

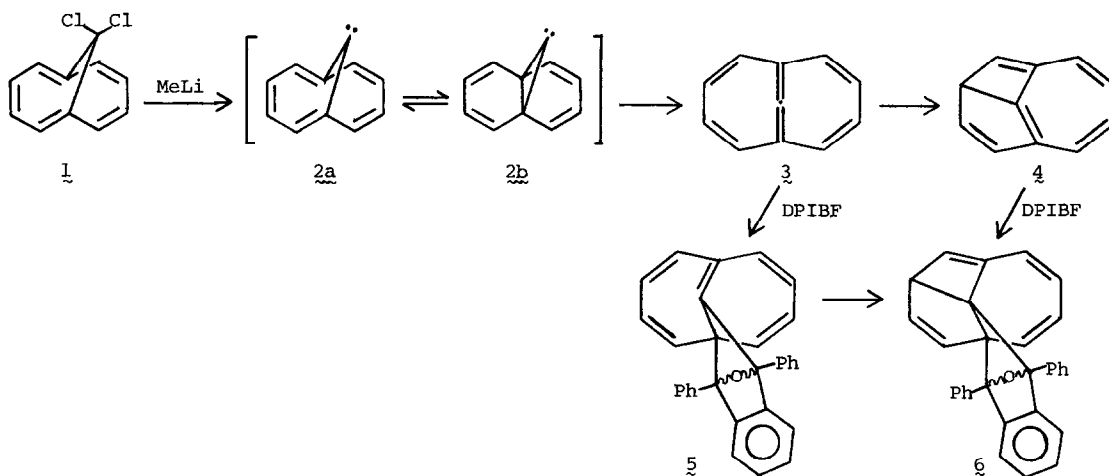
ON THE QUESTION OF ALLENE FORMATION FROM  
TRICYCLIC CYCLOPROPYLIDENES<sup>1</sup>

by Philip Warner<sup>\*2</sup> and Suae-Chen Chang

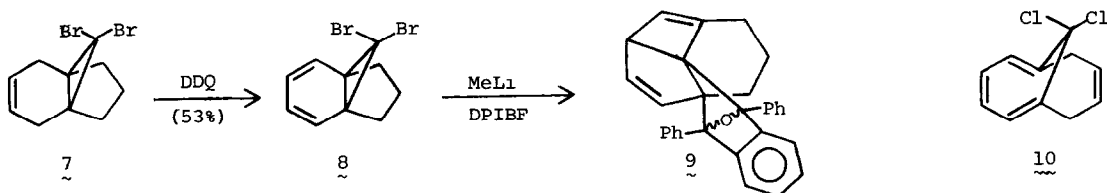
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**Abstract:** The carbenoid or carbene derived from 8 undergoes dimerization or trapping with DPIBF. The allene mechanism previously proposed was made doubtful by the finding that stereoisomeric carbenes 20a and 20b give stereoisomeric products without crossover.

Carlton, *et al.*,<sup>3a</sup> showed that 1 undergoes reaction with MeLi to afford dimer(s); in the presence of diphenylisobenzofuran (DPIBF), Diels-Alder adducts were obtained. They proposed a mechanistic scheme in which a carbene or carbenoid (written<sup>3a</sup> as 2) opened to an allene (3). The allene was envisioned to either internally cyclize (to 4) and then externally cycloadd to yield 6, or possibly react in the reverse fashion (*i.e.*, via 5). It would seem that 3+4 is more "allowed" than 5+6, and should also be favored over 3+5 on a kinetic basis.<sup>4</sup>

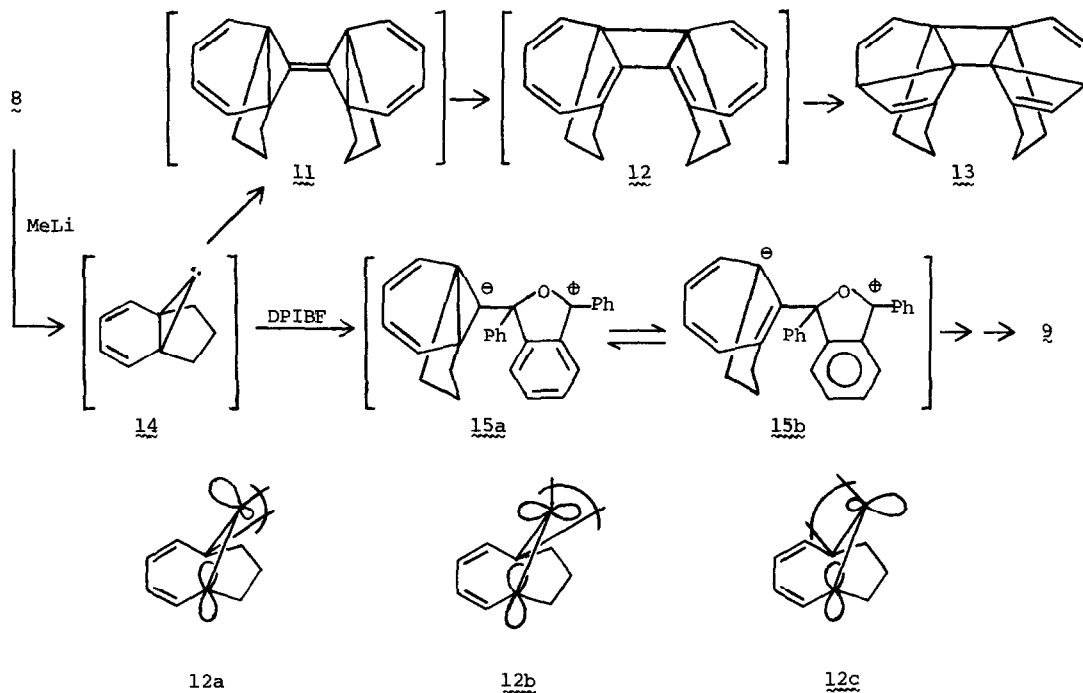


We now report that treatment of 8<sup>5</sup> with MeLi in ether at either -78° or room temperature gives one isolable dimer (22% yield), the structure of which is unknown.<sup>5d</sup> Similar treatment of 8 in the presence of DPIBF provides two adducts in a 2:1 ratio (24%). We have assigned their structures as 9 based on their close spectral resemblance to 6.<sup>5b,c</sup>



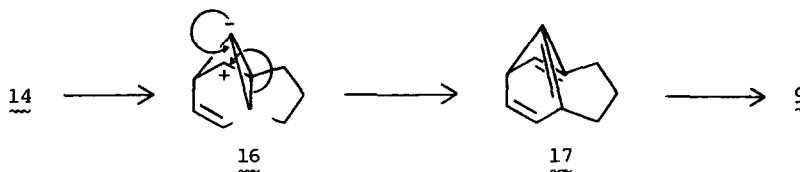
The similar reactions of 8 and 1 indicates that only one diene moiety (viz., in 2b or 3) is necessary to effect the observed reactions (as already demonstrated by Levin's<sup>3b</sup> study of the reaction of 10 with MeLi), but no comment can be made on the role of 2a vs. 2b. However, some new mechanistic conclusions can be drawn.

First of all, the possibility that dimer formation occurs via a carbene dimer<sup>6</sup> (e.g.,  $8 \rightarrow 11 \rightarrow 13$ ) and that trapping proceeds by way of zwitterion 15 can apparently be rejected. To do so requires a detailed look at the structure of the bridgehead double bonds of 12 (or the analogous one derived from closure of 15). The situation depicted by 12a-c is as follows:

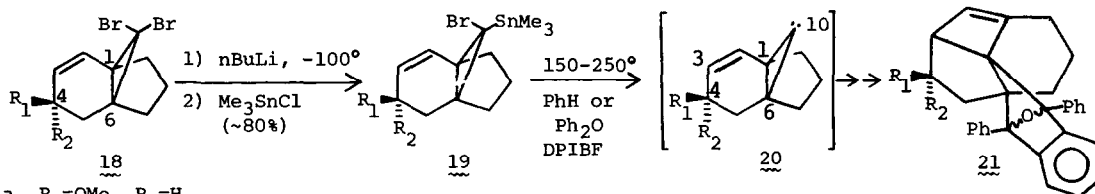


12b represents the unrehybridized,<sup>7</sup> nearly perpendicular olefin structure, not found in any bridgehead olefins<sup>8</sup> (12b is particularly poor due to the extra bond angle strain imposed by the cyclobutane ring). Contrariwise, 12a represents the rehybridized form which would be trans-cyclohexenoid,<sup>9</sup> while 12c depicts the more stable trans-cycloheptenoid isomer. However, 12c is incapable of internal cyclization without substantial atomic movement and overlap loss in the transition state; were it to be formed, it would probably dimerize or be trapped.<sup>10</sup> Obviously, the same arguments mitigate against the pathway involving 5, since the analogous intermediate from 15 has apparently been excluded.

What likely pathways are left for the formation of 9? Most viable are the allene mechanism, and the zwitterionic mechanism<sup>11</sup> depicted below. Additionally, there is the question of the involvement of free carbenes vs. carbenoids (i.e.,  $\alpha$ -bromoanions related to 14). Pursuant to our study of the effects of  $L_1^+$  complexation on the reactions of the



carbenoids derived from 18a,<sup>12a</sup> we felt the pyrolytic decomposition<sup>13a</sup> of 19 would generate carbenes (20) without the complication of  $\alpha$ -bromoanion intervention. Thus both 18a and 18b (available from the corresponding alcohol<sup>12b</sup>) were converted to the  $\alpha$ -bromo trimethyltin derivatives,<sup>13b</sup> from which the predominant isomers, 19a and 19b, were isolated. Pyrolysis



a,  $R_1 = \text{OMe}$ ,  $R_2 = \text{H}$

b,  $R_1 = \text{H}$ ,  $R_2 = \text{OMe}$

of 19a or 19b in  $\text{Ph}_2\text{O}$  at  $250^\circ$  for 1 minute in the presence of 1.1 eq. DPIBF (ca. 0.1M) resulted in the formation of 21 (2 isomers in each of the "a" and "b" series) without any detectable crossover (pmr and glc analysis). Similar reaction of 19a in benzene ( $150^\circ$ ,  $t_{1/2} \approx 100'$ ) also produced only 21a, even when the [19a] and [DPIBF] were 0.002M.<sup>14</sup> Assuming we could have observed 21b only if it constituted 5-10% of the product mixture, the minimum energy difference between that required for DPIBF trapping and epimerization at  $C_4$  is ca. 8 kcal/mole. Operationally, this indicates that an allene intermediate, at least in the classical sense,<sup>15</sup> is not involved in the formation of 21 (or, presumably, 6 or 9). There remains the question of when is an allene an allene (e.g., how much  $C_1-C_6$  bond breaking in 20 is required before one has an "allene", and to what extent may this be preceded by or coincide with  $C_3-C_{10}$  bonding)? We are attempting to answer this question.

#### REFERENCES AND FOOTNOTES

1. We gratefully acknowledge partial support from the National Science Foundation.
2. Fellow of the Alfred P. Sloan Foundation, 1976-80.
3. (a) J. B. Carlton, R. H. Levin and J. Clardy, *J. Am. Chem. Soc.*, **98**, 6068 (1976);  
(b) J. B. Carlton and R. H. Levin, *Tetrahedron Lett.*, 3761 (1976).
4. (a) Levin's supposition<sup>3a</sup> that initial dimerization of 3 could provide only 2 dimers is in error, since the dimerization could initially produce the 1,3-dimethylene-cyclobutane type structure;<sup>4b</sup> (b) J. E. Baldwin and R. A. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).

5. (a) 8: mp 73-74°; pmr (CCl<sub>4</sub>): δ1.1-3.0 (m, 6H), 5.5-6.3 (AA'BB', 4H); uv (c-C<sub>6</sub>H<sub>12</sub>): λ<sub>max</sub> 235 (ε=1600) nm; calcd. for C<sub>10</sub>H<sub>10</sub>Br<sub>2</sub>: m/e 287.9150; found: m/e 287.9149; (b) 9a (16%): mp 207-209 (d); pmr (CCl<sub>4</sub>): δ1.0-2.0 (m, 6H), 3.0 (br. s, 1H), 5.05 (d, 1H), 5.65 (dd, 1H), 5.9 (s, 1H), 6.95-7.3 (m, 14H); calcd. for C<sub>30</sub>H<sub>24</sub>O: m/e 400.1827; found: m/e 400.1817; (c) 9b (8%): mp 155-157°; pmr (CCl<sub>4</sub>): δ0.7-2.2 (m, 6H), 2.97 (br. s, 1H), 5.64 (br. s, 2H), 5.84 (br. s, 1H), 6.9-7.9 (m, 14H); found for C<sub>30</sub>H<sub>24</sub>O: m/e 400.1846; (d) dimer (C<sub>20</sub>H<sub>20</sub>): mp 93-95°; pmr (CCl<sub>4</sub>): δ1.08-2.45 (m, 12H), 3.55 (m, 2H), 5.32 (d, 2H, J=5), 5.86 (s, 2H), 6.13 (dd, 2H, J=5, 2); cmr (CDCl<sub>3</sub>): δ152.5 (rel. area 1), 139.2 (7.6), 136.2 (7.1), 134.4 (6.7), 59.3 (1.3), 56.5 (6.2), 28.6 (8.2), 27.5 (15.1); calcd. for C<sub>20</sub>H<sub>19</sub> (P-1): m/e 259.1487; found: m/e 259.1485.
6. Such a possibility was considered and found not to be readily excludable in a related case [R. A. LaBar and W. M. Jones, J. Am. Chem. Soc., 96, 3645 (1974)].
7. (a) W. L. Mock, Tetrahedron Lett., 475 (1972); (b) L. Radom, J. A. Pople and W. L. Mock, ibid., 479 (1972).
8. R. Keese, Angew. Chem. Int. Ed., 14, 528 (1975).
9. (a) J. R. Wiseman and W. A. Pletcher, J. Am. Chem. Soc., 92, 956 (1970); (b) P. Warner and S. Lu, ibid., 98, 6752 (1976).
10. P. Warner, R. La Rose, C. Lee and J. C. Clardy, ibid., 97, 5507 (1975).
11. (a) This type of nucleophilic attack of the π bond upon the carbene center is favored theoretically; <sup>11b</sup> (b) W. W. Schoeller and U. H. Brinker, J. Am. Chem. Soc., 100, 6012 (1978).
12. (a) P. Warner and S.-C. Chang, Tetrahedron Lett., 3981 (1978); (b) P. Warner, W. Boulanger, T. Schleis, S.-L. Lu, Z. Le and S.-C. Chang, J. Org. Chem., 43, 4388 (1978).
13. (a) D. Seyferth and F. M. Armbrrecht, Jr., J. Am. Chem. Soc., 91, 2616 (1969); (b) D. Seyferth, R. L. Lambert, Jr. and M. Massol, J. Organomet. Chem., 88, 255 (1975).
14. As expected, the rate of loss of 19a remained constant as the concentration was varied.
15. For a similar stereochemical experiment which was used to exclude an allene, see W. R. Moore and B. J. King, J. Org. Chem., 36, 1877 (1971).

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