

STEREOSELECTIVE INSERTION OF TETRASUBSTITUTED CYCLOPROPYLIDENE INTO A CARBON - HYDROGEN BOND<sup>1</sup>

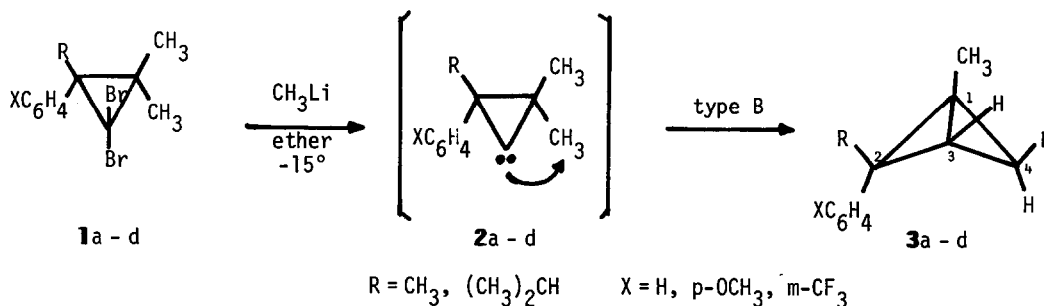
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It has been observed that the treatment of tetrasubstituted gem-dibromocyclopropanes with methyl lithium brought about the exclusive formation of bicyclobutanes rather than allenes.<sup>2-5</sup> In these reactions, the divalent carbon of the intermediate cyclopropylidene inserted selectively into a carbon-hydrogen bond of an alkyl group which geminated to the sterically bulkiest group among the four substituents<sup>4,5</sup> (Insertion type A).



This communication deals with an entirely different selectivity from hitherto known reactions and a facile synthesis of endo-2-aryl bicyclobutanes **3a-d** via aryltrialkylcyclopropylidenes **2a-d** generated from corresponding gem-dibromocyclopropanes **1a-d**. In the intermediates **2a-d**, the divalent carbon did not insert into R group, but the methyl group which is cis to phenyl group (Insertion type B).



Treatment of 1,1-dibromo-2-phenyl-2,3,3-trimethylcyclopropane (**1a**) with methyl lithium in ether at  $-15^\circ$  gave a single product, 1,2-dimethyl-endo-2-phenylbicyclobutane (**3a**), in a 76 % yield. Satisfactory spectroscopic analyses were obtained for **3a** [mass spectrum  $m/e$  158 ( $M^+$ ); nmr ( $\text{CCl}_4$ )  $\delta$  ppm 0.65 (s., 1H, endo-4-H), 1.32 (s., 3H, exo-2- $\text{CH}_3$ ), 1.35 (broad s., 2H, 3-H and



Table I. The Reaction of **1a-d** with Methylolithium<sup>a</sup>

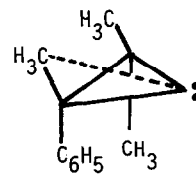
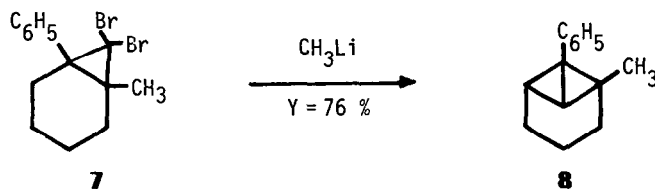
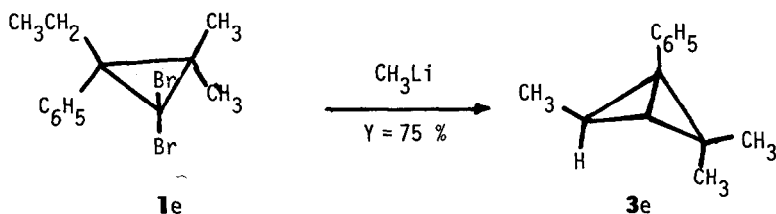
	X	R	Yield (%) of Product <sup>b</sup>	nmr of <b>3a-d</b> ( $\delta$ -ppm) <sup>c</sup>
<b>1a</b>	H	CH <sub>3</sub>	76 ( <b>3a</b> )	0.65 (s., 1H), 1.32 (s., 3H), 1.35 (br s., 2H), 1.69 (s., 3H), 7.10 (br s., 5H)
<b>1b</b>	m-CF <sub>3</sub>	CH <sub>3</sub>	74 ( <b>3b</b> )	0.63 (s., 1H), 1.37 (s., 3H), 1.40 (br s., 2H), 1.70 (s., 3H), 7.30-7.61 (m., 4H)
<b>1c</b>	p-OCH <sub>3</sub>	CH <sub>3</sub>	87 ( <b>3c</b> )	0.62 (s., 1H), 1.29 (br s., 2H), 1.32 (s., 3H), 1.68 (s., 3H), 3.73 (s., 3H), 6.6-7.1 (m., 4H)
<b>1d</b>	H	(CH <sub>3</sub> ) <sub>2</sub> CH	71 ( <b>3d</b> )	0.43 (d., J=1.3 Hz, 1H), 0.88 (d., J=3.1 Hz, 6H), 1.25 (d., J=1.3 Hz, 1H), 1.34 (d., J=1.3 Hz, 1H), 1.72 (s., 3H), 1.58-1.85 (m., 1H), 7.08 (br s., 5H)

a; The reaction was carried out in ether at -15 °.

b; Isolated yields.

c; In carbon tetrachloride: s.; singlet, br s.; broad singlet, d.; doublet, m.; multiplet.

On the contrary, when R group in **1** was ethyl, the selectivity of insertion differed remarkably and showed the insertion of type A. Thus, the bicyclobutane obtained from 1,1-dibromo-2-phenyl-2-ethyl-3,3-dimethylcyclopropane (**1e**) was **3e**, in which the divalent carbon did not insert into *cis*-methyl group, but ethyl group. A similar phenomenon was observed in the transformation of **7** to **8**.



Although the selectivity of insertion of the divalent carbon described in this communication is not necessarily explainable, it may be one of the factors controlling the selectivity that the instability of the central carbon-carbon bond in the bicyclobutanes<sup>9</sup> bearing

a phenyl substituent on the bridgehead makes the transition state such as **9** unfavorable, though the transition state **9** is deeply related to the insertion of type A.

The strange behaviors of **1e** and **7** might be resulted from the delicate balance among reactivity of the divalent carbon,<sup>9</sup> steric effect in the transition state,<sup>5,10</sup> and stability of the products.<sup>8</sup>

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#### References and Notes

- 1) Small Ring Compounds XXXI. Part XXX: T. Shono and I. Nishiguchi, *Tetrahedron*, **30**, 2183 (1974).
- 2) W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, **1970**, 2365.
- 3) W. R. Moore and J. B. Hill, *ibid.*, **1970**, 4553.
- 4) D. W. Brown, M. E. Hendrick, and M. Jones, Jr., *ibid.*, **1973**, 3951.
- 5) D. P. G. Hamon and V. C. Trenerry, *ibid.*, **1974**, 1371.
- 6) **3a-d**<sub>2</sub>, mass spectrum  $m/e$  160 ( $M^+$ ); nmr ( $CCl_4$ )  $\delta$  = 0.65 (s., 0.31H), 1.32 (s., 3.0H), 1.35 (br s., 0.72H), 1.69 (s., 3.0H), 7.10 (br s., 5.0H).
- 7) All the products described herein showed satisfactory spectroscopic and elemental analyses.
- 8) The products **3e** and **8** are rather unstable in comparison with **3a-d** and **6a,b**. The former bicyclobutanes decomposed in a few hours at room temperature, while the latter compounds could be stored at room temperature for a week with negligible decomposition.
- 9) The reactivity of cyclopropylidene as to the insertion into carbon-hydrogen bonds was reported to follow the order of tertiary > secondary > primary. See (a) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. E. Allen, Jr., *J. Am. Chem. Soc.*, **94**, 7761 (1972); (b) R. B. Reinartz and G. J. Tonken, *Tetrahedron Lett.*, **1973**, 4013.
- 10) Insertion of the divalent carbon of cyclopropylidenes into the methine carbon-hydrogen bond of isopropyl group may cause severe steric crowding in the transition state. See ref. 5).