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A PRECAUTION ON THE PREPARATION OF 4-BROMOCYCLOPENTENE BY THE HYDRIDE REDUCTION OF CYCLOPENTADIENE DIBROMIDE

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Extensive current activity in regard to the π-route to non-classical carbonium ions and other studies employing 4-substituted cyclopentenes compels us to warn others of the serious hazard involved in the preparation of 4-bromocyclopentene by the method of Bartlett and Rice (1). In this procedure 4-bromocyclopentene is prepared by the lithium aluminum hydride reduction of the crude 3, 5-dibromocyclopentene. An ether solution of the dibromide (2.66 moles) is added slowly to the ether solution of the hydride (1.3 moles) cooling by an ice bath. The reaction mixture is stirred overnight at room temperature, then refluxed for 36 hours and worked up in the usual manner.

On our fourth occasion of running this reaction, approximately one hour after the addition of the dibromide was completed, the mixture exploded shattering the glass apparatus and causing a brief fire. Assuming the explosion was due to fortuitous circumstances the reaction was attempted a fifth time. In this case, 45 minutes after the addition of the dibromide was complete, a violent explosion occurred completely destroying the hood above the bench level -- the sides and top were blown out, the steel door was sprung from its tracks and the safety glass blown out and hurled 18 feet across the room. On one occasion Bartlett and Rice encountered a fire during the course of this reaction (2).

We urge others to use utmost caution in employing this reaction or to adopt alternate procedures for the preparation of 4-substituted cyclopentenes. Synthetically useful derivatives of Δ^3-cyclopentenol prepared by hydroboration of cyclopentadiene (3) have been reported (3, 4). 4-Bromocyclopentene can be prepared from the alcohol by the phosphorous tribromide-pyridine method (5). Cyclopentene-4-carboxylic acid and derivatives are available through cycloalkylation of malonic ester (6).

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