*- **crotyl chlorides** were prepared from the corresponding alcohols and phsophorus trichloride in the presence of pyridine.[9] The *trans* product had b.p. 84.2–84.0° and $n^{25}D$ 1.4326, and the *cis* had b.p. 85.0–85.8° and $n^{25}D$ 1.4360.

To establish the stereochemical purity of the isomeric chlorides, a method based on their reduction to butenes by lithium aluminum hydride was used.[12] Such reductions of allylic *chlorides* occur with complete retention of configuration about the carbon–carbon double bond.[13] A 2-g. sample of the chloride in 5 ml. of tetrahydrofuran was added dropwise to a suspension of 1.6 g. of lithium aluminum hydride in 9 ml. of tetrahydrofuran. Several samples of the gas which was evolved were trapped in a 3-ml. gas collection U-tube during the course of the reaction. The contents of the collector were then subjected to gas–liquid chromatography on a column prepared by suspending a 1:1 mixture of benzonitrile and silver nitrate on a firebrick base. The eluting gas was helium, and the column temperature was 0°. The detection system consisted of a Gow Mac conductivity cell with a tungsten filament. The products were identified by comparing their emergence times with those of samples of pure hydrocarbons obtained from the Matheson Co. Within the limits of error the composition of all gas samples (as calculated from peak areas) collected during the course of reaction of a halide sample with the hydride was the same. The elution times of the various hydrocarbons and the percentage compositions of the hydrocarbon mixtures obtained by reducing the *cis*- and *trans*-chlorides are given in Table I.

cis- **and** *trans*-**Cinnamyl Chlorides.**—*trans*-Cinnamyl alcohol,[14] m.p. 32°, was prepared by the reduction of commercial cinnamaldehyde with sodium borohydride.[15] The *cis*-alcohol, b.p. 97–100° (1 mm.), $n^{17.2}D$ 1.5752, was prepared by catalytic hydrogenation of 3-phenyl-2-propyn-1-ol[16] as described previously.[14] The infrared spectrum of the *cis* product showed no absorption (in the region of 965 cm.$^{-1}$) characteristic of *trans*-1,2-disubstituted ethylene.[17] The *cis*- and *trans* chlorides, b.p. 69–73° (2 mm.) and 94° (2 mm.), respectively, were prepared from the corresponding alcohols using phosphorus trichloride and pyridine.[14] The

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(3) (a) H. Conroy and R. A. Firestone, *J. Am. Chem. Soc.*, **75**, 2530 (1953); **78**, 2290 (1956); (b) D. Y. Curtin and H. W. Johnson, Jr., *ibid.*, **76**, 2276 (1954); (c) D. Y. Curtin and R. J. Crawford, *ibid.*, **79**, 3156 (1957).

(4) E. N. Marvell and J. L. Stephenson, *J. Org. Chem.*, **25**, 676 (1960).

(5) B. E. Norcross and W. N. White, Abstracts of Papers Presented before the Division of Organic Chemistry of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 15-O.

(6) S. J. Rhoads and R. L. Crecelius, *J. Am. Chem. Soc.*, **77**, 5057 (1955).

(7) For example see (a) J. Kincaid and D. S. Tarbell, *ibid.*, **61**, 3085 (1939); (b) D. S. Tarbell and J. Kincaid, *ibid.*, **62**, 728 (1940); (c) W. N. White, D. Gwynn, R. Schlift, C. Girard and W. Fife, *ibid.*, **80**, 3271 (1958); (d) H. L. Goering and R. R. Jacobson, *ibid.*, **80**, 3277 (1955), as well as refs. 3c, 5, 6.

(8) W. N. White and B. E. Norcross, *ibid.*, **83**, 1968 (1961).

(9) *Cf.* L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1940).

(10) M. Schechter, N. Green and F. B. LaForge, *ibid.*, **74**, 4902 (1952).

(11) (a) E. Muckermann, *Ber.*, **42**, 3449 (1909); (b) L. Carpino, *J. Am. Chem. Soc.*, **80**, 599 (1958).

(12) The authors are indebted to Professor L. F. Hatch for suggesting this method and to Professor R. K. Brinton for invaluable guidance in perfecting the analytical method.

(13) L. F. Hatch, P. D. Gardner and R. E. Gilbert, *J. Am. Chem. Soc.*, **81**, 5943 (1959).

(14) L. F. Hatch and H. E. Alexander, *ibid.*, **72**, 5643 (1950).

(15) W. G. Brown and S. W. Chaiken, *ibid.*, **71**, 122 (1949).

(16) T. Y. Lai, *Bull. soc. chim. France*, **53**, 685 (1933).

(17) R. N. Jones and C. Sandorfy in A. Weissberger's, "Technique of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 378–383.

TABLE I

G.L.C. ANALYSIS OF HYDROCARBONS OBTAINED FROM THE CROTYL CHLORIDES

Hydrocarbon	Elution time, min.	Composition chloride, % *cis*[a]	*trans*
Satd. hydrocarbons	3	..	0.1
trans-2-Butene	13.7	2.3	95.0
Isobutene	26.0	..	0.1
cis-2-Butene	49.2	97.6	4.8[b]

[a] The reduction product from the *cis*-chloride was shown to contain about 0.1% of 1-butene by separating the hydrocarbons on a series of two columns, the first of which contained a packing of dinonyl phthalate on firebrick and the second of which was the benzonitrile–silver nitrate column already described. When only the silver nitrate column is used, *cis*-2-butene and 1-butene are eluted simultaneously. [b] This may contain some 1-butene.

infrared spectrum of the *cis* product showed some absorption around 965 cm.$^{-1}$. As discussed later it was estimated that this chloride contained from 10–20% of its geometric isomer.

***cis*- and *trans*-γ-methylallyl phenyl ethers** were prepared from the corresponding crotyl chloride and phenol by the general method outlined by Goering and Jacobson[7d] for preparation of allyl phenyl ethers. The *trans* product[7d] had b.p. 58–62° (1–2 mm.), $n^{25}\mathrm{D}$ 1.5180. The *cis* isomer, obtained in 71% yield, had b.p. 63–65° (1 mm.), $n^{25}\mathrm{D}$ 1.5212.

Anal. Calcd. for (*cis*) $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.94; H, 8.34.

***cis*- and *trans*-γ-methylallyl 2,6-dimethylphenyl ethers** were prepared from the corresponding crotyl chloride and 2,6-dimethylphenol. The procedure was that used in preparing the phenyl ethers except that it was necessary to extract the crude products with Claisen alkali (alcoholic potassium hydroxide) rather than with aqueous base to remove phenolic contaminants. The *trans* isomer[18] had b.p. 79–81° (2 mm.), $n^{25}\mathrm{D}$ 1.5060. The *cis* isomer, obtained in 40% yield, had b.p. 88–89° (2 mm.), $n^{25}\mathrm{D}$ 1.5080.

Anal. Calcd. for (*cis*) $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.71; H, 8.98.

***cis*-and *trans*-γ-phenylallyl phenyl ether** were prepared from *cis*-and *trans*-cinnamyl chlorides by the general procedure of Goering and Jacobson.[7d] The *trans* product,[19] after three recrystallizations from an ethanol–water mixture, had m.p. 67.5–68.5°. The product obtained from the *cis*-chloride (in 46% yield) had b.p. 143–148° (2 mm.), $n^{19}\mathrm{D}$ 1.5964.

Anal. Calcd. for (*cis*) $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.61; H, 6.90.

The *cis*-ether, as prepared from *cis*-chloride samples which showed some infrared absorption at 965 cm.$^{-1}$ because of contamination with the geometric isomer, also showed some absorption at this wave length. A quantitative estimate of the amount of *trans* impurity in the *cis* ether was made by comparing the intensity of this peak in the *cis* sample with that of the intense 965 cm.$^{-1}$ peak in the spectrum of the *trans* ether. The spectra of the two ether samples were determined on a Beckman IR4 infrared spectrophotometer with double beam operation using carbon disulfide as the solvent with sodium chloride prisms. The sample of "*cis*-ether" used in rate work was, on this basis, assigned a *cis* to *trans* ratio of 84/16. The rate constants reported later were calculated after correcting to eliminate the contribution of the *trans* contaminant to the over-all reaction rate.

The ultraviolet spectra of the *cis*- and *trans*-γ-phenylallyl ethers in 95% ethanol were almost identical and showed the intense absorption maximum in the neighborhood of 250 mμ (molecular extinction coefficient 19,000) of substances containing the cinnamyl radical.[20]

The Kinetic Studies.—The rates of Claisen rearrangement of the several ethers were investigated by a modification of the procedure used previously by Kincaid and Tarbell.[7a] For a typical run eight identical 5-ml. samples of a solution of the particular ether in diphenyl ether were sealed in glass tubes under nitrogen. Eastman Organic Chemicals white label diphenyl ether was used without further purification. The phenyl allyl ether concentrations of the starting solutions at room temperature were of the order of 0.37–0.52 *M*. The tubes were then heated in the vapor of a refluxing liquid of appropriate boiling point. The temperature of the vapor was recorded using a thermometer accurate to ±0.1°. The liquids used for the vapor baths were cyclohexanol, 1,2-propanediol, tetrahydronaphthalene and *m*-nitrotoluene. It was established by separate experiment that from 300 to 400 seconds, depending on the bath temperature, was required for temperature equilibration of the rate samples. Timing was started after the equilibration period was completed. Sample tubes were removed from time to time and cooled and the contents were analyzed for phenolic material.[21] The mixtures of unreacted ether and of phenolic product were transferred to a round-bottom flask with a standard taper joint with the aid of a small amount (about 1 ml.) of pyridine; 2 ml. of a standardized solution of acetic anhydride in pyridine was added. A short condenser plugged at the upper end with a glass stopper was attached to the flask, and the contents were heated under pressure (all joints were greased) on a steam-bath for 1 hour. Reproducible results were not obtained unless a closed system was used. After cooling the flask in a Dry Ice-bath, its contents were diluted with water, and the mixture was titrated with 0.2 *M* sodium hydroxide to a *p*H of 8.6 using a Beckman *p*H meter. The results were subject to slight corrections which were based on blank titrations of mixtures of 2.6 ml. of pyridine, 4.6 ml. of diphenyl ether and distilled water, the latter in the same amount used in diluting the acetylation products of the rate samples before titration. The phenol content of the rate samples was calculated from the difference between the quantity of acetic anhydride added in the analysis and that recovered by titration (as acetic acid).

Rate constants *k* (see eq. 1) were calculated from the slopes of the straight lines obtained by plotting values of the

$$kt = 2.303 \log (E_0)/(E) \qquad (1)$$

logarithms of the phenyl allyl ether concentrations (*E*) of the rate samples *versus* the corresponding reaction times. All reactions were followed to at least two-thirds of completion. The conformance of the experimental data to eq. 1 was exceptionally good throughout the course of the reactions.

As mentioned previously, the rate data for *cis*-γ-phenylallyl phenyl ether were subject to a correction for the contribution of the contaminating *trans* isomer to the over-all rate. The amount of phenol produced from the *trans* contaminant at any given reaction time was calculated from the initial concentration of that isomer (as evaluated by infrared spectrophotometry) and the known rearrangement rate constant for the *trans* compound. The latter was measured directly or was calculated for the temperature in question from the rate constants and activation energies which are later reported for *trans*-γ-phenylallyl phenyl ether. The ether concentration at a particular reaction time, as evaluated by volumetric analysis, could then be modified so that it included only the contribution of the *cis* isomer to the total value.

The Rearrangement Product of *cis*-γ-Methylallyl Phenyl Ether.—A 4-ml. sample of *cis*-γ-methylallyl phenyl ether was heated in a sealed tube under nitrogen at 186° for 25 hours (the time required to produce 80% rearrangement as estimated from the rate constant for the reaction in diphenyl ether at this temperature). The entire sample was then used for the preparation of a 3,5-dinitrobenzoate derivative of the phenolic product (by the pyridine method[22]). White needles, which melted at 64–65° after three recrystallizations from pentane, were obtained.

Anal. Calcd. for $C_{17}H_{14}N_2O_6$: C, 59.65; H, 4.12. Found: C, 59.72; H, 4.25.

This product was characterized as the 3,5-dinitrobenzoate of 2-(α-methylallyl)-phenol by comparing its melting point with an authentic sample of the derivative prepared from

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[18] E. N. Marvell, A. V. Logan, L. Friedman and R. W. Ledeen, *J. Am. Chem. Soc.*, **76**, 1922 (1954).

[19] C. D. Hurd and L. Schmerling, *ibid.*, **59**, 107 (1937).

[20] L. J. Andrews and S. L. Linden, *ibid.*, **69**, 2091 (1947).

[21] A. Verley and F. Bolsing, *Ber.*, **34**, 3354 (1901).

[22] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 211–212.

the phenol obtained by heating *trans*-γ-methallyl phenyl ether.[23] The *trans*-ether was heated in a sealed tube under nitrogen at 186° for 11.5 hours, and the 3,5-dinitrobenzoate, m.p. 61-63°, was prepared from the product as described above. The mixed m.p. of the two samples of the derivative of the rearrangement product of the *cis*- and *trans*-ethers was 62.5-64°. The infrared spectra of the two samples were identical.

That the *cis*-ether did not isomerize to its *trans* isomer during the course of the rearrangement was illustrated by an experiment in which a 3-ml. sample of the *cis* isomer was first heated at 186° under nitrogen for 14 hours (time for 60% rearrangement). The sample was then dissolved in ether, and the solution was extracted twice with 6 *N* sodium hydroxide. After drying the ether phase over sodium sulfate, the solvent was evaporated. The residual α-methylallyl phenyl ether had an infrared spectrum in carbon disulfide which was identical with that of the starting material and which completely lacked the peak at 965 cm.$^{-1}$ characteristic of the *trans* double bond in the *trans*-γ-methylallyl phenyl ether.

The Rearrangement Product of *cis*- and *trans*-γ-Methylallyl 2,6-Dimethylphenyl Ether.—A 6-ml. sample of the *trans* isomer of this ether was heated at 186° under nitrogen for about 35 min. (long enough to cause about 60% rearrangement). A sample of the 3,5-dinitrobenzoate of the phenolic product (2,6-dimethyl-4-(γ-methylallyl)-phenol) was prepared, as described above, from 3 ml. of the resultant mixture. After three recrystallizations from ethanol this material melted at 117.5-118.5° (lit.[15] m.p. 117.9-118.6°). The infrared spectrum of the 3,5-dinitrobenzoate in carbon disulfide was found to have a fairly strong band at 965 cm.$^{-1}$, an indication that the 4-γ-methylallyl substituent is substantially *trans* in its geometry. A *trans* band has been observed previously in the spectrum of the free phenol as obtained by Claisen rearrangement.[18]

A diethyl ether solution of the remaining 3 ml. of the mixture obtained by heating the original ether was subjected to repeated extraction with Claisen alkali. The ether phase was then evaporated. The infrared spectrum of the residue, in carbon disulfide, was found to be essentially identical with respect to the position and intensities of all peaks with that of the original *trans*-ether.

A similar experiment was conducted in which a sample of *cis*-γ-methylallyl 2,6-dimethylphenyl ether was subjected to about 60% rearrangement by heating under nitrogen for 1.5 hours at 186°. A portion of the resultant mixture was used to prepare a 3,5-dinitrobenzoate of the phenolic product. After three recrystallizations from ethanol, this melted from 107-111°. The infrared spectrum of this derivative was identical, with respect to the positions of the absorption peaks, with that of the derivative obtained from the rearrangement product of the *trans*-ether.

The remainder of the mixture obtained from heating the *cis*-ether was dissolved in diethyl ether, and the solution was extracted with Claisen alkali. The residue remaining after evaporation of the ether was found to have a small but definite infrared absorption peak at 965 cm.$^{-1}$ in contrast to the starting ether which contained no *trans* contaminant. The spectrum of this material lacked a band at 3350 cm.$^{-1}$ (characteristic of a hydroxyl group). Thus the 965 cm.$^{-1}$ band cannot be ascribed to traces of *trans*-2,6-dimethyl-4-(γ-methylallyl)-phenol which escaped extraction with Claisen alkali. The possibility that the isomerization of the *cis*-ether to *trans*-ether was promoted by Claisen alkali in the extraction process was eliminated on the basis of an experiment in which the pure *cis*-ether was shaken for 4 hours with Claisen alkali. The ether, which was recovered by extraction with diethyl ether followed by evaporation of the solution, had no infrared peak at 965 cm.$^{-1}$.

Apparently then the *cis*-ether is partially isomerized to the *trans*-ether during the course of the Claisen rearrangement. It was estimated by comparing the absorption intensities (at 965 cm.$^{-1}$) of the pure *trans*-ether and of *cis*-ether recovered after partial rearrangement as described above that the *cis* sample contained about 10% of the *trans* contaminant.

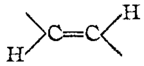
The Rearrangement Product of *cis*-γ-Phenylallyl Phenyl Ether.—A sample of 2-(α-phenylallyl)-phenol was prepared for comparison purposes by refluxing a solution of *trans*-γ-phenylallyl phenyl ether in N,N-diethylaniline for 4 hours. The details of the procedure are essentially those reported by Claisen and Tietze.[24] Some of the product (b.p. 150-153° (1.5 mm.), n^{25}D 1.5940) was converted[22] to its phenylurethan derivative, m.p. 93-95° (lit.[19] m.p. 93-94°).

A solution of 6.5 g. of *cis*-γ-phenylallyl phenyl ether in 28 ml. of N,N-diethylaniline was refluxed for 13 hours. Even after a brief heating period the solution was very darkly colored. Because of difficulties with product coloration no attempts were made to check (as was done with other *cis*-ethers) the infrared spectrum of unreacted ether reisolated after a substantial portion of a sample of *cis*-ether had undergone thermal rearrangement to the phenol.

The cooled reaction mixture was diluted with 40 ml. of ligroin and then extracted with three 25-ml. portions of 3 *M* hydrochloric acid and then with four 25-ml. portions of 1 *M* sodium hydroxide. The basic extract was acidified with 0.5 *M* sulfuric acid to the congo red end-point. The mixture was then ether extracted, and the dried ether layer was distilled. A yield of 1.9 g. (29%) of 2-(α-phenylallyl)-phenol was obtained, b.p. 150° (1.5 mm.), n^{25}D 1.5952. The infrared spectra of this sample of phenol and of its phenylurethan, m.p. 91.5-93°, were identical with those of the corresponding compounds prepared from the *trans*-ether.

Results

The several ethers, the rearrangement rates of which were investigated, were prepared by reaction of the sodium salts of the appropriate phenols with *cis*- or *trans*-γ-methylallyl or γ-phenylallyl chlorides (crotyl and cinnamyl chlorides). The preparative methods used in obtaining the *cis*- and *trans*-halides were similar to those described elsewhere.[9,14] Only in the case of *cis*-γ-phenylallyl phenyl ether was there any evidence that the ether samples were contaminated with their geometric isomers. This material displayed a weak infrared absorption band at 965 cm.$^{-1}$, characteristic of the



grouping. Presumably the *trans*-ether impurity (estimated to be present to the extent of 16%) was derived from *trans*-cinnamyl chloride formed through partial allylic rearrangement during the conversion of *cis*-cinnamyl alcohol to *cis*-cinnamyl chloride. The high stereochemical purity of the geometric isomers of crotyl chloride was conveniently demonstrated by reducing samples of the halides to the corresponding *cis*- and *trans*-2-butenes, which can be distinguished readily by gas-liquid chromatography.

In Table II the rate constants, *k* (eq. 1), at various temperatures and the energies and entropies of activation for Claisen rearrangement of the ethers in diphenyl ether are listed. The rate constants are similar in magnitude to those reported previously by Goering and Jacobson[7d] for rearrangement of a number of ring-substituted phenyl allyl ethers and of various isomeric methylallyl phenyl ethers in diphenyl ether. Also the values of the energies and entropies of activation observed in the present investigation for reaction of the γ-methylallyl ethers of phenol and 2,6-dimethylphenol are closely similar to those reported by Goering and Jacobson. In the one instance (*trans*-γ-methylallyl phenyl ether) in which the authors repeated the kinetic work of Goering and

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[23] W. M. Lauer and H. E. Ungnade, *J. Am. Chem. Soc.*, **58**, 1392 (1936).

[24] L. Claisen and E. Tietze, *Ber.*, **58**, 279 (1925).

Jacobson, though by a different experimental procedure, the two sets of results were in very good agreement (see Table II). The entropies of activation for the γ-phenylallyl phenyl ethers are more negative than those for the γ-methylallyl ethers, and in the case of the *trans* isomer the observed energy of activation is significantly lower than that customarily found for the methylallyl ethers.

TABLE II

RATE CONSTANTS, ENERGIES AND ENTROPIES OF ACTIVATION FOR CLAISEN REARRANGEMENT IN DIPHENYL ETHER

(Ether)$_i$[a] mole/l.	Temp., °C.	k, sec.$^{-1}$	E_a, kcal./mole	ΔS^*, e.u.
trans-$C_6H_5OCH_2CH{=}CHCH_3$[b,c]				
0.517	186.5	2.32 ± 0.05	32.2	−12.4
.517	207.6	11.0 ± .4		
.518	186.5	1.87 ± .02	30.8	−16.0
.518	207.8	8.33 ± .23		
		Av.	31.5	−14.2
cis-$C_6H_5OCH_2CH{=}CHCH_3$[b]				
0.522	187.1	1.36 ± 0.04	31.5	−15.2
.522	208.5	6.29 ± .10		
.519	186.6	1.24 ± .02	32.4	−13.4
.519	207.9	5.96 ± .06		
		Av.	32.0	−14.3
trans-$C_6H_5OCH_2CH{=}CHC_6H_5$[b]				
0.368	186.7	3.75 ± 0.04	24.8	−27.7
.368	208.0	12.4 ± .03		
.444	187.1	3.37 ± .05	25.0	−27.5
.444	208.5	11.4 ± .2		
		Av.	24.9	−27.6
cis-$C_6H_5OCH_2CH{=}CHC_6H_5$				
0.372	208.5	2.73 ± 0.08	29.2	−21.7
0.372	234.3	12.9 ± 0.2		
trans-2,6-$(CH_3)_2C_6H_3OCH_2CH{=}CHCH_3$				
0.432	160.9	3.78 ± 0.06	29.5	−13.6
0.432	186.3	25.0 ± 0.5		
cis-2,6-$(CH_3)_2C_6H_3OCH_2CH{=}CHCH_3$				
0.434	161.0	1.29 ± 0.05	30.6	−13.2
0.434	186.5	9.25 ± 0.14		

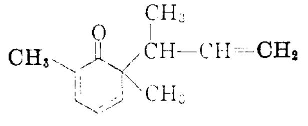
[a] Initial ether concentrations of rate samples at room temperature. [b] Two different batches of ether were prepared. The first two runs were made using one of these ether samples and the other sample was used for the second two runs. [c] For *trans*-γ-methylallyl phenyl ether Goering and Jacobson[7d] list these values for reaction in diphenyl ether (determined by a dilatometric method): $k(184.85°) = 1.61 \pm 0.02$ sec.$^{-1}$, $E_a = 31.7$ kcal. mole, $\Delta S^* = -12$ e.u.

The rate constant for the *trans*-γ-methylallyl phenyl ether in the region of 200° is somewhat less than twice as large as that for the *cis* isomer, and the energies and entropies of activation for rearrangement of the two ethers to 2-(α-methylallyl)-phenol are the same within experimental error. In the case of the γ-phenylallyl phenyl ethers, the rate constant for the rearrangement of the *trans* isomer to 2-(α-phenylallyl)-phenol at 208° is about four times that for the *cis*.[25] The energy of activation for the *cis* isomer is about 4 kcal./mole greater than that for the *trans*, and the entropy of activation for the *trans* compound is of the order of 6 e.u. more negative than that for the *cis*. These entropy differences for the two phenylallyl isomers can be explained on the assumption (see the introductory remarks) that the γ-phenyl substituent, unlike the γ-methyl group, is sufficiently bulky so that close approach of the γ-carbon and the *ortho* carbon to which migration occurs is less favored for the *cis* than for the *trans* isomer. Thus in the case of the *trans* isomer the activated complex is structurally more constrained and is formed with more entropy loss than is that of the *cis* ether. As is the case, such a difference in activation entropies should be correspondingly reflected in activation energies.[26]

The reactions of the *cis*-γ-substituted allyl ethers are, however, apparently not subject to the pronounced steric retardation to be anticipated were the carbon of the migrating group to approach the *ortho* position very closely in the activation process. It seems reasonable, therefore, that a substantial portion of the energy of activation for these rearrangements must be expended in the weakening of the α-carbon–oxygen bond.

In a broad sense the relative reactivities of the *cis*- and *trans*-γ-methylallyl 2,6-dimethylphenyl ethers with respect to *para* rearrangement are similar to those observed for the *ortho* rearrangements of the isomeric γ-methylallyl phenyl ethers. Again the *trans* compound is somewhat, though not markedly so, more reactive than the *cis* in the region of 200°, and the energies and entropies of activation for the two isomers are about the same. Clearly a methyl group in the *ortho* position of the phenyl ring creates no serious steric barrier opposing the migration of the substituted allyl group to that position to form the dienone intermediate[3a] of the *para* rearrangement.

Actually, however, the conversion of the γ-methylallyl dimethylphenyl ether to the dienone III probably is not uniquely the rate-controlling step of the over-all reaction to produce a phenol. The fact that *cis*-γ-methylallyl 2,6-dimethylphenyl ether is partially isomerized to its *trans* isomer during the course of the Claisen rearrangement (see the Experimental section) can best be explained on the assumption that the dienone III can undergo competitive reactions to form *para* rearrangement product and to reform[3c] γ-methylallyl 2,6-dimethylphenyl ether. The reaction to regenerate the ether must be stereoselective with respect to production of the *trans* isomer since the *trans*-ether remains free of its *cis* isomer during the course of the *para* rearrangement. It seems highly unlikely that the conversion of the *cis*- to the *trans*-ether takes place by a process (not involving the dienone intermediate) in which the bond between ether oxygen and the methylallyl group is not



III

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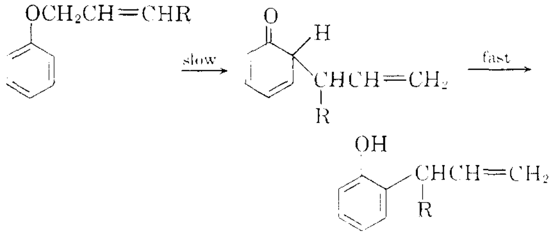
[25] The rate constants for rearrangement of the *trans* isomers of γ-methylallyl and γ-phenylallyl ethers of *p*-methoxyphenol and of 3,5-dimethylphenol are also reported[8] to be only slightly larger than those for the corresponding *cis* isomers in the neighborhood of 200°.

[26] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., p. 345.

broken. Were this the case, *cis*-γ-methylallyl phenyl ether might be expected to undergo partial conversion to its *trans* isomer during Claisen rearrangement. This does not happen.[27]

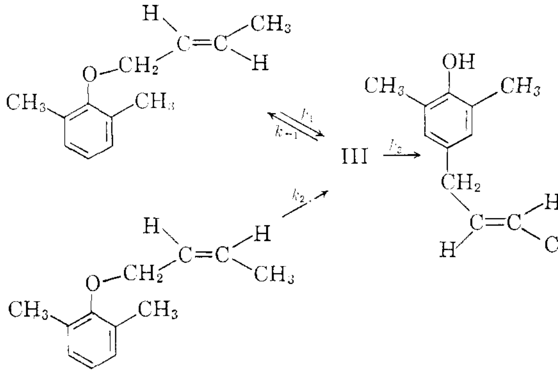
It is probable that in the ortho rearrangement the conversion of dienone to phenolic product is rapid as compared to the conversion of ether to dienone (eq. 2)



(2)

The more complex reaction scheme for the *cis*- and *trans*-γ-methylallyl 2,6-dimethylphenyl ethers is depicted in eq. 3.

It should be noted that the γ-methylallyl group in the 4-position of the phenolic product has the *trans* configuration (see the Experimental section). If a steady state is established with respect to III, the experimental rate constant, k, for rearrangement of the *trans* isomer to a phenol is actually $k_1k_3/(k_{-1} + k_3)$. That is, k is a satisfactory measure of the magnitude of k_1 (the rate constant of primary interest in this investigation) only when $k_{-1} << k_3$. Also the rate constant k for formation of phenolic product from the *cis*-ether is related to



(3)

the concentrations of *cis* (C) and *trans* (T) ether and to their sum (E) in the reaction mixture at any time by the expression

$$k(\mathrm{E}) = k_3[k_2(\mathrm{C}) + k_1(\mathrm{T})]/(k_{-1} + k_3) \qquad (4)$$

The validity of k as a measure of k_2 is again dependent on the magnitude of k_{-1} relative to that of k_3. In this regard it is significant that the unreacted ether recovered after more than half of the *cis*-ether had rearranged was found to contain only a relatively small percentage of the *trans* isomer. On the other hand, Curtin and Crawford[3d] have shown that in the region of 75–100°, 6-allyl-2,6-dimethyl-2,4-cyclohexadienone was rearranged to a phenol only about 2.8 times as fast as it isomerized to the corresponding phenyl allyl ether. Clearly the rate and thermodynamic constants listed in Table II for the *cis*- and *trans*-γ-methylallyl 2,6-dimethylphenyl ethers must be used for interpretive purposes with some reserve.

[27] It should be noted, however, that Marvel and Stephenson[4] have observed some *cis–trans* isomerization of an ether as an adjunct of the *ortho* rearrangement.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, O.]

The *ortho*-Claisen Rearrangement. II. The Rearrangement of *cis*- and *trans*-γ-Substituted Allyl Aryl Ethers[1]

BY WILLIAM N. WHITE AND BRUCE E. NORCROSS[2,3]

RECEIVED SEPTEMBER 6, 1960

The rates of rearrangement of *cis*- and *trans*-γ-methylallyl *p*-methoxyphenyl ethers and *cis*- and *trans*-γ-phenylallyl *p*-methoxyphenyl ethers have been determined. For each pair the *trans* isomer rearranged faster than the *cis* isomer. These results suggest that the transition state of the Claisen rearrangement has a preferred conformation I in which the atoms most intimately involved in the reaction have a spatial relationship vaguely resembling that of the chair form of the cyclohexane ring.

Introduction

Ever since Claisen's studies in the early 1900's on the rearrangement which bears his name, much interest has been shown in the nature of the transition state and the intermediates leading to the products of this reaction. Claisen,[4] in 1925, on the basis of extensive studies, suggested a possible mechanism:

> Der Vorgang würde dann folgender sein: In dem Masse, wie durch die sich erhöhende Temperatur der Zusammenhang zwischen dem Allyl und dem Sauerstoff gelockert und schliesslich, bei einem bestimmten Temperaturgrad, ganz aufgehoben wird, tritt durch gleichzeitig erfolgenden Bindungswechsel im Kern, eine neue Valenz am Orthokohlenstoffatom hervor, von der das Allyl im selben Augenblick, wo es sich von dem Sauerstoff völlig ablöst, an dem räumlich am nächsten gelegenen γ-Kohlenstoffatom erfasst wird. Damit tritt auch der Grund für die Verschiebung der Doppelbindung im Allyl von β,γ nach α,β klar hervor. Nach erfolgtem Eintritt des Allyls in den Kern schnellt dann das System aus der ketoniden Form wieder in die phenolide zurück.

This postulation has been shown to be correct in all its details.

Thus the Claisen rearrangement[5] (eq. 1) has been shown to be kinetically first order, unimolecular,

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[1] This investigation was supported by a research grant NSF-G7345 from the National Science Foundation.

[2] National Science Foundation Predoctoral Fellow, 1958–1960.

[3] From the thesis submitted by Bruce E. Norcross in partial fulfillment of the requirements for the Doctor of Philosophy Degree at The Ohio State University.

[4] L. Claisen and E. Tietze, *Ber.*, **58B**, 275 (1925).

[5] For excellent reviews on this subject see: D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc.,