Tetrahedron Letters No. 43, pp.4023 - 4024, 1971. Pergamon Press. Printed in Great Britain.

ON THE MECHANISM OF THE THERMAL REARRANGEMENT OF 2-BROMOCYCLOBUTANONE KETALS.

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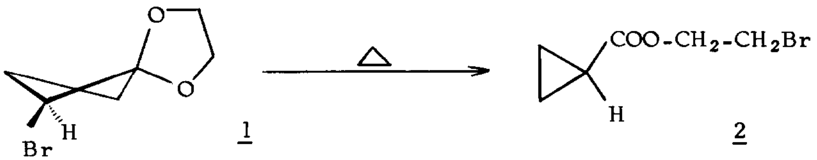
(Received in UK 30 July 1971; accepted for publication 28 September 1971)

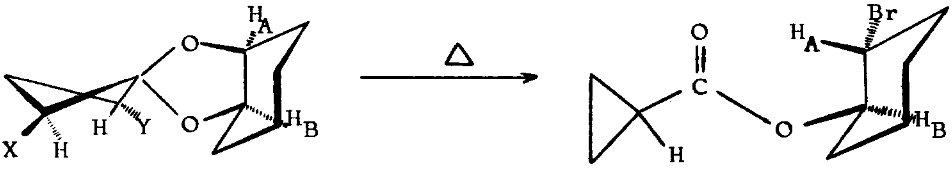
It is known that 2-bromocyclobutanone hydrate (1), hemi-ketals (2) and ketals (3) undergo practically quantitative thermal ring contraction into cyclopropanecarboxylic acid or esters. (E.g., 1 ⟶ 2 (3)).



1 2

Formally analogous rearrangements have been observed from chlorocyclopropanone ketals (4) and 2-bromotropone ketals (5) ; but attempts to extend this reaction to 2-bromo-cyclopentanone and -cyclohexanone ketals have failed (3). Due to the facility with which the former substrates undergo rearrangement, it has been suggested that such isomerisations might be concerted and could follow a well defined stereochemical pathway (see 5, 6, 7). Thus, to be thermally allowed by orbital symmetry (8), a possible 2a + 2s + 2a pathway for 1 ⟶ 2 would require retention at the carbon atom which is the migration site for the halogen (5, 6, 7).

We wish to report experimental evidence that such a thermal ring contraction actually involves complete inversion at the carbon atom undergoing the bromine substitution.



3 syn X = Br Y = H
anti Y = Br X = H

4 trans

The ketal 3 was prepared from cis-1,2 cyclohexanediol and 2-bromocyclobutanone (refluxed in C_6H_6 + p-TsOH, 15 hours, and distillated : b.p. 75° / 0,5 mm). NMR measurements indicate the presence of both syn and anti isomers (~50 - 50) : δ ($CDCl_3$) (ppm) 1.70 (m, 8 H), 2.25 (m, 4 H), 4.40 (m, CHBr) and two multiplets : 4.20 (H_A, H_B of the anti isomer) and 3.30 (H_A, H_B of the syn isomer). On heating (in a sealed tube, 180°, 10 mn) the mixture of (*syn* + *anti*) ketals 3 undergoes quantitative ring contraction into a unique 2-bromocyclohexyl cyclopropanecarboxylic ester 4 (m.p. : 33°). The structure of the rearranged product was determined from spectroscopic data : IR $\nu_{c=o}$ (film) : 1730 cm^{-1} ; NMR δ ($CDCl_3$) (ppm) 0.90 (m, 4 H), 1.80 (m, 9 H), 4.00 (m, 1 H) and 4.85 (m, 1 H). Double irradiation successively at δ 1.76 and 1.65 ppm gives rise to two doublets respectively at δ 4.10 and 4.90 ppm with J_{AB} = 9.30 cps implying a *trans* configuration for H_A and H_B of 4.

Pure samples of the *trans* ester 4 (m.p. 33°) and the *cis* isomer (liq.) were synthetized by addition at room temperature of cyclopropanecarboxylic acid chloride to *trans* and *cis* 2-bromocyclohexanol separately. The melting point and spectroscopic data of the *trans* ester entirely confirm that the configuration of ester 4 is *trans* and that it is the unique product of the ring contraction. (In the *cis* ester the H_A and H_B signals are quite different : two well separated multiplets at δ 4.45 (1 H) and 4.80 ppm (1 H) are observed ; and double irradiation at δ 8.20 ppm gives rise to two doublets with J_{AB} = 2.70 cps). Heated separately at 180°, under the conditions which lead to ring contraction in 3, the *trans* 4 and *cis* esters are recovered unchanged.

The stereochemistry of the ring contraction thus involves complete inversion at the migration terminus whatever the configuration of the bromine atom of 3.

The rate constant and reaction order of the ring contraction carried out in decalin at 150° have been determined by measuring the ratio of the areas of the proton signals of 4 at δ 4.85 ppm and of 3 at δ 4.40 ppm. A plot of 1/[ketal 3] versus time (*syn* and *anti* isomers ring contract at approximatively the same rate) is sufficiently linear for the reaction to be considered as being of second order implying therefore *an intermolecular transfer of the halogen*. The rate constant : k = 0.11.10^{-3} M^{-1}.sec^{-1} in decalin is only slightly affected when the solvent is changed to one of greater polarity. For example we found $k' \approx 3.33.10^{-3}$ M^{-1}.sec^{-1} in nitrobenzene or in isobutyric acid. ($k'/k \approx 30$). These results and the specificity of the ring contraction imply that a true carbonium ion intermediate is improbable (see for instance (9), and also (7)).

However that may be such ring contractions do not involve a concerted valence reorganization under the control of orbital symmetry.

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