I-STRAIN AND THE UNSYMMETRICAL BROMONIUM ION GOVERNING ORIENTATION IN ELECTROPHILIC ADDITION TO ISOPROPYLIDENECYCLOALKANES

Anthony J. Sisti

Department of Chemistry, Adelphi University, Garden City, New York

(Received in USA 2 July 1970; received in UK for publication 14 July 1970) The rearrangement of the magnesium salts of halohydrins to ketones is a well known synthetic method (1). Recently (2) the reaction has offered a simple new procedure for ring expansion. Geissman and Akawie (1) have convincingly demonstrated that an epoxide interpretation for the rearrangement is untenable since the reaction proceeds smoothly only when the hydroxyl and halo groups are cis. During a study intended to demonstrate general synthetic applicability of the ring expansion reaction an approach to 1-(1-bromo-1methylethyl)-l-cycloalkanols became imperative. Accordingly, isopropylidenecyclohexane and isopropylidenecyclopentane (3) (0.15 mole) were treated with NBS and water at 15-20° (4) producing halohydrins^{*}, ir (film), 3460 cm⁻¹ and 3480 cm⁻¹ (hydroxyl groups) respectively, both of which gave instant precipitates with alcoholic silver nitrate. Isopropylidenecyclohexane halohydrin was dissolved in anhydrous benzene (300 ml.), converted to its magnesium salt (2) and then decomposed in refluxing benzene (1 hr). After workup (2) distillation produced exclusively methyl 1-methylcyclohexyl ketone (13.8 g 66%) b.p. 68-70°/ 7mm (Lit. (5) b.p. 80-85°/16mm), vpc (20% Carbowax 4' column, 130° and 150°) showed a single compound, nmr (CCl₄) τ 8.0 and 9.0 (singlets, methyl groups), ir (film), 1700 cm⁻¹ (carbonyl group), 2,4-dinitrophenylhydrazone, m.p. 131-132° (Lit. (6) m.p. 132°) and semicarbazone, m.p. 183-185° (Lit. (6) m.p. 186-187°).

The halohydrins were handled under the mildest conditions during workup and were used immediately.

3305

Thus, the halohydrin I, had the structure indicated. It is noteworthy to mention that when 1-chlorocyclohexyl methyl ketone was treated with methylmagnesium iodide it yielded the magnesium salt of the halohydrin from which by subsequent decomposition it gave exclusively methyl 1-methylcyclohexyl ketone (5). Isopropylidenecyclopentane halohydrin, on the other hand, when decomposed (as



above 1/2 hr reflux) yielded the ring enlarged ketone, 2,2-dimethylcyclohexanone, (10.2g 54%) b.p. 55-57°/9mm (Lit. (7) b.p. $169-170^{\circ}/768mm$), vpc^{**} (20% Carbowax 4' column, 150°) showed 95% purity, nmr, (CCl₄), τ 8.98 (singlet two methyl groups), ir (film), 1710 cm⁻¹ (carbonyl group) and 2,4-dinitrophenylhydrazone, m.p. 139-140° (Lit. (7) m.p. 140-142°) admixture produced no depression. Thus, <u>the halohydrin II</u>, possessed, <u>in this case</u>, the structure indicated.



Since the reaction of NBS and water with an olefin proceeds via the bromonium ion (8) the results herein appear best rationalized by invoking the concept of I-strain (9) and the postulated unsymmetrical bromonium ion (or bromocarbonium ion), which recent reports indicate as best describing the reactions of unsymmetrical olefins with positive bromine (10). *** From isopropylidenecyclopentane the unsymmetrical bromonium ion, III, should be more stable than IIIa since it would essentially maintain sp² character on the ring carbon atom and thereby avoids or minimizes four bond oppositions (two H to Br and two H to

^{**} Vpc revealed the presence of a 5% contaminant presumably methyl 1-methyl-

isopropyl oppositions) as present in IIIa. The reduction of angle strain is not of appreciable importance (120° to 109°) as compared to conformational

strain since IIIa then would be preferred. From isopropylidenecyclohexane, IV should be more stable than IVa since the former has essentially sp³ character on the ring carbon atom thus considerably reducing the two bond oppositions (two adjacent equatorial hydrogens with the isopropyl group) which would be present in IVa. The reduction of angle strain (120° to 109°) would be an additional factor favoring IV over IVa. As far as is known these examples appear to be the first demonstrating the effects of I-strain governing orientation in an electrophilic addition reaction.

IV a

Further studies are presently being undertaken with other rings and other reaction types.

^{**} cyclopentyl ketone based upon the same retention time as an authentic sample, and the nmr, (CCl₄), τ 8.0 and 8.8 two small singlets. It is believed the ketone arose from rearrangement of small amounts of epoxide.
*** Attempts to account for the products by comparison of carbonium ion sta-

^{***} Attempts to account for the products by comparison of carbonium ion stabilities based on electrical considerations do not here seem relevant since both (exo and endocyclic) would be tertiary and should be of comparable stabilities.

- M. Tiffeneau and B. Tchoubar, <u>Compt. rend.</u> <u>198</u>, 941 (1934); T. A. Geissman and R. I. Akawie, <u>J. Amer. Chem. Soc.</u>, <u>73</u>, 1993 (1951); A. S. Hussey and R. R. Herr, <u>J. Org. Chem.</u>, <u>24</u>, 843 (1959).
- A. J. Sisti, Tetrahedron Letters, 5327 (1967); A. J. Sisti, <u>J. Org. Chem.</u>,
 33, 453 (1968); A. J. Sisti, <u>J. Org. Chem.</u>, <u>33</u>, 3953 (1968).
- 3) R. Siegmann, M. Beers and H. Huisman, Rec. Trav. Chim., 83, 67 (1964).
- 4) C. O. Guss and R. Rosenthal, J. Amer. Chem. Soc., <u>77</u>, 2549 (1955).
- 5) O. Sakur, Compt. rend., 208, 1092 (1939).
- 6) H. Pines and J. Marechal, J. Amer. Chem. Soc., 77, 2819 (1955).
- 7) P. S. Adamson, A. M. Marlow and J. L. Simonsen, J. Chem. Soc., 774 (1938).
- 8) E. E. Van Tamelen and K. B. Sharpless, Tetrahedron Letters, 2655 (1967).
- 9) H. C. Brown, R. S. Fletcher and R. B. Johannesen, J. Amer. Chem. Soc., 73, 212 (1951).
- 10) D. R. Dalton, V. P. Dutta and D. C. Jones, J. Amer. Chem. Soc., <u>90</u>, 5498 (1968).