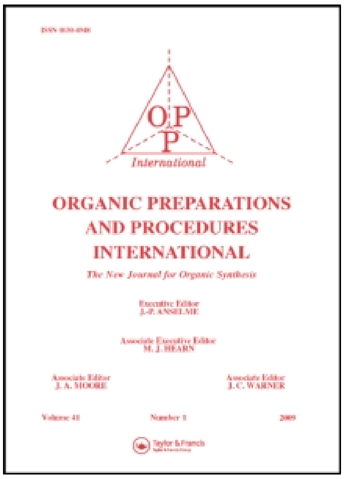

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REDUCTION OF 1,1-DICHLOROBENZOCYCLOBUTENES

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REDUCTION OF 1,1-DICHLOROBENZOCYCLOBUTENES

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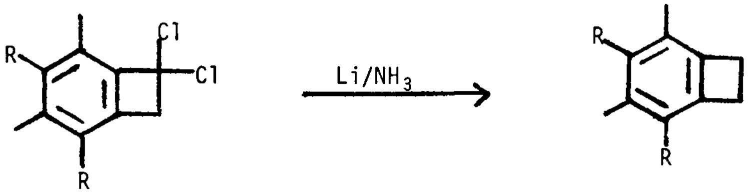
We wish to report that lithium in liquid ammonia is an effective reagent for reducing halogens from the four-membered ring of benzocyclobutenes, without giving appreciable amounts of ring-opened products.

Substituted 1,1-dichlorobenzocyclobutenes are readily available through the thermal 1,4-elimination of hydrogen chloride from adjacent methyl and trichloromethyl groups.[1-3] For example, 1 is obtained in high yield by heating trichloromethylpentamethylbenzene[4] to 115-120°. For reasons which need not be detailed here, we sought a general method for reducing appreciable quantities of 1 and related compounds directly to benzocyclobutenes. Hydrocarbon 2 was previously[2] prepared by hydrolysis of 1 to the ketone, followed by Wolff-Kishner reduction (overall yield



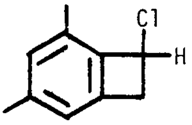
1, R=CH_3
3, R=H

2, R=CH_3
4, R=H

38%). The method is not entirely satisfactory because cyclobutanones undergo ring-opening in strongly alkaline media.[5]

Addition of an ether solution of 1 to excess lithium in liquid ammonia at -75° resulted in complete reduction to 2 (78%), together with a small amount of hexamethylbenzene. The latter could be removed by sublimation. Similar reduction of 3 gave 4[6] in 61% yield. It seems likely that this constitutes a general method for removing one or more halogens from the four-membered ring of benzocyclobutenes.

Other reduction methods were less successful. With Raney Ni and hydrogen at 2 atm, 3 gave only 25% of 4, together with 73% of the mono chlorobenzocyclobutene 5.[7] With zinc and acetic acid, 3 gave 4 (14%), 5 (21%) and the ketone 6 (38%).[2]



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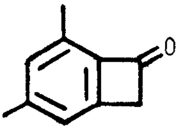

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Lithium aluminum hydride was ineffective in reducing 3, and the sodium borohydride-diglyme-base procedure for trapping and reducing carbonium ions[8] gave mainly (68%) recovered 3, with some 5 (27%) and isodurene (5%).

Clearly the best method, of those tried, for removing all the halogens is the lithium-ammonia reduction. Catalytic hydrogenolysis may be synthetically useful for obtaining monohalides (*i.e.*, 5) from dihalides.

Experimental

2,3,4,5-Tetramethylbicyclo[4.2.0]octa-1,3,5-triene (2). A solution of 30 g (0.131 mole) of 1[2] in 250 ml of anhydrous ether was added with stirring over 75 min to a solution of 7.4 g (1.06 mole) of lithium in 900 ml of liquid NH_3. The reaction mixture was kept at -75° (dry ice-isopropanol) throughout the addition. After 60 min additional stirring, the cold bath was removed, 60 g (1.13 mole) of ammonium chloride was added and the ammonia was allowed to evaporate overnight. The residue was dissolved in 250 ml of ether and 250 ml of water. The organic layer was dried ($MgSO_4$) and evaporated to give 17.5 g of a yellow solid which by vpc (5' X .38" OV-225[9] column, 190°, 200 ml He/min) consisted of 94% 2 (rt 4.0 min) and 6% hexamethylbenzene (rt 5.2 min). The product could be purified by recrystallization (pet. ether) or sublimation (75° at 0.15 mm) to give product with 98.5% purity by vpc (yield 78%; the 1.5% impurity is hexamethylbenzene).

8-Chloro-2,4-dimethylbicyclo[4.2.0]octa-1,3,5-triene (5). Raney nickel (4-5 g) was added to a solution of 3.57 g (0.0178 mole) of 3 in 120 ml of hexane, and the mixture was shaken on a Parr apparatus at room temperature under 2 atm of hydrogen. Hydrogen uptake was slow. The reaction was monitored by vpc and was stopped after 21 hours. The solution was filtered, the solvent was distilled and the residue was purified by preparative vpc (SE 30 column, 167°) to give 0.58 g (25%) of 4[6] and 2.15 g (73%) of 5.[7] After 21 hours, the conversion of 5 → 4 proceeds slowly, even if the solution is filtered and fresh catalyst is added.

Acknowledgement. We are indebted to the National Institutes of Health for financial support.

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6. *Anal*: Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.88; H, 9.15. Compound **4** showed a parent peak at m/e 132 and an nmr spectrum with bands at τ 7.93 (3H, s), 7.78 (3H, s), 7.03 (4H, s), 3.55 (1H, s) and 3.45 (1H, s), consistent with the assigned structure.

7. *Anal*: Calcd. for $C_{10}H_{11}Cl$: C, 72.1; H, 6.6; Cl, 21.3. Found: C, 72.4; H, 6.8; Cl, 20.8. Compound **5** showed parent peaks at m/e 168, 166. The nmr spectrum is distinctive and constitutes particularly strong evidence for the structure. It shows two aryl methyls at τ 7.81 and 7.74 (sharp singlets), two aryl protons at τ 3.46 and 3.33 (broadened singlets), the CHCl proton from τ 4.77-4.95 and the remaining cyclobutane protons as a pair of AB doublets (J=14 Hz) centered at τ 6.85 and 6.34; the lower branch was further split by 4.5 Hz and the upper by about 1.5 Hz, through coupling with the proton centered at τ 4.86. This spectrum is very much like those reported for similar compounds in ref. 2.

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