RING EXPANSION OF UNSATURATED CYCLOPROPANES WITH TRIALKYLBGRANES

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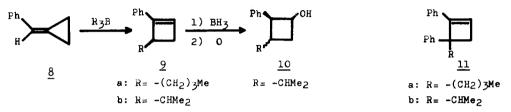
Trialkylboranes have proven to be a versatile reagent for organic synthesis. This communication describes the novel reactions of trialkylboranes with diphenylcyclo-propenone and alkylidenecyclopropanes to give ring-expanded products, indenones and cyclobutenes, respectively.

A mixture of diphenylcyclopropenone²(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°, 1%), 3-(1-ethoxyethyl)-2-phenyl-1-indenone (2c, 11%) and the unchanged 1 (62%). The structure of 2a was determined by spectral data including aromatic solvent induced shift (ASIS)⁵ of nmr, and by comparison of the reduction product 3 with the authentic sample prepared from 4. The structure of 2c was based on spectra. 7

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

The formation of <u>2c</u> 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-ethoxy-ethyl radical has not been established. Tributylborane gave similar results (<u>2b</u>, 17%).

A solution of benzylidenecyclopropane 9(8, 0.70 g, 5.4 mmol) and tributylborane (1.0 g, 5.4 mmol) in THF (10 ml) was heated to reflux for 60 hours under nitrogen atmosphere. Treatment of the reaction mixture with alkaline hydrogen peroxide and the subsequent preparative glc gave 2-butyl-1-phenylcyclobutene 3,10(9a, 19%) and the unchanged 8,35%. Hydrogenation of 9a gave 1-butyl-2-phenylcyclobutene. Irradiation of 0.27 M solution of tributylborane and 8 in cyclohexane produced 9a in 15% yield. Oxygen-catalyzed reaction gave a complex mixture including 9a, analysis of which being underway. Thermal and photochemical reaction of 8 with triisopropylborane



gave similar results (9b, 21% and 5% respectively). Hydroboration of 9b gave 3-iso-propyl-2-phenylcyclobutanol (10). A solution of diphenylmethylenecyclopropane and trialkylborane in THF was heated to reflux for 40 hours under nitrogen atmosphere to afford 4-alkyl-1,4-diphenylcyclobutene(1la: 15%, 1lb: 33%) corresponding to 9 in the case of $8.^{11}$

References and Notes

- 1. H. C. Brown, Accts. Chem. Res., 2, 65 (1969); Chem. Britain, 7, 458 (1971).
- 2. R. Breslow, J. Posner and A. Krebs, <u>J. Amer. Chem. Soc.</u>, <u>85</u>, 234 (1963).
- 3. All new compounds gave correct analyses.
- 4. Nmr (CCl₄) δ ppm: 7.24 (s) 9H, 3.34 (m) 1H, 1.38 (d) 6H; ASIS $\delta_{\text{CCl}4}-\delta_{\text{C6H6}}=18\text{Hz}$, (Me and CH of i-Pr); ms: m/e (rel intensity %), 248 (M⁺, 100), 233 (70); ir (liq film): 1708cm⁻¹; uv (EtOH): 250, 420 nm.
- 5. N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Org. Chem. Illustrations from the Steroid Field," Holden-Day, Inc., San Francisco, 1964.
- N. Campbell and E. Ciganek, <u>J. Chem. Soc.</u>, 3834 (1956); J.Koo, <u>J. Amer. Chem. Soc.</u>, 75, 1891 (1953).
- 7. Nmr (CCl₄) 8 ppm: 7.37 (m) 9H, 4.73 (t) 1H, 3.40 (m) 2H, 1.63 (d) 3H, 1.10 (t) 3H; ir (liq film): 1708, 1100 cm⁻¹; ms: m/e (rel intensity %), 278 (M⁺, 78), 207 (100).
- 8. G. W. Kabalka, H. C. Brown, A. Suzuki, S. Homma, A. Arase and M. Itoh, <u>J. Amer.</u> Chem. Soc., <u>92</u>, 710 (1970)
- 9. K. Sisido and K. Utimoto, Tetrahedron Letters, 3267 (1966).
- 10. The structure of <u>9a</u> was based on spectral data; nmr (CCl₄) & ppm: 7.27 (m) 2H, 6.98 (s) 3H, 6.17 (s) 1H, 2.0-2.9 (m) 5H, 1.4 (m) 4H, 0.93 (t) 3H; ms: m/e (rel intensity %), 186 (M⁺, 43), 143 (100); ir (liq film): 2940, 1499, 748, 705 cm⁻¹; uv (EtOH): 225, 264, 272, 282 nm.
- 11. Mechanistic studies of this reaction are progressing.