

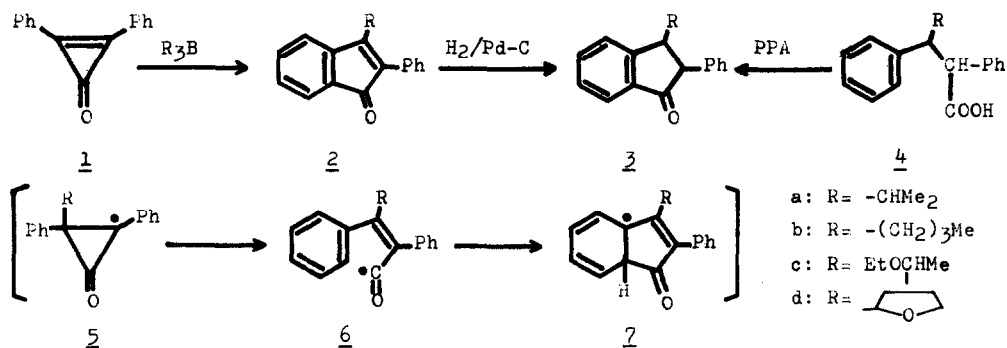
RING EXPANSION OF UNSATURATED CYCLOPROPANES WITH TRIALKYLBORANES

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Trialkylboranes have proven to be a versatile reagent for organic synthesis.¹ This communication describes the novel reactions of trialkylboranes with diphenylcyclopropanone and alkylidenecyclopropanes to give ring-expanded products, indenones and cyclobutenes, respectively.

A mixture of diphenylcyclopropanone² (1, 0.50 g, 2.5 mmol) and triisopropylborane (0.70 g, 5.0 mmol) dissolved in benzene-ether (1:1, 20 ml) was stirred under nitrogen atmosphere at room temperature for 4 days and then was treated with water (5 ml) at room temperature. Chromatographic separation on silica gel column gave 3-isopropyl-2-phenyl-1-indenone³ (2a, mp 107.5-109°, 13%), 3-(1-ethoxyethyl)-2-phenyl-1-indenone (2c, 11%) and the unchanged 1 (62%). The structure of 2a was determined by spectral data⁴ including aromatic solvent induced shift (ASIS)⁵ of nmr, and by comparison of the reduction product 3 with the authentic sample⁶ prepared from 4. The structure of 2c was based on spectra.⁷



Treatment of 1 with triisopropylborane under oxygen catalysis⁸ in benzene-THF (1:1) solution gave 2a in 52% yield but no 2d corresponding to 2c in the above case. As the reactive species under oxygen-catalyzed conditions is considered to be isopropyl radical,⁸ the reaction may be explained, as shown in the above equation, to involve radical addition affording 5, rearrangement to 7 via 6, and aromatization to 2.

The formation of 2c in the former case suggests that the reaction in the absence of catalytic oxygen also proceeds via radical mechanism but the exact origin of 1-ethoxyethyl radical has not been established. Tributylborane gave similar results (2b, 17%).

