Tetrahedron Letters No. 27, pp 2561 - 2564, 1973. Pergamon Press. Printed in Great Britain.

CHEMISTRY OF ORGANODITINS. I.

STEREOCHEMISTRY OF DEHALOGENATION OF VICINAL DIHALIDES.

Henry G. Kuivila and Charles H.-C Pian

Department of Chemistry, State University of New York at Albany, Albany, N.Y. 12222

(Received in USA 23 April 1973; received in UK for publication 29 May 1973)

In a previous paper we reported on the relative rates, stereochemistry and mechanism of dehalogenation of vicinal dibromides by tri-n-butyltin hydride.[1] Only minor amounts of simple reduction occurred, the dibromides were more reactive than simple monobromides, and *anti*-elimination dominated in some cases. Furthermore the degree of stereoselectivity was found to depend upon the concentration of tri-*n*-butyltin hydride, indicating that it can play a role in the product-determining step. Vicinal dichlorides or chlorobromides underwent simple reduction as the major course of reaction. We report here preliminary results of a similar study using hexabutyditin as the debrominating agent. Organoditins have been previously shown to react with organic halides. The reactions may occur thermally at rather high temperatures,[2] or may be catalyzed by peroxides,[2a] copper metal,[3] or by irradiation.[4]

We have observed that dehalogenation of vicinal dihalides, which has been reported to occur thermally in the case of stilbene dihalides,[2c] can be initiated by azobisisobutyronitrile, by benzoyl peroxide, and photochemically. We chose the latter form of initiation for this initial study on the mechanism because the reactions could be conducted at ambient temperature, and the products were free of substances formed from initiator fragments. Simple dihalides such as 2,3-dibromo-(or chloro)-propanol and 1,2,3-trichloropropane underwent facile reaction when irradiated in Pyrex with a medium pressure mercury vapor lamp with an equimolar amount of hexa-*n*-butyltin (HBDT) (neat) as indicated by formation of yields of organotin halide ranging from 68% to 88%. No volatile three-carbon compounds could be observed by glpc This suggests that the reaction products polymerized under the reaction conditions. On the other hand, when a mixture of diastereomers of 2,3-dichlorobutane was photolyzed under similar conditions 88% of the ditin appeared as tri-*n*-butyltin chloride, 40% of 2-butenes with a *trans*/*cis* ratio of 2/1. In contrast with the reaction of this chloride with tri-*n*-butyltin hydride,[1] no 2-chlorobutane was detected This result suggests the possibility of protecting double bonds in synthetic procedures by chlorination, followed by dechlorination by this reaction

n-Butane and 1-butene were found as products in all experiments Their formation in these photochemically initiated reactions and of benzene when hexaphenylditin (HØDT) is used appears to be general, and probably results, as suggested by Wilputte-Steinert and Nasielski,[5] by fragmentation of the "hot" triorganotin radicals before reaction with halide into the organic radical and di-n-butyltin or diphenyltin. Di-n-butyltin was found in the non-volatile portions of our product mixtures.

Upon reaction of equimolar amounts of HBDT and meso-2,3-dibromobutane 39% of 2-butenes with a trans/cis ration of 2.90 was detected. No 2-bromobutane was detected. The dl-dibromide yielded 36% of the same mixture with a trans/cis ratio of 1.12. Thus, some stereoselectivity is shown in the reaction. Preliminary results of a more extensive study made with the diastereomeric 2,3-dibromo-4-methylpentanes are shown in the table It is evident that the reaction shows stereoselectivity which increases with the initial concentration of HBDT, with the trans/cis ratio in the product ranging from 0.85 from the threo-dibromide at the lowest HBDT/dibromide concentration ratio to 7.50 from the erythro-dibromide with the highest HBDT/dibromide ratio used. These results indicate a proclivity toward anti-elimination with increased ditin concentration, and suggest participation by the ditin in the product-determining step of the elimination.[6] Monoolefins have been shown to undergo isomerization during the course of debromination of vicinal dibromides[1] and during the course of addition of organotin hydrides to olefins [7] Consequently the degrees of stereoselectivity shown in the present work can be taken to be minimum values in view of the apparent free radical nature of the mechanism involved. This is shown to be the case for 3-methyl-2-butene. In a typical experiment the cis isomer was irradiated in the presence of tri-n-butyltin hydride under the conditions of the debromination experiments and was isomerized to a mixture containing 30% of the trans isomer.

Discussion of mechanism of the ditin induced dehalogenation is best deferred pending the outcome of additional work. One possibility is a chain mechanism analogous to the proposed by Hokomi and Sakurai for the dehalogenation of ethylene dibromide by disilanes and digermanes.[7]

Table 1

Debromination of 2,3-dibromo-4-methylpentanes with Hexa-_n_-butylditin[a]

	ditin	% consumption		% yield olefin	
isomer	dibromide	ditin	dibromide	<u>trans</u>	<u>cis</u>
<u>threo</u>	1.00	65.7	100	38.7	45.4
	1.90	48.4	100	27.1	62.4
	3.73	37.5	100	25.9	72.6
	0.91	86.8	81.0	78.3	16.1
	1.56	60.4	91.8	79.8	13.7
	3.21	49.2	100	83.7	85.1
	4.89	38.9	100	85.1	11.3

[a] Induced by irradiation through Pyrex with medium pressure mercury vapor lamp.

References

1. R. J. Strunk, P. M. DiGiacomo, K. Aso and H. G. Kuivila, J. Amer. Chem. Soc., 92 (1970)2849

2. a) G. A. Razuyeav, N. S. Vyazankin, and O. A. Shchepetkova, Tetrahedron, 18 (1962), b) G. A. Razuyaev, Yu. I. Dergunov and N. S. Vyazankin, Zh. Obshch. Khim., 32 (1962) 2515. c) H. Shirai, Y. Sato, and M. Niwa, Yakugaku Zasshi, 90 (1969) 1232, Chem. Abstr., 74 (1971) 3368q, d) H. Shirai, Y. Sato, and J. Tani, ibid., 90 (1970) 59, Chem. Abstr., 72 (1970) 90593 j

3. G. A. Razuvaev, O. S. D'yachkovskaya, and V. I. Fionov, Dokl. Akad. Nauk SSSR 177 (1967) 1113

4. a) G. A. Razuvaev, N. S. Vyazankin, E. N. Gladyshev, and I. A. Borodavko, Zh. Obshch. Khim., 32 (1962) 2154, b) R. D. Chambers, H. C. Clark, and C. J. Willis, Chem. and Ind., (1960) 76.

5. L. Wilputte-Steinert and J. Nasielski, J. Organometal. Chem., 24 (1970) 113.

6. As the reactions were carried out neat it could be argued that the trend in the stereoselectivity is due to change in solvent, with the less polar solvent (high ditin/dibromide ratio) favoring _anti_ elimination. This possibility is obviously subject to experimental test.

7. H. G. Kuivila and R. Sommer, J. Amer. Chem. Soc., 89 (1967) 5616.

8. A. Hosomi and H. Sakurai, J. Amer. Chem. Soc., 95, 1384 (1972).

Acknowledgement

We express our appreciation to the National Science Foundation for financial support, and to M & T Chemicals Inc., for gifts of organotins.

Key Words

Free radical elimination, organotins