Tetrahedron Letters No.16, pp. 1499-1503, 1967. Pergamon Press Ltd. Printed in Great Britain.

SUBSTITUENT EFFECTS ON SUSPECTED PHENONIUM ION REACTIONS

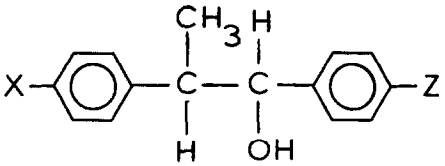
Charles A. Kingsbury and D. C. Best

Chemistry Department, Iowa State University

Ames, Iowa 50010

(Received 14 January 1967)

We wish to report an nmr study of the alcohol-halide conversion in the 1,2-diphenyl-1-propyl system, with regard to the effect of substituents on the stereochemistry of the reaction. This study has bearing on the



controversy concerning the phenonium ion. Cram[1] has recently presented the case for the phenonium ion in which stereochemical grounds played a prominent role in deciding the mechanism. Brown[2] and co-workers have criticized this work on the basis of kinetic studies and prefer a conformational argument to explain the retention of configuration observed in the 3-phenyl-2-butyl system. Other studies[3,7] have shown that a β-aryl group may shield one side of the open ion from attack of the nucleophile. Thus, configuration may be retained without participation.

The present reaction under study could possibly involve a stable benzylic open carbonium ion or a bridged ion or both of these. The elegant isotope studies of Collins[3] and co-workers would seem to favor an open carbonium ion over the bridged species in such a situation as this.

The stereochemistry of the conversion to chloride by con. HCl at 0°C. is easily studied by nmr by observation of the methyl resonance absorption. In the threo series of compounds this uniformly occurs ca. 1.5 ppm whereas in the erythro series this absorption occurs at 1.2 ppm. Integration gives the erythro to threo ratio (accuracy is assumed to be ± 6%). Starting materials are easily differentiated from products in the threo series but some difficulty occurs in the erythro. The erythro and threo chlorides do not interconvert under the reaction conditions.

Table I shows the stereochemistry of the product as X and Z are varied. The reaction is stereoselective rather than stereospecific (runs 1-4, 6-8) since both erythro and threo starting materials give predominantly threo product. Thus it is likely that common intermediates exist. The equilibration studies of Cram and Elhafez[4] have shown that the erythro isomer is slightly more stable than the threo. Thus the least stable isomer is the predominant product in the above runs.

An explanation of the results, similar to that of Cram,[4] can be given with the aid of Diagram 1. Beginning with threo ROH, with a strongly electron donating substituent X=p-OCH_3 predominantly threo RCl possibly via pathway 1 → 3 → 4 is observed. However, path 1 → 2 → 3 → 4 cannot be excluded. Erythro ROH cannot yield the trans phenonium ion 3 directly, and path 1 → 2 → 3 → 4 may be important. The open ion 2 must be formed initially, then undergo internal rotation before 3 is formed. It is noteworthy that the stereoselectivity is lower for the erythro series of compounds. Thus capture of the open ion (path 1 → 2 → 4, 5) must compete favorably with internal rotation. The latter pathway increases in importance as X becomes poorly electron donating.

TABLE I

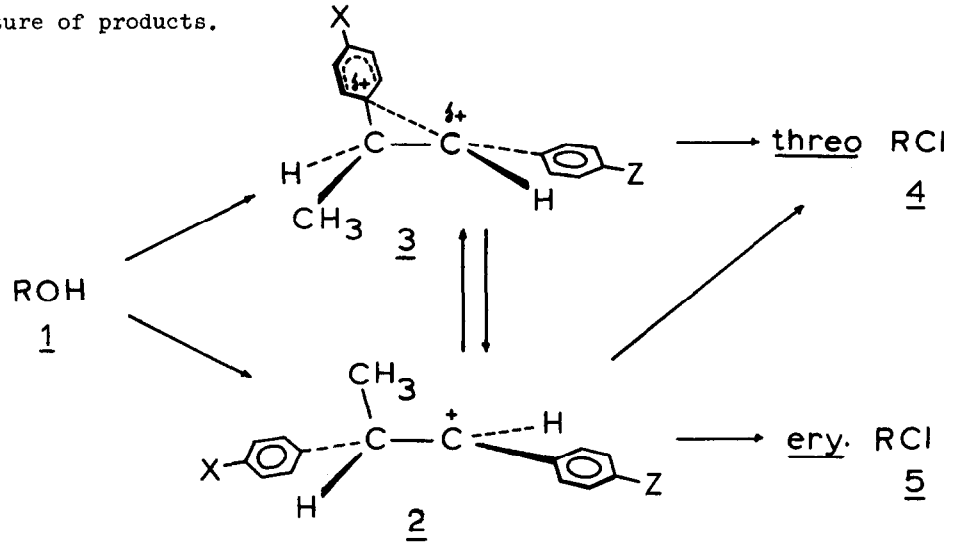
Stereochemistry of Reaction Products from Substituted 1,2-Diphenyl-1-propanols with con. HCl/LiCl at 0°C.

	Threo X	ROH Z	Rx Time (hr.)	RCl % Erythro	RCl % Threo	Comments
(1)	p-CH_3O	H	1	11%	89%	rx complete
(2)	o-CH_3O	H	6	2%	98%	rx complete
(3)	H	H	1.5	20%	80%	rx complete
(4)[a]	p-Cl	H	12	37%	62%	ca. 60% reaction
(5)	H	CH_3O	0.2	46%	54%	rx complete
	Erythro X	**ROH Z**				
(6)	p-CH_3O	H	6.8	26%	74%	rx complete
(7)	o-CH_3O	H	8.25	29%	71%	rx complete
(8)	H	H	6.5	33%	66%	rx complete
(9)	p-O_2N	H	9.1	60%	40%	rx complete
(10)	H	CH_3O	1.75	60%	40%	rx complete

[a] At 25°C rather than 0°C.

In runs 2 and 7, X = o-OCH_3, participation by the methoxy function may be involved. The stereoselectivity is near maximum (98%) in the case of the threo isomer.

In two cases the bridged ion 3 does not appear to be involved. In the first case (run 9) the bridged aryl group would be destabilized by a p-nitro group and tends not to be formed. In the second case (runs 5 and 10) the open ion 2 is markedly stabilized by a methoxy function. In both cases pathway 1 → 2 → 4, 5 appears to be dominant yielding close to the equilibrium mixture of products.



Winstein and co-workers[5] have reported a kinetic study in the substituted β-phenylethyl system. Solvolysis was accelerated with electron donating substituents. The stereochemical results of this study complement these kinetic results.

Although some sort of shielding effect,[1,6,7] or else a complex with the attacking acid[8] might be invoked to explain the results, it appears that the stereoselective reaction is best accommodated by product formation from the bridged ion as originally postulated by Cram. It also appears that bridged ions and open ions can indeed co-exist peacefully as hypothesized by Brown and

coworkers.[2]

Acknowledgement

This work is supported in part by NSF Grant GP 3551

References

(1) D. J. Cram, J. Am. Chem. Soc., 86, 3767 (1964).

(2) H. C. Brown, K. Morgan, and F. Chloupek, ibid., 87, 2137 (1965).

(3) C. J. Collins, "Advances in Physical-Organic Chemistry," Vol. 2, Academic Press, London, 1964, p. 1, and references cited therein.

(4) D. J. Cram and F. A. Abd Elhafez, J. Am. Chem. Soc., 76, 30 (1954), ibid., 75, 340 (1953).

(5) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, ibid., 75, 147 (1953).

(6) Reference 3, p. 43.

(7) B. Murr and C. Santiago, J. Am. Chem. Soc., 88, 1827 (1966).

(8) G. Russell, private communication.