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Cyclopropyloxetanes
Reactions of 5-Oxaspiro[2.3]hexane with Hydrogen Halides

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The title cyclopropyloxetane reacted with aqueous hydrogen chloride, bromide, and iodide to give mixtures of the corresponding 1-(halogenomethyl)-1-(hydroxymethyl)cyclopropane and 1-halogeno-1-(hydroxymethyl)cyclobutane.

(Keywords: Bicyclobutonium ion; Cyclopropyl carbinyl cation; Molecular rearrangement; Oxetane)

Cyclopropyloxetane. Reaktion von 5-oxaspiro[2.3]hexan mit Halogenwasserstoffsäuren

Das im Titel genannte Cyclopropyloxetan reagiert mit wäßriger HCl, HBr und HI zu den entsprechenden 1-(Halogenmethyl)-1-(hydroxymethyl)cyclopropanen und 1-Halogen-1-(hydroxymethyl)cyclobutanen.

Introduction

Although the exceptionally wide variety of acid-catalysed rearrangements of cyclopropyl epoxides has been studied[1] in some detail, only one of the homologous cyclopropyl oxetanes has been examined and the reports of the reactions of this compound, 5-oxaspiro[2.3]hexane (**2**), with hydrogen bromide and hydrogen chloride vary.

Searles and *Lutz* obtained[2] 4-bromo-2-(bromomethyl)-1-butanol (**1**) from the cyclopropyl oxetane **2** on reaction with gaseous hydrogen bromide; using aqueous hydrogen bromide, *D'yachenko* and *Lukina* obtained[3] 1-(bromomethyl)-1-(hydroxymethyl)cyclopropane (**3**) and an unidentified product. With aqueous hydrogen chloride, the former workers claimed to get 1-chloro-1-(hydroxymethyl)cyclobutane (**4**) and the latter, 1-(chloromethyl)-1-(hydroxymethyl)cyclopropane (**6**).

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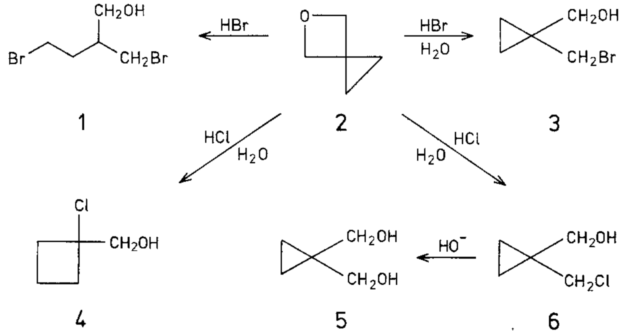
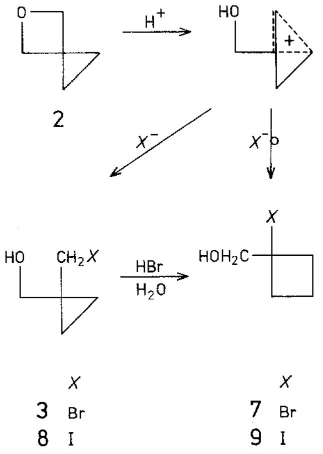
We have re-examined these reactions of the cyclopropyl oxetane **2** and also its reaction with hydrogen iodide.



Results and Discussion

The reaction of 5-oxaspiro[2.3]hexane (**2**) in benzene with gaseous hydrogen bromide afforded **3** while aqueous hydrogen bromide afforded this product **3** plus 1-bromo-1-(hydroxymethyl)cyclobutane[4] (**7**); the bromobutanol **1** was not observed. The cyclopropyl carbinol **3** was converted into the cyclobutyl carbinol **7** by aqueous hydrogen bromide but not by gaseous hydrogen bromide.



The cyclopropyl oxetane **2**, on reaction with aqueous hydrogen chloride, did not give exclusively **4** or **6**, as reported[2,3], but a mixture of both, consisting mainly of the latter (89%). This cyclopropane **6** underwent basic hydrolysis to give 1,1-bis(hydroxymethyl)cyclopropane (**5**), identical with a sample prepared by the method of *Hutchins* et al.[5]. 5-Oxaspiro[2.3]hexane **2** reacted with aqueous hydrogen iodide to give in low yield (20%), a mixture of 1-(hydroxymethyl)-1-(iodomethyl)cyclopropane (**8**) (75%) and 1-(hydroxymethyl)-1-iodocyclobutane (**9**) (25%); both products decomposed rapidly out of solution and elemental analyses could not be obtained.

Experimental

^{1}H-NMR spectra, in $CDCl_3$ with *TMS* as internal standards, were obtained for all products. Chemical shifts are given in ppm (δ) and coupling constants in Hz. OH signals were identified by deuteriation. M.p.s were taken on a hot-stage apparatus and are uncorrected. The usual work-up consisted of diluting the reaction mixture with water, drying the extract over anhydrous sodium sulphate, removing the solvent, and fractionating the residue by thin layer chromatography on silica gel. Products are mentioned in order of decreasing R_f values.

1-(Bromomethyl)-1-(hydroxymethyl)cyclopropane (**3**)

Hydrogen bromide was passed through a solution of **2** (0.91 g) in dry benzene (20 ml) for 0.5 h at 0 °C. The usual work-up gave **3** as an oil[3] (0.3 g). (Found: C 36.7, H 5.3%. Calculated for C_5H_9BrO: C 36.4, H 5.5%.) NMR: 0.72–0.85, m, $—CH_2CH_2—$; 3.53, s, CH_2Br; 3.60, s, CH_2O; 3.96, s, OH.

1-Bromo-1-(hydroxymethyl)cyclobutane (**7**)

2 (2.23 g) was added dropwise to hydrobromic acid (10 ml; 48%) at 0 °C. The mixture was stirred for 3 h and worked-up as usual, giving **7** as an oil[4] (0.75 g). NMR: 1.76–3.04, , $—CH_2CH_2CH_2—$; 2.38, s, OH; 3.84, s, OH. Also obtained was **3** (0.2 g).

The cyclobutane **7** (0.1 g) in dry pyridine (5 ml) reacted with 3,5-dinitrobenzoyl chloride (0.1 g) to give (1-bromocyclobutyl)methyl 3,5-dinitrobenzoate (0.47 g), m.p. 77–78 °C. (Found: C 39.6, H 2.9, N 7.7%. $C_{12}H_{11}BrN_2O_6$ requires: C 40.1, H 3.1, N 7.8%.) NMR: 1.95–3.02, m, $—CH_2CH_2CH_2—$; 4.83, s, CH_2O.

The cyclopropane **3** (65 mg) was added dropwise to hydrobromic acid (5 ml; 48%) at 0 °C. After 3 h, the usual work-up gave 22 mg **7** and 26 mg of unreacted **3**.

1-Chloro-1-(hydroxymethyl)cyclobutane (**4**) *and 1-(chloromethyl)-1-(hydroxymethyl)cyclopropane* (**6**)

2 (1.5 g) was added dropwise to hydrochloric acid (10 ml; 32%) at 0 °C and stirred for 3 h. The usual work-up gave the cyclobutane **4** as an oil[2] (72 mg). NMR; 1.85–2.85, m, $—CH_2CH_2CH_2—$; 2.71, s, OH; 3.76, s, CH_2O. The cyclopropane[3] **6** (589 mg) was also obtained. NMR: 0.61, s, $—CH_2CH_2—$; 3.56, s, CH_2Cl; 3.61, s, CH_2O: 4.78, s, OH.

6 (150 mg) in dry pyridine (5 ml) reacted with 3,5-dinitrobenzoyl chloride (150 mg) to give (1-chloromethylcyclopropyl)methyl 3,5-dinitrobenzoate (86 mg), m.p. 90–92 °C. (Found: C 46.2, H 3.8, Cl 11.3, N 8.7%. $C_{12}H_{11}ClN_2O_6$ requires: C 45.8, H 3.5, Cl 11.3, N 8.9%.) NMR: 0.89, s, $—CH_2CH_2—$; 3.67, s, CH_2Cl; 4.55, s, CH_2O.

1,1-Bis(hydroxymethyl)cyclopropane (**5**)

6 (50 mg) was added dropwise to aqueous methanolic potassium hydroxide (10 ml; 1 *M*) and refluxed for 2 h. The usual work-up gave the cyclopropane **5** as an oil[5] (22 mg). NMR: 0.49, s, —CH_2CH_2—; 3.63, s, 2 × CH_2O; 4.10, s, 2 × OH.

1-(Hydroxymethyl)-1-iodocyclobutane (**9**) *and 1-(hydroxymethyl)-1-(iodomethyl)cyclopropane* (**8**)

2 (2.18 g) was added dropwise to hydriodic acid (10 ml; 56%) at 0 °C and stirred for 3 h. The usual work-up gave the cyclobutane **9** as an oil (0.27 g). NMR: 1.90-2.98, m, —$CH_2CH_2CH_2$—; 2.56, s, OH; 3.73, s, CH_2O. Also obtained was the cyclopropane **8**, an oil (0.83 g). NMR: 0.61-1.02, m, —CH_2CH_2—; 3.40, s, CH_2I; 3.62, s, CH_2O; 4.84, s, OH.

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