

The *ortho* Claisen Rearrangement. IX.
The Effect of Solvent on the Substituent Effect^{1,2}

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The rate of the *ortho* Claisen rearrangement is subject to both solvent^{1a,3} and substituent^{1a,d,e,h,3} effects. Electron-donating groups and polar solvents increase the rate of the reaction. In view of this sensitivity of the rearrangement to both solvent and structure, a determination of the relation of solvent change to substituent effect might permit conclusions about the rela-

interpolation and extrapolation and are shown in Table II. The rate constants were correlated by using Hammett's equation and σ^+ values. The reaction constants, ρ , in each solvent are included in Table II.

Table II shows that there is only a small change in ρ with solvent variations that produce an overall rate effect of 22- to 39-fold. This implies that the internal electronic demands of the reaction site on the substituents remains about the same in all solvents. Since solvent effects are intramolecular in nature while substituent effects are intramolecular and more closely associated with the reaction center, it might have been anticipated that medium effects on the reaction constant would not be large. The variation in ρ is in the direction expected—as solvent polarity increases and the energy of the transition state is lowered, a smaller stabilizing contribution from the substituents is required and so ρ is smaller.

TABLE I
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR REARRANGEMENT OF ALLYL *p*-X-PHENYL ETHERS

X	Solvent	$k \times 10^6$ (sec ⁻¹)		$\Delta H \pm \sigma, b$	$\Delta S \pm b, c$
		T_1	T_2		
NO ₂	Tetradecane	0.166 ± 0.002 ^d	0.972 ± 0.026 ^e	33.9	-10.5
	Carbitol ^f	1.03 ± 0.09 ^e			
	28.5% EtOH-H ₂ O	0.732 ± 0.012 ^h	4.09 ± 0.01 ⁱ	28.3	-15.6
Br	Tetradecane	0.439 ± 0.003 ^d	2.25 ± 0.05 ^e	30.5	-16.2
	Carbitol ^f	2.48 ± 0.06 ^e	9.46 ± 0.3 ^e	29.8	-14.8
	28.5% EtOH-H ₂ O	1.14 ± 0.03 ^h	6.11 ± 0.13 ⁱ	27.6	-16.4
CH ₃	Tetradecane	0.728 ± 0.002 ^f	3.30 ± 0.02 ^e	33.1	-9.8
	Carbitol ^f	4.71 ± 0.04 ^f	18.8 ± 0.2 ^e	30.3	-12.6
	28.5% EtOH-H ₂ O	2.23 ± 0.01 ^h	10.7 ± 0.3 ⁱ	26.2	-18.5
OCH ₃	Tetradecane	2.13 ± 0.01 ^d	11.8 ± 0.1 ^e	33.0	-7.7
	Carbitol ^f	8.66 ± 0.09 ^e	35.7 ± 0.1 ^e	29.9	-12.1
	28.5% EtOH-H ₂ O	5.82 ± 0.16 ^h	29.3 ± 0.1 ⁱ	26.5	-15.8

^a In kcal/mol. ^b The average deviation of ΔH is ±0.2 kcal/mol and that of ΔS is ±0.3 eu. ^c In cal/(deg mol). ^d $T = 177.7 \pm 0.1^\circ$. ^e $T = 199.7 \pm 0.1^\circ$. ^f EtOCH₂CH₂OCH₂CH₂OH. ^g $T = 180.9 \pm 0.1^\circ$. ^h $T = 170.7 \pm 0.1^\circ$.

TABLE II
RATES OF REARRANGEMENT OF ALLYL *p*-X-PHENYL ETHERS AT 181°

Solvent	$k \times 10^6$ (sec ⁻¹) ^a					
	NO ₂	Br	CH ₃	OCH ₃	ρ^b	r^c
Tetradecane	2.34	5.98	7.94	28.3	-0.67	0.97
Carbitol ^d	10.3	27.7	44.2	91.6	-0.61	0.99
28.5% EtOH-H ₂ O	90.9	134	233	621	-0.53	0.95

^a $T = 181.0^\circ$. ^b Reaction constant obtained with σ^+ values. ^c Correlation coefficient. ^d EtOCH₂CH₂OCH₂CH₂OH.

tive importance of solvent and substituents in stabilizing the transition state.

In order to investigate this problem, the rates of rearrangement of four allyl *p*-X-phenyl ethers in three solvents, tetradecane, carbitol, and 28.5% ethanol-water, were compared. The relevant experimental data are summarized in Table I. Rate constants at the common temperature of 181° were obtained by

(1) Previous papers in this series: (a) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Amer. Chem. Soc.*, **80**, 3271 (1958); (b) W. N. White and B. E. Norcross, *ibid.*, **83**, 1968 (1961); (c) *ibid.*, **83**, 3265 (1961); (d) W. N. White and W. K. Fife, *ibid.*, **83**, 3846 (1961); (e) W. N. White and C. D. Slater, *J. Org. Chem.*, **26**, 3631 (1961); (f) *ibid.*, **27**, 2908 (1962); (g) W. N. White and E. F. Wolfarth, *ibid.*, 3509 (1961); (h) W. N. White, C. D. Slater, and W. K. Fife, *ibid.*, **26**, 627 (1961); (i) W. N. White and E. F. Wolfarth, *ibid.*, **35**, 2196 (1970).

(2) This investigation was supported by Grants G-7345 and GP-1970 from the National Science Foundation.

(3) H. L. Goering and R. R. Jacobsen, *J. Amer. Chem. Soc.*, **80**, 3277 (1958).

Experimental Section

Preparation of Allyl *p*-X-Phenyl Ethers.—These compounds were prepared by the procedure previously described.^{1a} Immediately prior to final distillation, the allyl ether was dissolved in Skellysolve B and chromatographed on a column of activity grade I alumina using Skellysolve B as eluent. The solvent in the eluate was evaporated and the residue was distilled. The physical properties of the products agreed with those recorded in the literature.^{1a}

Solvents.—Tetradecane and carbitol were separately distilled through a 45-cm Vigreux column. Center cuts having boiling ranges of less than a degree were selected for the kinetic measurements. The 28.5% ethanol-water solvent was prepared by diluting 30.0 ml of absolute ethanol to 100.0 ml with water.

Kinetic Measurements.—The spectrophotometric procedure previously described^{1a} was employed.

Registry No.—Allyl *p*-nitrophenyl ether, 1568-66-7; allyl *p*-bromophenyl ether, 25244-30-8; allyl *p*-methylphenyl ether, 23431-48-3; allyl *p*-methoxyphenyl ether, 13391-35-0.