Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.62. Found: C, 85.62; H, 7.46.

Benzoyl mesityl ketoxime. The nitrosation method of Weissberger and Glass[4] was followed using 4.75 g. (0.02 mole) of α-mesitylacetophenone and 1.5 g. (0.035 mole) of butyl nitrite. Benzoyl mesityl ketoxime was obtained as a white solid, m.p. 158–159° (from ethanol); yield 2.0 g. (37%).

Anal. Calcd. for $C_{17}H_{17}NO_2$: C 76.38; H 6.41; N, 5.24. Found: C, 76.92, 76.59; H, 6.45, 6.21; N, 5.32.

Reaction of benzoyl mesityl ketoxime with benzenesulfonyl chloride and base. The reaction was run in the manner described above using 0.9 g. (0.0033 mole) of benzoyl mesityl ketoxime, 0.73 g. (0.004 mole) of benzenesulfonyl chloride, and 0.66 g. (0.016 mole) of sodium hydroxide in 25 ml. of water. The ether extracts of the alkaline solution yielded a yellow oil which was chromatographed as before to yield 0.15 g. (31%) of mesitonitrile (identified by its infrared spectrum) and 0.4 g. (67%) of a solid, m.p. 127–129°, believed to be *benzoyl mesityl ketoxime benzoate.* Infrared bands: $\gamma_{C=O}$ 1650 cm.$^{-1}$,$\gamma_{C=O}$ 1745 cm.$^{-1}$ Recrystallization was effected from ethanol.

Anal. Calcd. for $C_{24}H_{21}NO_3$: C, 77.61; H, 5.70; N, 3.77; Found: C, 77.23, 77.65; H, 6.23, 6.18; N, 3.52.

Acidification of the alkaline solution yielded 0.05 g. (12%) of benzoic acid.

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The *ortho*-Claisen Rearrangement. VII. The Rearrangement of Allyl *p*-Tolyl-2,6-d_2 Ether[1]

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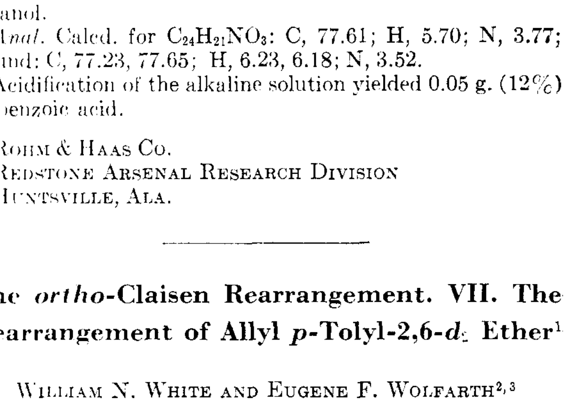
The sequence of reaction steps comprising the *ortho*-Claisen rearrangement is usually written as:



It has been suggested[4] that neither step 1 nor step 2 is reversible and that step 1 is slow and rate-determining. This appears to be an eminently reasonable assumption since enolization (step 2) is ordinarily a very facile reaction whereas the breaking and forming of carbon-oxygen and carbon-carbon bonds (step 1) does not occur so easily.[5] Indeed this has usually been tacitly assumed in the interpretation of kinetic studies of this reaction.[6,7] However, it was desirable to demonstrate that the above kinetic scheme is a true representation of the facts.

This demonstration could be accomplished by determining whether there was a kinetic isotope effect in the rearrangement of allyl *p*-tolyl-2,6-d_2 ether or whether isotope fractionation occurred in the rearrangement of a mixture of allyl *p*-tolyl-2,6-d_2 ether and ordinary allyl *p*-tolyl ether. A kinetic isotope effect would indicate that the step involving carbon-hydrogen bond breaking must determine, at least in part, the over-all rate of reaction. Isotope fractionation would occur if step 1 was reversible and step 2 was rate-controlling.

RESULTS AND DISCUSSION

Allyl *p*-tolyl-2,6-d_2 ether was prepared by a sequence of reactions starting with *p*-toluidine. A sample of *p*-toluidine was heated at 120° for ten hours with deuterium chloride in deuterium oxide. This treatment was repeated with a fresh portion of deuterium oxide four times. The deuterated toluidine was diazotized and the diazonium solution decomposed to yield *p*-cresol-2,6-d_2. The cresol was converted to allyl *p*-tolyl-2,6-d_2 ether by treatment with allyl bromide in the presence of potassium carbonate.

Combustion of the 3,5-dinitrobenzoate of the *p*-cresol-2,6-d_2 to water followed by reduction of the water to hydrogen and mass spectrometric analysis of the latter showed that the cresol contained 1.51 atoms of deuterium per molecule. A sample of the *p*-cresol-2,6-d_2 was brominated to 2,6-dibromo-*p*-cresol. A similar analysis of the 3,5-dinitrobenzoate of this substance revealed 0.003 atom of deuterium per molecule of 2,6-dibromo-*p*-cresol. This indicates that almost all of the deuterium was incorporated into the 2- and 6- positions of *p*-cresol.

The kinetics of rearrangement of allyl *p*-tolyl-2,6-d_2 ether and allyl *p*-tolyl ether were determined spectrophotometrically in carbitol as solvent. The specific rate constants for the rearrangement of these ethers at three temperatures are listed in Table I. The reactions were followed to 72–75% completion in each case, with seven points being determined in each run. The activation parameters were calculated by standard methods[8] and are also listed in Table I. Using the deviation listed for the individual rate constants, the mean statistical error

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(2) General Electric Foundation Fellow, 1960–61.

(3) From the thesis submitted by Eugene F. Wolfarth in partial fulfillment of the requirements for the Degree of Doctor of Philosophy at The Ohio State University.

(4) H. Schmid, *Helv. Chim. Acta*, **20**, 13 (1957).

(5) However, it has been shown that 6-allyl-2,6-dimethyl-2,4-cyclohexadienone rearranges with incredible ease to allyl 2,6-dimethylphenyl ether (the reverse of step 1) and 4-allyl-2,6-dimethylphenol [D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957)].

(6) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

(7) W. N. White and B. E. Norcross, *J. Am. Chem. Soc.*, **83**, 1968 (1961) and W. N. White and W. K. Fife, *J. Am. Chem. Soc.*, in press.

(8) A. A. Frost and R. G. Pearson, *Kinetics and Mechanisms*, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 95–97.

TABLE I

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REARRANGEMENT OF ALLYL *p*-TOLYL ETHERS

t°	Allyl *p*-Tolyl Ether $k \times 10^5$ sec.$^{-1}$	Allyl *p*-Tolyl-2,6-d_2 Ether $k \times 10^5$ sec.$^{-1}$
199.70 ± 0.1	15.73 ± 0.66	15.86 ± 0.14
180.30 ± 0.05	3.94 ± 0.05	4.08 ± 0.07
160.30 ± 0.05	0.784 ± 0.004	0.761 ± 0.007
$\Delta H^{\ddagger a}$	30.1	30.5
$\Delta S^{\ddagger b}$	−13.1	−12.3

[a] Kcal./mole. [b] Cal./deg./mole.

calculated[9] for the enthalpy and entropy of activation is ± 0.8 kcal./mole and ± 0.9 cal./deg./mole, respectively. Therefore, within the experimental error, the rate constants and activation parameters of the deuterated and nondeuterated allyl *p*-tolyl ethers are essentially identical. This indicates that the breaking of the *ortho* carbon-hydrogen bond is not kinetically important, and therefore, that the first step of the reaction is rate-determining. In the first step the *ortho* carbon changes in hybridization from sp^2 to sp^3, so a small secondary isotope effect was expected, but was not observed experimentally.

Further substantiation of the above conclusions was obtained from the observation that when a 1:3 mixture of allyl *p*-tolyl-2,6-d_2 ether and allyl *p*-tolyl ether was rearranged to the extent of 50%, no isotope fractionation occurred. This was proved by the identity of the infrared spectra of the original ether mixture and of the ether recovered from partial reaction.

It is therefore evident that equation (1) correctly represents the kinetic pattern of the *ortho* Claisen rearrangement.

EXPERIMENTAL

Preparation of p-cresol-2,6-d_2. A solution of 10 g. of *p*-toluidine (Eastman Kodak) in 25 cc. of concd. hydrochloric acid was placed in a 20 × 900-mm. heavy walled Pyrex combustion tube sealed at one end. Excess hydrochloric acid was removed by maintaining the tube at 50° and 4 mm. pressure overnight. To the dry amine salt was added 10 cc. of 99.7% deuterium oxide and the tube was sealed. The tube was thermostated at 120° for 10 hr. It has been shown[10] that at this temperature, equilibrium for the *ortho* positions is established in 6–8 hr. The water was removed under reduced pressure at 50° and the exchange repeated four more times.

The solid residue (*p*-toluidine-2,6-d_2 hydrochloride) was taken up in water and made slightly basic. The free amine was collected by filtration and dried. A solution of 10 g. (94 moles) of this amine in 300 cc. of water containing 12.4 g. (126 moles) of sulfuric acid was cooled to 3° with stirring. A solution of 7.2 g. (105 moles) of sodium nitrite in 15 cc. of water was added dropwise (a test for nitrous acid was obtained after 15 min.). Excess nitrous acid was destroyed by addition of 4 g. of urea. The diazonium solution was added to boiling water in a flask set up for rapid steam distillation. The addition was complete in 30 min. A total of 3 l. of distillate was collected. After salting out, the product was extracted with petroleum ether (b.p. 65–70°), dried over magnesium sulfate, and distilled. There was obtained *p*-cresol-2,6-d_2, b.p. 90–95° at 15 mm. in 66.5% yield.

Deuterium analysis. Using the procedure of Phillips and Keenan,[11] a small portion of the *p*-cresol-2,6-d_2 was converted to the 3,5-dinitrobenzoate, m.p. 184–188°, reported[11] 188.6°. After diluting with normal *p*-cresyl 3,5-dinitrobenzoate to give a deuterium content in the range of 0.6%, sufficient sample was burned in a modified combustion train to give 3–4 mg. of water. The water was collected in a 10-cm. length of 2-mm. glass tubing with the aid of a Dry Ice trap. The tubing was then sealed. The water was released into an evacuated break-seal tube containing 2–3 g. of zinc dust. This tube was heated at 400° for 4 hr. to reduce the water to hydrogen. The resulting gas was introduced into a mass spectrometer and the relative intensities of the H—H and H—D peaks determined. The spectrometer was calibrated with hydrogen gas of known deuterium content.

Anal. Calcd.: 0.576% D for 2.00 atoms D/molecule. Found: 0.434% D for 1.51 atoms D/molecule.

A small portion of the *p*-cresol-2,6-d_2 was dissolved in water and excess bromine added. The precipitated 2,6-dibromo-*p*-cresol was taken up in ether, dried over magnesium sulfate, and the solvent removed. The 3,5-dinitrobenzoate ester was prepared as before and recrystallized from 1:1 benzene–petroleum ether to yield colorless crystals, m.p. 219–220.1°.

Anal. Calcd. for $C_{14}H_8Br_2N_2O_6$: C, 36.55; H, 1.75; N, 6.09. Found: C, 36.54; H, 1.82; N, 5.98.

Combustion of the sample, reduction of the water produced, and mass spectrometric analysis showed there was 0.003 atom % excess deuterium per molecule. Thus essentially all the incorporated deuterium is located at the *ortho* positions.

Preparation of allyl p-tolyl ethers. Both the allyl *p*-tolyl- and allyl *p*-tolyl-2,6-d_2 ethers were prepared as described previously.[6] Immediately prior to the final distillation, the ethers were chromatographed on Woelm I alumina, using petroleum ether (b.p. 65–70°) as eluant.

Kinetic measurements. The rearrangement kinetics of these ethers were determined spectrophotometrically in carbitol solvent in exactly the same manner as described by White *et al.*[6]

Isotope fractionation study. A mixture of one part of allyl *p*-tolyl-2,6-d_2 ether and three parts of normal ether was prepared and its infrared spectrum determined with a Perkin-Elmer Model 21 spectrophotometer, using sodium chloride optics and a 0.03-mm. fixed cell. A portion of the mixture (1 g.) was dissolved in 10 cc. of carbitol, sealed in a Pyrex test tube, and heated at 180° for a period corresponding to one half-life. The quenched sample was taken up in 40 cc. of petroleum ether (b.p. 65–70°) and washed eight times with 30-cc. portions of water and then with 30 cc. of 10% sodium hydroxide. After a final wash with 30 cc. of brine, the petroleum ether solution was dried over magnesium sulfate, and the solvent was removed. The infrared spectrum, taken in the same fixed cell, was identical to that of the starting mixture, indicating that no measurable isotopic fractionation had occurred.

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