

TABLE I

Run No.	Solvent	Base		T , °C.	Yield, %	Net steric course
		Nature	Concn., N			
1	(CH ₃) ₂ COH	(CH ₃) ₃ COK	0.30	100	83	80% Ret.
2	<i>n</i> -C ₄ H ₉ OH	<i>n</i> -C ₄ H ₉ OK	0.30	100	72	68% Ret.
3	C ₂ H ₅ OH	C ₂ H ₅ OK	0.37	100	58	60% Ret.
4	CH ₃ OH	CH ₃ OK	0.30	100	73	44% Ret.
5	HOCH ₂ CH ₂ OH	HOCH ₂ CH ₂ OK	0.085-1.00	100	21-48	15-37% Ret.
6	H ₂ O	HOK	0.30-1.1-9.7	100	27-58	2% Inv.-10% Inv.-70% Ret.
7	(CH ₃) ₂ COH ^a	(CH ₃) ₃ COK	0.16	53	78	92% Ret.
8	(CH ₃) ₂ COH ^a	(CH ₃) ₄ N ⁺ OH ⁻	0.16	53	59	60% Ret.
9	HOCH ₂ CH ₂ OH ^b	HOCH ₂ CH ₂ OK	0.34	25	52	48% Ret.
10	HOCH ₂ CH ₂ OH ^b	(CH ₃) ₄ N ⁺ OH ⁻	0.34	25	50	46% Ret.
11	(CH ₃) ₂ SO	HOCH ₂ CH ₂ OK	0.088	53	51	37% Ret.
12	(CH ₃) ₂ SO	(CH ₃) ₄ N ⁺ OH ⁻	0.11	53	42	34% Ret.

^a Solutions 0.32 M in water. ^b Solutions 0.68 M in H₂O.

amide (+)-I, m.p. 112-112.2°, $[\alpha]_{546}^{25} +32.6^\circ$ (*c* 9, dioxane), was prepared from (+)-II, $[\alpha]_{546}^{25} +12.8^\circ$ (*l* = 1 dm., neat), by the usual method. Repeated recrystallization of grossly optically impure (-)-I from ether-pentane gave optically pure (-)-I, m.p. 112.5-113°, $[\alpha]_{546}^{25} -35.4^\circ$ (*c* 9, dioxane). These data relate the configurations and maximum rotations of starting materials and products in reactions (1), (2) and (3).

Cleavage of sulfonamide (+)-I without base at 100° in water, *t*-butyl alcohol or dimethyl sulfoxide gave completely racemic III. Results obtained in the presence of base are summarized in Table I. Except in ethylene glycol and water, base concentrations were reached where an increase in base did not change stereospecificity. In ethylene glycol, retention increased regularly as base was increased (run 5). In water, as base concentration increased, the reaction occurred first with increasing net inversion and then with increasing net retention (run 6).

Oxidation of II with potassium periodate under conditions of runs 1, 3 and 4 gave results within experimental error of the corresponding cleavages of I. In water, oxidation of II without base at 100° gave 100% racemization, whereas at 0.012 to 0.30 M base, 30-32% inversion was observed (compare with run 6).

Treatment of (-)-2-phenyl-2-butylamine *p*-toluenesulfonate (95°, 3 M solution of sodium hydroxide in 90% water-10% ethanol) with hydroxylamine-O-sulfonic acid⁶ gave III (10%) with 32% net retention. Cleavage of I under the average conditions of the above reaction gave III (83%) with 37% net retention. Oxidation of II under the same average conditions gave III (10%) with 26% net retention. The stereochemical results vary enough with concentrations of hydroxylamine, base and sodium sulfate to make the three results within experimental error of one another.

These data suggest several conclusions: (1) The same intermediate, probably RN₂H, is produced in all three of the reactions employed. (2) This intermediate partitions between a base-catalyzed anionic elimination reaction to give III somewhat stereospecifically, and a homolytic elimination to give racemic III. (3) Generation

(6) A. Nickon and A. Sinz, *J. Am. Chem. Soc.*, **82**, 753 (1960).

of a proton donor at the front of the carbanion in the base-catalyzed reaction of RN₂H provides for the retention mechanism, whereas a nitrogen molecule as a shield at the front of the carbanion provides for the inversion mechanism.⁷ (4) In relatively non-polar solvents the homolytic cleavage of RN₂H can be eliminated, but not in water or ethylene glycol. (5) In water, different intermediates are involved in the anionic cleavage depending on whether I or II are starting materials.

- (7) Compare nitrogen as leaving group with carbon and hydrogen. (a) D. J. Cram, J. L. Mateos, F. Hauck, A. Langemann, K. R. Kopecky, W. D. Nielsen and J. Allinger, *ibid.*, **81**, 5774 (1959); (b) D. J. Cram, C. A. Kingsbury and B. Rickborn, *ibid.*, **83**, 3688 (1961). (8) Eastman Kodak Fellow, 1961-1962.

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EVIDENCE FOR PARALLEL CONTROL OF REACTION RATE AND STEREOCHEMISTRY *via* THE ELECTROSTATIC INFLUENCE OF REMOTE SUBSTITUENT DIPOLES

Sir:

We wish to report evidence we have obtained in studies of sodium borohydride reduction of 4-substituted cyclohexanones indicating that, in systems where rate variations are strongly governed by remote substituent effects, parallel control of product stereochemistry also is exercised. Furthermore, the existence of a field effect of this nature appears to be unexpected in view of assumptions to the contrary applied in various interpretations of rate and stereochemical effects.¹⁻⁶

The rates of reduction obtained by use of the kinetic method devised by Brown and co-workers⁷ are presented in the accompanying data table. The existence of a linear free energy relationship

- (1) W. G. Dauben, G. J. Fonken and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).
(2) W. G. Dauben and R. E. Bozak, *J. Org. Chem.*, **24**, 1596 (1959).
(3) A. H. Beckett, N. J. Harper, A. D. J. Balon and T. H. E. Watts, *Tetrahedron*, **6**, 319 (1959).
(4) W. M. Jones and H. E. Wise, Jr., *J. Am. Chem. Soc.*, **84**, 997 (1962).
(5) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).
(6) E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960).
(7) H. C. Brown, O. H. Wheeler and K. Ichikawa, *Tetrahedron*, Vol. 1, 214 (1957).