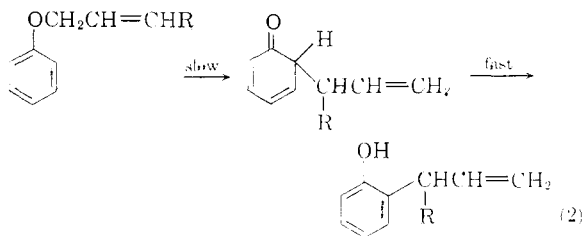broken. Were this the case, cis-γ-methylallyl phenyl ether might be expected to undergo partial conversion to its trans isomer during Claisen rearrangement. This does not happen.[27]

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 $k_1 k_3/(k_{-1} + k_3)$. That is, k is a satisfactory measure of the magnitude of k_1 (the rate constant of primary interest in this investigation) only when $k_{-1} \ll k_3$. Also the rate constant k for formation of phenolic product from the cis-ether is related to

(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.

(3)
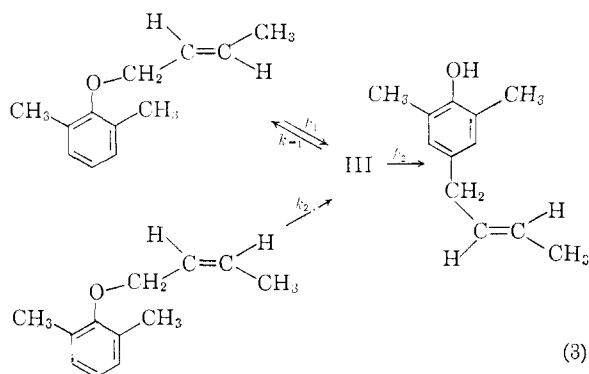
the concentrations of cis (C) and trans (T) ether and to their sum (E) in the reaction mixture at any time by the expression

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

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.

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]

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 Zusammen-

hang 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 Ortho-kohlenstoffatom 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,

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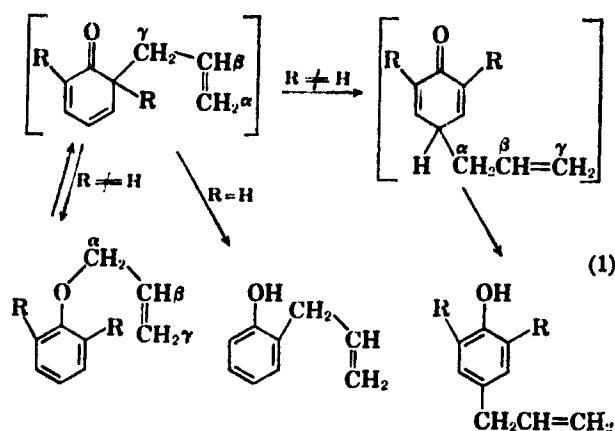
(5) For excellent reviews on this subject see: D. S. Tarbell in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc.,

(1)

intramolecular, and to involve the indicated inversion of the allyl side chain. The intermediate has been trapped from the reaction mixture and synthesized independently in some cases in which R ≠ H.

However, Claisen's mechanism, while grossly describing the over-all aspects of the transition state, does not define the geometrical relationships of the rearranging atoms. In the closely related para-Claisen rearrangement (eq. 1, R ≠ H), the suggestion[6] has been made that in the transition state, the carbon atoms of the side chain must lie in a plane parallel to that of the ring system, in order to allow the two carbon atoms becoming bonded to each other to be within bonding distance. For the ortho-rearrangement transition state[7] molecular models show that two different extreme conformations are available to the allyl fragment. One conformation (I)[8] has the α-carbon of the allyl side chain superimposed over the oxygen atom

I*   II*
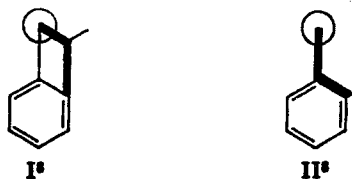
of the aromatic nucleus, and the γ-carbon atom over the ortho position to which it will become attached, while the β-carbon atom is directly over no atom of the benzenoid nucleus. In the other (II), however, all three carbon atoms of the chain are directly superimposed over the atoms of the phenoxy group: α-carbon over the oxygen, β-carbon over the 1-carbon and α-carbon over the 2-carbon of the ring. Although this latter conformation involves strong steric repulsions, it might be preferred electronically if overlap of the p-orbitals on the β-carbon of the allyl group and the 1-carbon of the ring results in stabilization. It is

New York, N. Y., 1945, pp. 1–48; D. J. Cram in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 295–303; and E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, pp. 644–649.

(6) S. J. Rhoads, R. Raulins and R. D. Reynolds, J. Am. Chem. Soc., 76, 3456 (1954).

(7) W. N. White, D. Gwynn, R. Schlitt, C. Girard and W. Fife, ibid., 80, 3271 (1958).

(8) In this representation, a heavy angular line is used to indicate the allyl side chain which is in a plane above and nearly parallel to that of the benzene ring.

the purpose of this research to distinguish experimentally between these two possible transition state conformations.

This distinction can, in principle, be made by a kinetic study of a series of cis- and trans-γ-substituted allyl aryl ethers. If conformation I best represents the transition state, then one would

I (trans)   II (trans)

I (cis)   II (cis)
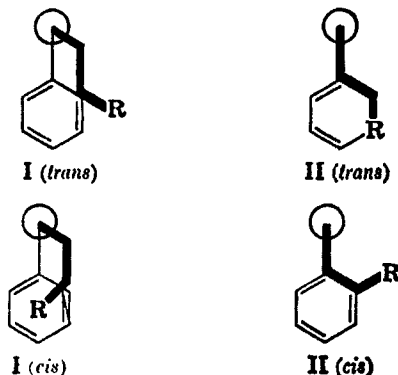
expect on the basis of potential steric hindrance in the transition state that the trans isomer would rearrange more rapidly than its cis isomer. Conversely, if II best represents the transition state, then the cis isomer would be expected to rearrange more rapidly than its trans partner.

Experimental

Preparation of trans-γ-Methylallyl Aryl Ethers.—Crotyl alcohol, b.p. 120–121° (760 mm.), was prepared in 48.4% yield from crotonaldehyde and sodium borohydride.[9] Crotyl chloride, b.p. 84.0–85.0° (760 mm.), was prepared in 33% yield from crotyl alcohol.[10]

A mixture of 16.1 g. (0.18 mole) of crotyl chloride (trans-1-chloro-2-butene), 27.0 g. (0.20 mole) of potassium carbonate, 0.3 mole of substituted phenol and 200 ml. of dry acetone was refluxed for 10 hours. This slurry was cooled, treated with 200 ml. water, and extracted with three 100-ml. portions of ether. The combined ether extracts were washed with three 25-ml. portions of 10% aqueous sodium hydroxide, two 25-ml. portions of Claisen alkali,[11] three 25-ml. portions of saturated brine, then were dried over magnesium sulfate, and distilled.

trans-γ-Methylallyl p-methoxyphenyl ether, b.p. 87.5–88° (2 mm.), was obtained in 72% yield.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.99; H, 7.93.

trans-γ-Methylallyl 3,5-dimethylphenyl ether, b.p. 82.5–83.0° (2 mm.), was obtained in 34% yield.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.97; H, 9.15.

Preparation of cis-γ-Methylallyl Aryl Ethers.—A mixture of 0.25 mole of substituted phenol, 41.6 g. (0.35 mole) of propargyl bromide (3-bromopropyne), 48.3 g. (0.33 mole) of potassium carbonate and 200 ml. of dry acetone was refluxed for 10 hours. This slurry was cooled, treated with 200 ml. of water, and extracted with three 100-ml. portions of ether. The combined ether extracts were washed with three 25-ml. portions of 10% aqueous sodium hydroxide, three 25-ml. portions of saturated brine, then dried over magnesium sulfate, and distilled to yield a propargyl aryl ether.

2-Propynyl p-methoxyphenyl ether,[12] b.p. 84–85° (2 mm.), was obtained in 54% yield.

(9) S. W. Chaikin and W. G. Brown, J. Am. Chem. Soc., 71, 122 (1949).

(10) L. F. Hatch and S. S. Nesbitt, ibid., 72, 727 (1950).

(11) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Edition, D. C. Heath and Co., Boston, p. 310.

(12) Ether radicals named according to rule 55.1, Comptes Rendus de la Quinsieme Conference, Union Internationale de Chimie Pure et Applique, September, 1949.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.20; H, 6.41.

2-Propynyl 3,5-dimethylphenyl ether, b.p. 72–73° (1.5 mm.), was obtained in 93% yield.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.67; H, 7.85.

To a solution of 0.23 mole of sodium amide from the reaction of 5.4 g. (0.23 mole) of sodium with 500 ml. of liquid ammonia[13] was added rapidly 0.07 mole of a 2-propynyl aryl ether in 50 ml. of dry ether. This solution was stirred for 5 minutes; then 33.2 g. (0.23 mole) of methyl iodide in 50 ml. of dry ether was added dropwise over a period of 1 hour, and the solution was stirred for 4 hours (2 hours at Dry Ice-acetone-bath temperatures, followed by 2 hours at the reflux temperature of ammonia). To this solution was added 100 ml. of dry ether, after which the ammonia was driven off by heating to ether reflux. The ether solution of 2-butynyl aryl ether was washed with three 50-ml. portions of 5% aqueous hydrochloric acid, two 50-ml. portions of 10% aqueous sodium hydroxide, two 50-ml. portions of saturated brine, dried over magnesium sulfate, and distilled.

2-Butynyl *p*-methoxyphenyl ether, b.p. 101–103.5° (1.5 mm.), was obtained in 61% yield.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.81; H, 7.01.

2-Butynyl 3,5-dimethylphenyl ether, b.p. 92–93° (1.5 mm.), was obtained in 59% yield.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.74; H, 8.08. Found: C, 82.68; H, 7.95.

To a solution of 10 g. of 2-butynyl aryl ether in 200 ml. of Skellysolve B was added 0.5 g. of Lindlar catalyst.[14] This mixture was allowed to absorb the calculated stoichiometric quantity of hydrogen at atmospheric pressure and room temperature. After being filtered to remove the Lindlar catalyst, the solution was distilled to yield the desired *cis*-α-methylallyl aryl ether.

cis-γ-Methylallyl *p*-methoxyphenyl ether, b.p. 88.0–89.0° (1 mm.), was obtained in 81% yield.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.14; H, 8.15.

cis-γ-Methylallyl 3,5-dimethylallylphenyl ether, b.p. 78–79° (2 mm.), was obtained in 75% yield.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.01; H, 9.14.

Preparation of *trans*-γ-Phenylallyl Aryl Ethers.—Cinnamyl bromide, b.p. 88–92° (1.5 mm), was obtained in 70% yield from dry hydrogen bromide and cinnamyl alcohol by the method of Fife.[15]

A mixture of 23.5 g. (0.12 mole) of cinnamyl bromide (1-phenyl-3-bromopropene), 27.6 g. (0.20 mole) of potassium carbonate, 0.20 mole of substituted phenol and 500 ml. of dry acetone was refluxed for 10 hours. This slurry was cooled, treated with 500 ml. of water, and extracted with three 100-ml. portions of ether. The combined ether extracts were washed with three 75-ml. portions of 10% aqueous sodium hydroxide, three 75-ml. portions of saturated brine, then dried over magnesium sulfate, and evaporated to dryness. The solid ethers were recrystallized to constant melting point.

trans-γ-Phenylallyl *p*-methoxyphenyl ether, m.p. 107.0–107.8° (from Skellysolve B and benzene), was identical to a sample previously synthesized by Fife.[7]

trans-γ-Phenylallyl 3,5-dimethylphenyl ether, m.p. 63.0–63.8° (from Skellysolve F), was obtained in 39% yield.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.69; H, 7.61. Found: C, 85.73; H, 7.53.

Preparation of *cis*-γ-Phenylallyl Aryl Ethers.—Dibromocinnamic acid, m.p. 199–210°, prepared[16] in 97% yield, was converted[17] to phenylpropiolic acid, m.p. 136–138°, in 67% yield. This acid was then esterified,[18] using forcing

azeotropic conditions, to yield ethyl phenylpropiolate, b.p. 150–153° (16 mm.), in 92% yield. This ester was then reduced to α-phenylpropargyl alcohol (1-phenyl-1-propyne-3-ol), b.p. 90–92° (1 mm.), in 75% yield with lithium aluminum hydride at low temperatures.[19] This acetylenic carbinol was converted[20] to γ-phenylpropargyl bromide, b.p. 78–80°(1 mm.), in 58% yield.

A mixture of 30.0 g. (0.154 mole) of γ-phenylpropargyl bromide, 34.5 g. (0.25 mole) of potassium carbonate, 0.25 mole of substituted phenol and 400 ml. of acetone was refluxed for 10 hours. This slurry was cooled, treated with 400 ml. of water, and extracted with three 150-ml. portions of ether. The combined ether extracts were washed with three 50-ml. portions of saturated brine; dried over magnesium sulfate, and either distilled or evaporated to yield a 3-phenyl-2-propynyl aryl ether.

3-Phenyl-2-propynyl *p*-methoxyphenyl ether, m.p. 76.4–77.6° (from methanol), was obtained in 86% yield.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.91; H, 6.13.

3-Phenyl-2-propynyl 3,5-dimethylphenyl ether, b.p. 162–164° (1.5 mm.), was obtained in 85% yield.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.18; H, 7.12.

To a solution of 10 g. of 3-phenyl-2-propynyl aryl ether in 200 ml. of Skellysolve B was added 0.5 g. of Lindlar catalyst.[24] This mixture was allowed to absorb the calculated stoichiometric quantity of hydrogen at atmospheric pressure and room temperature. After being filtered to remove the Lindlar catalyst, the solution was distilled to yield the desired *cis*-α-phenylallyl aryl ether.

cis-γ-Phenylallyl *p*-methoxyphenyl ether, b.p. 154–155° (1.5 mm.), was obtained in 78% yield.[21]

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.15; H, 6.98.

cis-γ-Phenylallyl 3,5-dimethylphenyl ether, b.p. 148–148.2° (1 mm.), was obtained in 82% yield.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.69; H, 7.61. Found: C, 85.67; H, 7.78.

Isolation of Rearrangement Products.—In the cases of those allyl aryl ethers used in this study which had not been previously shown to yield the expected phenols on thermal rearrangement, large scale rearrangements were made in diphenyl ether in order to isolate and characterize the phenol produced. In general, 2 g. of the allyl aryl ether was dissolved in 20 g. of pure diphenyl ether, placed in a thick-walled 20 × 150 mm. lip-less Pyrex test-tube equipped with a sealed-on piece of 6 mm. glass tubing, degassed by repeated freezing and thawing under vacuum, and sealed under vacuum. These sealed tubes were then heated for 24 hours in boiling ethylene glycol (b.p. 195–197°), cooled, and opened. The resulting reaction mixture was treated in one of two ways, A or B, in order to obtain the product phenol.

In method A, the diphenyl ether solution was diluted by an equal volume of diethyl ether, and extracted with four 10-ml. portions of Claisen alkali. This basic solution was then extracted with three 10-ml. portions of ether to remove the diphenyl ether soluble in the methanolic alkali. The Claisen alkali solution was then neutralized, with cooling, with concentrated hydrochloric acid, and extracted with four 15-ml. portions of ether. The ether solution was then dried over magnesium sulfate, and either distilled or evaporated to dryness and the resulting solid phenol recrystallized. The major difficulty in this method was in obtaining pure phenol, uncontaminated by traces of diphenyl ether.

In method B, the diphenyl ether solution was diluted by an equal volume of Skellysolve B, and chromatographed through a 25 × 190 mm. column of Woelm I alumina, using a graded series of solvents to elute the phenol. The diphenyl ether came off the column very readily with pure

(13) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworth Scientific Publications, London, 1955, p. 193.

(14) (a) H. Lindlar, U. S. Patent 2,681,938; (b) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(15) W. Fife, Ph.D. Dissertation, The Ohio State University, 1960.

(16) M. Reiner, *J. Am. Chem. Soc.*, **64**, 2510 (1942).

(17) R. V. Paulson and W. S. MacGregor, *ibid.*, **73**, 679 (1951).

(18) W. Haerst and J. F. Thorpe, *J. Chem. Soc.*, **127**, 1245 (1925).

(19) E. B. Bates, E. R. H. Jones and M. C. Whiting, *ibid.*, 1854 (1954).

(20) (a) M. Tchao Yin Lai, *Bull. soc. chim.*, **53**, 1533 (1933); (b) M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

(21) Although the Lindlar catalyst has been reported to yield only *cis*-olefins from acetylenes, the remaining 22% of this reaction was the solid *trans* isomer. Successive attempts to isolate more *cis*-ether, using smaller quantities of catalyst, resulted in the isolation of *only* *trans* isomer.

TABLE I
PRODUCTS OF REARRANGEMENT

Phenol	Method	Yield, %	B.p. (mm.) or m.p., °C.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
2-(α-Methylallyl)-4-methoxy-	A	54	100–104 (2)	74.13	74.19	7.92	7.83
2-(α-Phenylallyl)-4-methoxy-	B	55	81.0–82.3	79.97	80.08	6.71	6.84
2-(α-Methylpropenyl)-3,5-dimethyl-	B	35	78.5–79.3	81.77	81.55	9.15	9.05
2-(α-Phenylpropenyl)-3,5-dimethyl-	A	45	86.6–87.2	85.69	85.98	7.61	7.5
	B	83					

TABLE II
DILATOMETER READINGS DURING REARRANGEMENT OF cis-γ-METHYLALLYL p-METHOXYPHENYL ETHER[a]

t[b]	H[c]	t[b]	H[c]	t[b]	H[c]
70	203.7	195	174.6	849	107.6
78	202.6	199	175.6	862	108.0
83	201.2	204	174.8	886	106.4
87	199.6	219	170.2	904	105.7
92	198.8	245	166.2	928	104.1
96	197.3	263	162.3	945	102.3
106	196.1	279	159.8	981	102.3
120	192.8	293	156.6	1007	100.8
133	189.7	312	153.2	1016	100.6
144	187.3	..	...	1043	98.2
156	184.8	837	108.1	1049	99.4
165	182.3	842	107.4	1062	98.2

[a] Run 61, $T = 207.19°$. [b] t in minutes. [c] H is height of liquid in dilatometer in mm.

TABLE III
APPLICATION OF GUGGENHEIM METHOD TO RATE DATA FOR cis-γ-METHYLALLYL p-METHOXYPHENYL ETHER[a]

H_1[b]	H_2[b,c]	$H_1 - H_2$	log $(H_1 - H_2)$	t_1[d]
204.6	106.2	98.4	1.9930	70
196.7	104.7	92.0	1.9638	100
189.8	103.4	86.4	1.9370	130
182.9	102.2	80.7	1.9069	160
176.4	101.0	75.4	1.8774	190
170.3	99.9	70.4	1.8476	220
164.6	98.9	65.7	1.8176	250

[a] Run 61, $T = 207.19°$, $k = 3.78 \times 10^{-5}$ sec.$^{-1}$. [b] Dilatometer reading in mm. [c] Δt between H_1 and H_2 was 800 min. [d] t_1 in min.

constant. A typical kinetic run is summarized in Tables II and III.

Rate data and kinetic parameters are summarized in Table IV.

TABLE IV
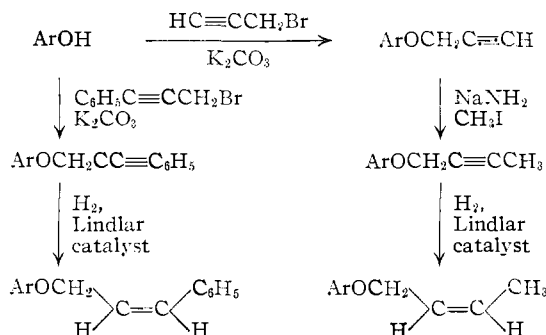SUMMARY OF KINETICS OF REARRANGEMENT OF cis- AND trans-γ-SUBSTITUTED ALLYL ARYL ETHERS

Substituents Ring	Chain	T, °C.	$k \times 10^5$, sec.
p-CH$_3$O	trans-γ-CH$_3$	184.99	2.24
		197.14	4.12
		200.27	4.98
		208.50	6.20
		209.16	6.62
		219.40	11.9
p-CH$_3$O	cis-γ-CH$_3$	200.11	2.40
		208.55	3.78
		219.40	5.61
p-CH$_3$O	trans-γ-C$_6$H$_5$	176.96	3.35
		184.54	6.88
		186.73	7.58
p-CH$_3$O	cis-γ-C$_6$H$_5$	183.54	3.44
		196.96	7.96
		208.55	22.4
3,5-(CH$_3$)$_2$	trans-γ-CH$_3$	200.20	4.96
		208.41	7.46
		229.74	19.6
3,5-(CH$_3$)$_2$	cis-γ-CH$_3$	208.66	3.96
		219.43	7.64
		229.73	14.1
3,5-(CH$_3$)$_2$	trans-γ-C$_6$H$_5$	184.90	4.98
		197.12	7.63
		217.88	17.5
3,5-(CH$_3$)$_2$	cis-γ-C$_6$H$_5$	208.66	4.56
		208.46	4.88
		219.48	7.53
		229.77	18.1

Skellysolve B. Generally a mixture of benzene and 10% methanol was required to remove the phenols from the column. These phenols could be readily followed on the column by their dull blue ultraviolet fluorescence. The physical properties, yields and analytical data of the phenols are summarized in Table I.

The products derived from γ-methylallyl and γ-phenylallyl 3,5-dimethylphenyl ethers were shown to be the o-propenyl phenols, rather than the o-allyl phenols, by their absorption in the 960–970 cm.$^{-1}$ region which is indicative of an internal double bond,[22] and the absence of any absorption in the 885–895 cm.$^{-1}$ region which is indicative of a terminal olefin.[22]

Kinetic Measurements.—Two dilatometers, A and B, were constructed as described by Goering and Jacobson.[23] Dilatometer B had a capillary volume about two-thirds that of A, and the same total volume as that of A. This feature allowed checks to be run on solutions of varying concentrations.

The constant temperature bath was also patterned after that of Goering and Jacobson,[23] and was capable of maintaining the temperature within 0.003°. However, initial experiments indicated that temperature fluctuations were introduced by the raising of the wooden door in the side of the insulated box. Therefore, the door was modified by introduction of a glass-ended rectangular tunnel, 12 inches by 2 inches, which permitted direct observation of the bath interior.

Concentrations of the allyl aryl ethers were adjusted to between 0.05 and 0.15 M to give a volume change corresponding to a decrease of about 20 cm. in the height of the meniscus in the dilatometer capillary. This decrease in height was measured with a cathetometer on an arbitrary scale.

Specific first-order rate constants were determined by first plotting meniscus height against time and smoothing the curve. At convenient time intervals, points were picked from this smooth decay curve, and Guggenheim's procedure[24] was applied to these to obtain a first-order plot and rate

(22) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34 ff.

(23) H. L. Goering and R. R. Jacobson, J. Am. Chem. Soc., 80, 3277 (1958).

(24) (a) E. A. Guggenheim, Phil. Mag., 2, 538 (1926). (b) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, 1953, pp. 48–49.

Results

The compounds chosen for this study were cis- and trans-crotyl 3,5-dimethylphenyl and p-methoxyphenyl ethers, and cis- and trans-cinnamyl 3,5-

dimethylphenyl and *p*-methoxyphenyl ethers.[25] The *trans*-crotyl compounds were synthesized by the reaction of the substituted phenol and crotyl chloride. The ethers were purified until there was no infrared absorption in the 885–895 cm.$^{-1}$ region, indicative of terminal olefin bonds.[22] However, they did show absorption in the 960–970 cm.$^{-1}$ region, indicating the presence of a 1,2-disubstituted *trans* double bond.[22] The *trans*-cinnamyl ethers were synthesized using *trans*-cinnamyl bromide and the substituted phenols, and were subjected to the same spectral criteria as the crotyl ethers.

Both *cis* series were synthesized by a similar route whose final step was the partial hydrogenation of an acetylene using Lindlar catalyst. These *cis*-olefins were then fractionated and scrutinized by

$$\text{ArOH} \xrightarrow[\text{K}_2\text{CO}_3]{\text{HC} \equiv \text{CCH}_2\text{Br}} \text{ArOCH}_2\text{C} \equiv \text{CH}$$

$$\left\downarrow \begin{array}{c} \text{C}_6\text{H}_5\text{C} \equiv \text{CCH}_2\text{Br} \\ \text{K}_2\text{CO}_3 \end{array} \right. \qquad \left\downarrow \begin{array}{c} \text{NaNH}_2 \\ \text{CH}_3\text{I} \end{array} \right.$$

$$\text{ArOCH}_2\text{CC} \equiv \text{C}_6\text{H}_5 \qquad\qquad \text{ArOCH}_2\text{C} \equiv \text{CCH}_3$$

$$\left\downarrow \begin{array}{c} \text{H}_2, \\ \text{Lindlar} \\ \text{catalyst} \end{array} \right. \qquad\qquad \left\downarrow \begin{array}{c} \text{H}_2, \\ \text{Lindlar} \\ \text{catalyst} \end{array} \right.$$

$$\begin{array}{c} \text{ArOCH}_2 \\ \diagdown \\ \text{H} \end{array} \diagup C = C \diagdown \begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{H} \end{array} \qquad \begin{array}{c} \text{ArOCH}_2 \\ \diagdown \\ \text{H} \end{array} \diagup C = C \diagdown \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{H} \end{array}$$

infrared analysis (*no* absorption in the 960–970 cm.$^{-1}$ region, but absorption in the 1295–1310 cm.$^{-1}$ region, indicative of a *cis*-1,2-disubstituted olefin[22]). The entire infrared spectra of a *cis–trans* pair were generally completely identical except for the specific *cis* and *trans* peaks.

The substituted allyl aryl ethers in diphenyl ether solution were heated in sealed tubes under the conditions used in the kinetic studies, and the base-soluble fraction isolated. In the *p*-methoxyphenyl series, the products of rearrangement were shown to be the expected *o*-allylphenols. In the 3,5-dimethylphenyl series, however, the products were the conjugated *o*-propenylphenols. The *o*-propenylphenols were distinguished from the *o*-allylphenols by the lack of infrared absorption in the 885–895 cm.$^{-1}$ region characteristic of a terminal double bond,[22] and the appearance of absorption in the 960–970 cm.$^{-1}$ region, characteristic of internal double bonds.[22]

Kinetics of rearrangement of *cis*- and *trans*-crotyl 3,5-dimethylphenyl ethers, *cis*- and *trans*-crotyl *p*-methoxyphenyl ethers, *cis*- and *trans*-cinnamyl 3,5-dimethylphenyl ether, and *cis*- and *trans*-cinnamyl *p*-methoxyphenyl ether were determined dilatometrically. The rate constants are summarized in Table IV.

The maximum error in the determination of these rate constants by the dilatometric method was estimated to be about 10%. Application of the equations of Purlee, Taft and DeFazio[26] to the

(25) The unsubstituted phenyl ethers were not used because preliminary experiments indicated that easily measurable reaction rates occurred at so high a temperature that side reactions introduced considerable error into the measurements.

(26) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *J. Am. Chem. Soc.*, **77**, 837 (1955).

data in Table IV show that the statistical error in $\Delta H^{\neq}$ would be about 9 kcal./mole and that in $\Delta S^{\neq}$ about 6 e.u./mole. The computation of these quantities would therefore be meaningless.

It is important to ascertain what effect the secondary isomerization of the allylphenols to the corresponding propenylphenols noted in the series of 3,5-dimethylphenyl ethers would have on the measured rate constants. Since the dilatometric procedure in this investigation depends upon differences in the relative partial molar volumes of the starting material and the product phenol, a comparison of the molar volumes of representative compounds allows an estimation of the effect of the double bond isomerization on the rate determination to be made. These comparisons show that the effect of double bond isomerization in the product results in a volume decrease as does the Claisen rearrangement. The effect of this on the measured rates would be to decrease the observed rate of reaction by increasing the final amount that the solution contracted in volume.

The possibility that *cis* to *trans* isomerization occurs preceding reaction must be eliminated. Burgstahler[29] reported that no *cis–trans* isomerization of a *cis* ether was observed when the ether was recovered after reaction had proceeded part way. In support of this, Marvell and Stephenson[30] report only a small percentage of *trans* ether formed after extensive Claisen rearrangements of a *cis* ether. However, more definite evidence is available in Table IV. If the *cis* to *trans* rearrangement were fast, followed by the rate-determining Claisen rearrangement of the *trans* ether formed, then both isomers of any pair would give the same rate constants. If, on the other hand, the *cis* to *trans* rearrangement were slow enough to be rate determining, then all *cis*-crotyl compounds should rearrange at the same rate, as should all *cis*-cinnamyl compounds, since the substitution on the aromatic nucleus should have no effect on this reaction, being not only removed sterically, but also isolated inductively by a methylene group in addition to the oxygen atom. If the *cis* to *trans* isomerization proceeded at some rate similar to that of the rearrangement of either the *cis* or *trans* ether, then the expression for the rate would be complex and linear first-order Guggenheim plots would not be obtained.

Discussion

The experimental approach used in this study to distinguish between Claisen rearrangement transition state conformations I and II depends on the creation of steric interaction of an alkyl substituent on the side chain with the bulk of the aromatic ring during the establishment of the rigid transition state. Thus, it is necessary to establish that the *o*-Claisen rearrangement is influenced by steric factors. In this regard, Alexander and Kluiber[27] have shown that there is an experimentally significant retention of optical activity in the rearrangement of (−)-*trans*-α,γ-dimethylallyl phenyl ether to 2-(α,γ-dimethylallyl)-phenol. Alexander and Kluiber,[28] and later Hart[29] interpreted the ob-

(27) E. R. Alexander and R. W. Kluiber, *ibid.*, **73**, 4304 (1951).

served asymmetric induction in terms of steric crowding in the transition state. Burgstahler[29] put this notion on firmer grounds by demonstrating that the Claisen rearrangement of either cis- or trans-α,γ-dimethylallyl vinyl ether and trans-α,γ-dimethylallyl phenyl ether leads essentially to only trans products. These data indicate that the transition state orientation is strongly influenced by steric crowding. In a recent communication, Marvell and Stephenson[30] reported that the rearrangement of either cis- or trans-α,γ-dimethylallyl phenyl ether yielded at least 90% trans product and a small but significant amount of cis product.

As is obvious, both conformations I and II have the plane of the allyl side chain parallel to that of the benzene ring. The possibility of conformations in which the plane of the allyl chain is not parallel to the aromatic system needs to be taken into consideration. As these two planes become progressively more non-parallel, the terminal substituents on the double bond of the allyl side chain become more interposed between the ortho-carbon atom (or its attached substituent) and the γ-carbon atom of the chain. This forces these two atoms which must become bonded to each other further apart. Even when the substituents are hydrogen atoms, the two carbons are not able, in this conformation, to approach within bonding distance of each other. Furthermore, the orbital being formed at the α-carbon atom of the allyl chain by breaking of the C–O bond will be orthogonal to and thus not overlap with the double bond orbital at the β- and γ-atoms. On the basis of these considerations, transition state conformations in which the planes of the allyl group and the aromatic ring deviate considerably from parallelism seem unlikely as possibilities for the transition state of the Claisen rearrangement.

If steric interactions in the transition state were the only factors influencing the rate of the Claisen rearrangement then the steric effect of cis and trans isomerism on the rates of rearrangement could be predicted according to whether conformation I or II best represented the transition state. As shown in Fig. 2, if conformation II best represented the transition state, then the steric interference in the transition state presented by the trans isomer's substituents would result in the cis isomer rearranging more rapidly than the trans. However, if the conformation was best represented by I, Fig. 2, then the transition state of the trans isomer would be less hindered than that of the cis isomer and thus the trans isomer would rearrange more rapidly.

These considerations neglect the nature of the initial state. In the substituted allyl phenyl ethers, the ground state conformation may be assumed to resemble in a general way the trans conformation of n-butane, in which the bulky groups are as far from one another as is possible.[31]

The amount of skew, or highly hindered, conformation of n-butane at 180° is 0.3%. This was estimated using the procedure given on p. 26 of ref. 31. In the substituted allyl aryl ethers, the percentage of the conformation corresponding to the even more hindered transition state would be considerably less. This amount is so low that it cannot affect the rate of reaction or the activation parameters determined for the rearrangement since the initial state of the ether consists for all practical purposes of conformations not resembling the transition state. The large negative entropies of activation usually observed for the Claisen rearrangement indicate that the change from initial to transition state involves a change from molecules with a favorable conformation to transition states with an unfavorable one. Thus, the conformational population of the initial state of the allyl aryl ether is such as to be without influence on the conclusions reached by consideration of steric effects on the transition states alone.

The ground states of cis- and trans-γ-substituted allyl aryl ethers will differ in energy approximately in the same way that simple cis and trans aliphatic and aromatic compounds have been shown to differ by means of heat of hydrogenation measurements. However, this energy difference will probably still persist in the transition state.

Thus, the effect of cis–trans isomerism on the rates of rearrangement of the γ-substituted ethers may be predicted from a consideration of the possible transition state conformations. In order to do this, four theoretically possible cases should be considered. (The term "energy" in the following discussion refers to free energy.)

A. Case I: Conformation II (Fig. 2) represents the transition state. In this situation the cis isomers would be expected to react the faster because of their less hindered transition states.

B. Case II: Conformation I (Fig. 2) represents the transition state. If this is so, then the unhindered transition state for the trans isomer would be sterically favored, and the trans isomer would react fastest.

C. Case III: Conformation I is preferred energetically but conformation II can be attained under conditions particularly unfavorable for I. In this case, the trans isomers will react through favored transition state I which is also less hindered, but the cis isomers will react for steric reasons through the ordinarily energetically unfavorable transition state II because it is less hindered. Even though steric interactions would be decreased in this way the energy requirements for reaction of the cis isomer would be higher than for the trans isomer so the cis isomer would react the slowest.

D. Case IV: Conformation II is preferred energetically, but conformation I can be attained under conditions unfavorable for II. In this case, the cis isomer can assume favored conformation II without any severe steric interactions and thus would react through transition state II. However, the trans isomers cannot get into conformation II with-

(28) H. Hart, J. Am. Chem. Soc., 76, 4033 (1954).

(29) (a) A. W. Burgstahler, Abstracts of Papers, 137th Meeting of the American Chemical Society, April 5–14, 1960, p. 1960; (b) A. W. Burgstahler, J. Am. Chem. Soc., 82, 4681 (1960).

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

(31) W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, 1956, pp. 7 ff.

out introducing strong non-bonding interactions into the system. Thus, the *trans* isomers will react through energetically unfavorable transition state I. The *trans* isomers would react more slowly than the *cis* isomers in this situation.

As can be seen from Table IV, for each *cis–trans* pair studied, the *trans* isomer rearranges more rapidly than its *cis* isomer. This indicates that case II or case III (above) describes the mechanistic situation. In each of these cases conformation I, the "elbowed-out" or "chair-form" conformation, is the preferred one for Claisen rearrangement.

In the case of the 3,5-dimethylphenyl ethers, an isomerization of the terminal double bond into conjugation with the aromatic ring is apparently occurring at the temperatures necessary for measurable rates. However, even for these pairs of isomers which apparently represent a more complicated kinetic situation, the rate relationship of *trans* and *cis* isomers is maintained (the *trans* isomers rearrange faster than the *cis* isomers).

These results indicate that of the four theoretical possibilities initially discussed, only those two involving conformation I as the preferred one for the transition state of the Claisen rearrangement may be considered. The data cannot be interpreted so as to differentiate between the possibility that all compounds react by conformation I (case II) and the alternative possibility that in a highly hindered environment, the transition state may be forced to take on the unpreferred conformation II (case III).

Thus, the rate data on the rearrangement of *cis*- and *trans*-γ-substituted allyl aryl ethers support acceptance of conformation I, the "elbowed-out" or "chair-form" conformation, as the preferred representation of the transition state of the Claisen rearrangement.

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Some Chemistry of [2.2]Metacyclophane. A Transannular Electrophilic Aromatic Substitution Reaction[1]

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The position at which an aromatic ring of [2.2]metacyclophane would be expected to undergo nitration was calculated using the method of partial rate factors to account for the effect of the side chains, and using the molecular orbital method to account for the effect of the other ring. Instead of the predicted product, there was isolated from the reaction a pyrene derivative which resulted from a simultaneous nitration and transannular ring closure of the forming aromatic carbonium ion. Other physical and chemical properties of the [2.2]metacyclophane are reported.

[2.2]Metacyclophane (I) was first prepared in 1899,[2] and its structure has been established beyond doubt, both by classical methods of organic chemistry,[2,3] and by X-ray crystallography.[4] Since the latter work has revealed the exact molecular structure, the compound furnishes an excellent case for the study of transannular resonance effects. These effects lead to results which can be both calculated theoretically and determined experimentally. A number of theoretical and experimental studies have been carried out in the past which were directed at the detection of transannular resonance.[5] In the present work the goal has been: first, by applications of the available theory, to reach some conclusions concerning the properties of [2.2]-metacyclophane; second to test these conclusions experimentally; and third, as it turns out, to reconcile the results.

The synthesis of [2.2]metacyclophane (I) has been improved considerably over that described in the literature.[3] Upon treating *m*-xylidene dibromide with phenyllithium under conditions of moderate dilution, a mixture of reaction products was obtained from which it was possible to isolate I in a yield of 39%.[6]

The theoretical studies were made in part on the basis of the simple molecular orbital theory, using certain approximations. Only the twelve π-electron system was considered initially. The resonance integrals were taken as equal to β for adjacent atoms in the same ring, and zero otherwise except for the one between carbons 8 and 16.[7] From the crystal structure[4] it is known that the benzene rings are approximately planar, and carbons 8 and 16 are separated by 2.689 Å. and have the axes of their *p*-orbitals colinear (from scale drawings). The magnitudes of both the 2pσ Slater and SCF overlap integrals for the system were estimated. Using the formula[8] $H_{ij} = 0.773 \beta (S_{ij}/1 + S_{ij})/(S/1 + S)$, where i and j refer to the pair of atoms in question, and S and $β$ are the values for benzene, the numerical value for the 2pσ exchange integral between carbons 8 and 16 was found to be 0.308 β (SCF) or 0.221 β (Slater). The other inter-ring exchange integrals were taken as equal to zero. The overlap integrals were neglected, as were the effects of the side chains. The matrix corresponding to the secular equations of the twelve π-electron system was diagonalized with the aid of

(1) Supported by a research grant from the National Science Foundation.

(2) M. Pellegrini, *Rec. trav. chim.*, **18**, 457 (1899).

(3) W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.*, 1114 (1951).

(4) C. J. Brown, *ibid.*, 3278 (1953).

(5) For leading references, see (a) D. J. Cram and R. H. Bauer, THIS JOURNAL, **81**, 5971 (1959).

(6) While this kind of a "Wurtz" reaction is well known (see for example C. S. Marvel and B. D. Wilson, *J. Org. Chem.*, **23**, 1483 (1958), and references therein) it has been stated that Compound I was not to be obtained by this method.

(7) The numbering system shown for I follows the suggestions of D. J. Cram and J. Abell, THIS JOURNAL, **77**, 1179 (1955).

(8) (a) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952); *Rec. Chem. Prog.*, **13**, 67 (1952); (b) M. Simonetta and S. Winstein, THIS JOURNAL, **76**, 18 (1954).