

# Efficient Pathway to the Tetracyclo[4.2.0.0<sup>2,8</sup>.0<sup>4,7</sup>]octane (Bishomoprismane) System by Carbenoid Insertion†

By MARK S. BAIRD\* and PETER SADLER

(Department of Organic Chemistry, The University, Newcastle upon Tyne NE1 7RU)

and JACQUES HATEM, JEAN-PIERRE ZAHRA, and BERNARD WAEGELL\*

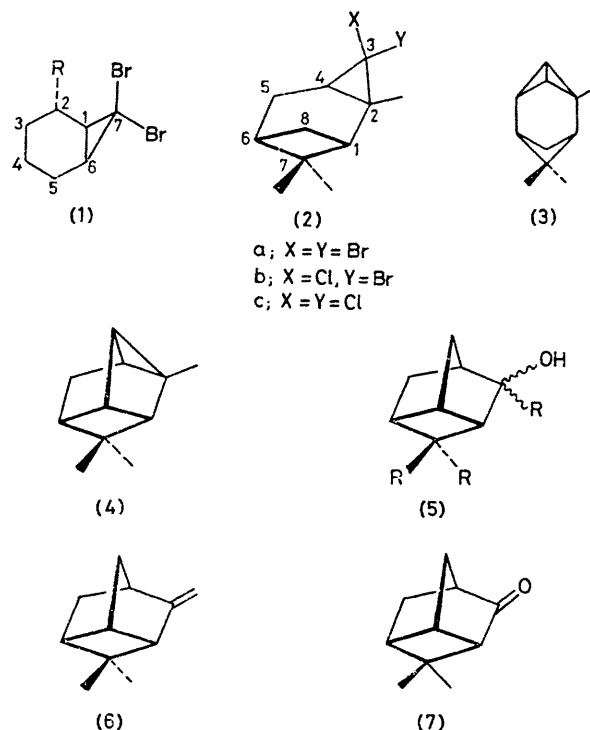
(Faculté des Sciences et Techniques de St-Jérôme, Laboratoire de Stéréochimie, associé au C.N.R.S., Rue H. Poincaré, 13397 Marseille, France)

**Summary** Reaction of (2a–c) with alkyl-lithium leads to (4), which rearranges to (6) on reaction with toluene-*p*-sulphonic acid, AgClO<sub>4</sub>-C<sub>6</sub>H<sub>6</sub>, or FeCl<sub>3</sub>-pyridine.

THE reaction of dibromides related to (1) with MeLi leads to cyclopropylidenes or related carbenoids<sup>1</sup> which generally insert into the C(2)–R bond<sup>2a</sup> to form bicyclo[1.1.0]butanes rather than into the C(3)–H bond. Efficient insertion into the C(3)–H bond has been reported for (1; R = OMe), when the 2-substituent is supposed to assist the reaction.<sup>2b</sup> The molecular conformation and in particular the carbene to C–H bond distances are, however, particularly important in these reactions, and we now report a highly specific insertion into the C(3)–H bond when this is close to the carbene centre.

Reaction of (2a)<sup>3</sup> {[α]<sub>D</sub>(CHCl<sub>3</sub>) + 25.9°} with MeLi-Et<sub>2</sub>O at 25–30 °C, followed by aqueous quenching led to (4) (94%), [α]<sub>D</sub> + 27.5°. Compound (4) was also obtained on treatment of (2b) with MeLi at 0 °C or (2c)<sup>4</sup> with EtLi at 25 °C (90 and 80%, respectively). The hydrocarbon showed eleven distinct signals in the <sup>13</sup>C n.m.r. spectrum [δ 48.6 (CH); 47.6 (CH); 36.4 (CH); 35.3 (C); 31.6 (CH); 30.9 (CH<sub>2</sub>); 27.0 (CH<sub>3</sub>); 26.8 (C); 25.6 (CH); 19.9 (CH<sub>3</sub>); and 19.0 (CH<sub>3</sub>) p.p.m.]. There was no upfield signal corresponding to a bicyclobutane such as (3)<sup>5</sup> and the spectrum was in complete agreement with structure (4). The 250 MHz <sup>1</sup>H n.m.r. spectrum exhibited three methyl singlets at δ (Me<sub>4</sub>Si) 0.76, 0.90, and 1.15, a seven-spin system which was resolved‡ into five bridgehead protons [δ 1.38 (m, including couplings of 6 and 3 Hz), 1.89 (dd, *J* 3 and 5 Hz), 2.05 (dd, *J* 4 and 6 Hz), 2.10 (ddd, *J* 4, 6.5, and 1.5 Hz), and 2.74 (ddd, *J* 6.5, 4.5, and 3 Hz)], and a methylene signal due to the protons on C(5) [δ 1.82 (ddd, *J* 12, 6.5, and 2 Hz) and 2.20 (dd, *J* 12 and 1 Hz)]. Coupling constants are in good agreement with those observed in related systems, in particular in pinanes<sup>6</sup> and tricyclo[3.3.1.0<sup>2,7</sup>]nonanes.<sup>7</sup> The efficient insertion into the C(8)–H bond to produce (4) rather than into the C(5)–H bond to form (3) or into the 2-Me group can be readily explained in terms of the geometry of (2). In the pinane-type skeleton the C(1)C(2)C(3)C(4)C(5) portion is considerably flattened by the C(7)-bridge;<sup>8</sup> consequently the *endo*-C(8)–H bond, which is nearly co-linear with the empty orbital of the carbenoid intermediate is most favourably placed for insertion.<sup>8</sup> In addition, the C(5)–H bond is less favourably placed than in (1).<sup>2a</sup>

Treatment of (4) with AgNO<sub>3</sub>-aqueous acetone led to a tertiary alcohol (5; R = Me) (20%), the n.m.r. spectrum of which was very similar to that of authentic (5; R = H).<sup>9</sup> The <sup>13</sup>C n.m.r. spectra of (4) and (5) were very similar apart from the expected changes at the reacting centres; this suggests that no skeletal rearrangement has occurred. Silver catalysed solvolysis of (3) in the normal manner<sup>10</sup> would lead to a secondary alcohol, a disubstituted cyclopropane, or considerable skeletal rearrangement, none of which was observed; however, solvolysis of (4) could readily lead to (5).§



Compound (4) also reacted with AgClO<sub>4</sub>-C<sub>6</sub>H<sub>6</sub> to give (6) (30%), [α]<sub>D</sub> - 4.88° [13C n.m.r.: δ 155.9 (C), 103.5 (CH<sub>2</sub>), 51.08 (CH), 45.6 (CH), 42.5 (CH), 40.8 (C), 40.4 (CH), 38.2 (CH<sub>2</sub>), 32.9 (CH<sub>2</sub>), 28.5 (CH<sub>3</sub>), and 20.0 (CH<sub>3</sub>) p.p.m.].

† The two groups of authors of this paper worked independently and became aware of the similarity of their work at the EUCHEM Conference on Electron Deficient Intermediates, Geneva, October, 1978.

‡ The spectrum was successfully simulated using the LAUCOM III programme (A. A. Bothner-By and M. S. Castellano, *J. Chem. Phys.*, 1964, **41**, 3863).

§ Compound (4) contains a *syn*-tricyclo[3.2.0.0<sup>2,4</sup>]heptane unit. Silver induced reactions of the corresponding *anti*-derivatives are known (L. A. Paquette and L. M. Leichter, *J. Org. Chem.*, 1974, **39**, 461; *J. Amer. Chem. Soc.*, 1971, **93**, 4922; 1972, **94**, 3653, and references therein).

The  $^1\text{H}$  250 MHz n.m.r. spectrum of (6) showed an *exo*-methylene group [ $\delta$  4.43 (br s) and 4.82 (br s)], a *gem*-dimethyl [ $\delta$  0.70 (s) and 1.21 (s)], four bridgehead hydrogen atoms [ $\delta$  3.03 (m), 2.71 (br s), 2.26 (dd,  $J$  5.5 and 4.5 Hz), and 1.96 (ddd,  $J$  7, 5, and 4.5 Hz)], and two AB-systems [ $\delta$  1.77 (dt,  $J$  12, 1.2, and 1.2 Hz) and 1.37 (ddd,  $J$  12, 7, and 2.5 Hz); 1.32 (br d,  $J$  11 Hz) and 1.27 (br d,  $J$  11 Hz)]. The same rearrangement occurred on reaction of (4) with *p*- $\text{MeC}_6\text{H}_4\text{-SO}_3\text{H-C}_6\text{H}_5$  (49%) or  $\text{FeCl}_3$ -pyridine (70%), and under

certain g.l.c. conditions. Compound (6) was further characterised by ozonolysis to give (7),  $[\alpha]_D -12^\circ$ ,  $\nu_{\text{max}}$  1735  $\text{cm}^{-1}$ . N.m.r. spectra of both (6) and (7) are in good agreement with those reported for other bicyclo[3.2.1.0<sup>3,6</sup>]-octanes.<sup>11</sup>

P.S. wishes to thank the S.R.C. and Bush Boake Allen for support.

(Received, 30th January 1979; Com. 085.)

<sup>1</sup> M. Jones and R. A. Moss, 'Carbenes,' Wiley, London, 1973; A. R. Allan and M. S. Baird, *J.C.S. Chem. Comm.*, 1975, 172.

<sup>2</sup> (a) L. A. Paquette and R. T. Taylor, *J. Amer. Chem. Soc.*, 1977, **99**, 5708; L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allan, *ibid.*, 1972, **94**, 7761, and references therein; (b) L. A. Paquette, G. Zon, and R. Taylor, *J. Org. Chem.*, 1974, **39**, 2677, and references therein.

<sup>3</sup> J. Graefe, L. M. Thank, and M. Mühlstädt, *Z. Chem.*, 1971, **11**, 252. The geometry of carbene addition to  $\alpha$ -pinene has been assigned by detailed n.m.r. studies (P. Brun, J. Casanova, J. Hatem, J. P. Zhara, and B. Waegell, *Org. Magnetic Resonance*, in the press) and attack occurs from the less hindered face; the formation of (4) from (2) provides absolute proof.

<sup>4</sup> J. Hatem and B. Waegell, *Tetrahedron Letters*, 1973, 2019, 2023; *ibid.*, 1971, 2069. Compound (2c) was prepared by the phase-transfer method.

<sup>5</sup> M. Christl and W. Buchner, *Org. Magnetic Resonance*, 1978, **11**, 461.

<sup>6</sup> A. J. Baretta, C. W. Jefford, and B. Waegell, *Bull. Soc. Chim. France*, 1970, 3899, 3985; P. Kaplan, C. O. Schule, D. Weisleder, and C. Kloppenstein, *J. Org. Chem.*, 1968, **33**, 1728; C. M. Holden and D. Whittaker, *Org. Magnetic Resonance*, 1975, **8**, 125.

<sup>7</sup> W. Frössl and P. Margaretha, *Helv. Chim. Acta*, 1976, **59**, 2244.

<sup>8</sup> R. C. Dobson, D. M. Hayes, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1971, **93**, 6188; E. A. Hill, *J. Org. Chem.*, 1972, **37**, 4008.

<sup>9</sup> R. R. Sauers and R. A. Parent, *J. Org. Chem.*, 1963, **28**, 605.

<sup>10</sup> L. A. Paquette, 'Metal Catalysed Reactions in Strained Ring Systems,' ch. 4, MTP International Review of Sciences, vol. 5, Alicyclic Compounds, Butterworths, London, 1973.

<sup>11</sup> R. R. Sauers, R. A. Parent, and S. B. Damie, *J. Amer. Chem. Soc.*, 1966, **88**, 2257; M. Geisel, C. A. Grob, R. P. Traber, and W. Tschudi, *Helv. Chim. Acta*, 1976, **59**, 2808.