Tetrahedron Letters No. 42, pp 3981 - 3984.
© Pergamon Press Ltd. 1978. Printed in Great Britain.

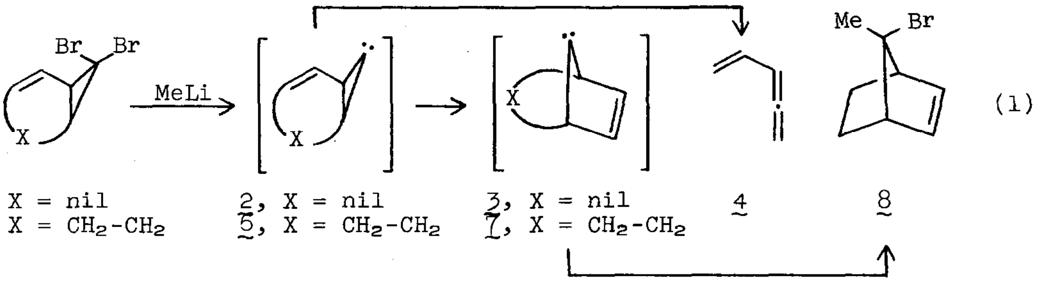
0040-4039/78/1015-3981$02.00/0

On the Purported Vinylcyclopropylidene to Cyclopentenylidene Rearrangement[1]

Philip Warner*[2] and Suae-Chen Chang

Department of Chemistry, Iowa State University, Ames, Iowa 50011

A recent review[3] cites the 2 to 3 conversion[4] as one of two known types of carbene-carbene rearrangements. The additional formation of bona fide carbene product 4[5] lends credence to the intermediacy of 2. More relevantly, 5 is converted uniquely to 8 by a process proposed[6] to involve 6 and 7, although none of the bona fide products from 7 were detected;[8] the stereoselectivity apparent in the formation of 8 remains unexplained. We now provide evidence which shows that these rearrangements do not involve carbenes,[9,10] but rather species in which bonding to lithium is necessary.[11]



1, X = nil
5, X = CH_2-CH_2

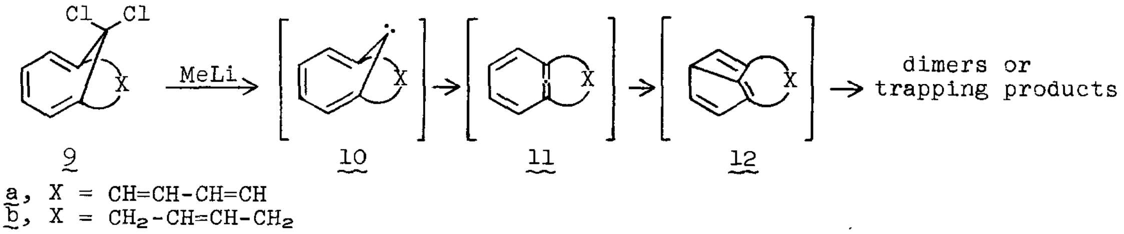
2, X = nil
5, X = CH_2-CH_2

3, X = nil
7, X = CH_2-CH_2

4

8

Our interest in bridgehead olefins generated from cyclopropanes[12] drew our attention to the purported formation of allenes 11a[13a] and 11b[13b] from 9a and 9b, respectively. We wondered whether the ultimate formation of 12 was a manifestation of cycloheptatrienylidene-cycloheptatetraene chemistry,[3] or rather related to the transformations of 1 and 5 (eqn. 1). This question remained unanswered by the observation that 10,10-dibromo[4.3.1]propella-2,4-



9

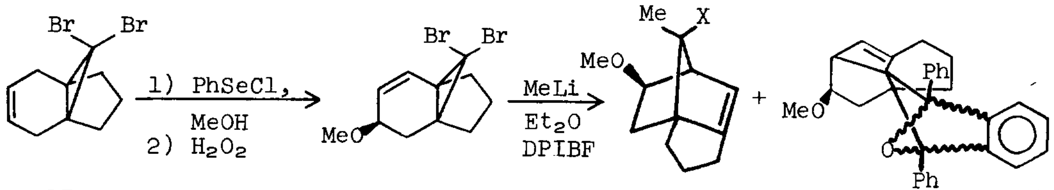
10

11

12

a, X = CH=CH-CH=CH
b, X = CH_2-CH=CH-CH_2

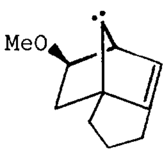
diene reacted analogously to 9 when treated with MeLi.[14] We thus focussed on 14,[15] synthesized in 77% yield from 13.[16]



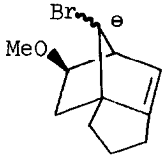
13 14 15, X=Br 16
17, X=I

Addition of MeLi to an ethereal solution of 14 and diphenylisobenzofuran (DPIBF) at -78° resulted in primarily 15 (49% isolated)[17] with small amounts of 16 visible in the pmr of the crude product. Reaction at room temperature provided the same products in the yields shown in Table I. To further probe the mechanism of the reaction, 14 was treated with MeLi in ether (DPIBF) in the presence of several different salts (Table I). The conclusions are that in the presence of Li^+ salts, or under less polar conditions [*e.g.*, low temperature or MeI solvent (vide infra)], the proportion of 15 increases at the expense of 16, while under generally more ionic conditions (including Br^-), the relative proportion of 16 increases.[18] Thus the reaction exhibits a common ion salt effect for Li^+ (but not Br^-), where the production of 15 is accentuated by the presence of Li^+. More dramatically, when MeLi is added to a solution of 14 (ether, DPIBF) which contains 12-crown-4-ether,[19] *no 15* results (15 is stable to the reaction conditions)--only 16 is formed! Thus if the Li^+ is forcibly removed from the initial carbenoid, 15 is not obtained (Table I).

But what is the pathway by which the methyl group is introduced? When the reaction of 14 with MeLi was performed in MeI as solvent, the products were 17 and 16 (in a 3:2 ratio); when the solvent was changed to CD_3I, the products were still 17 and 16--no deuterium was incorporated. Hence insertion of a rearranged norbornenylidene (18) into MeX is eliminated. Similarly excluded is an S_N2 displacement by 19 on MeX. The additional fact that 15 is

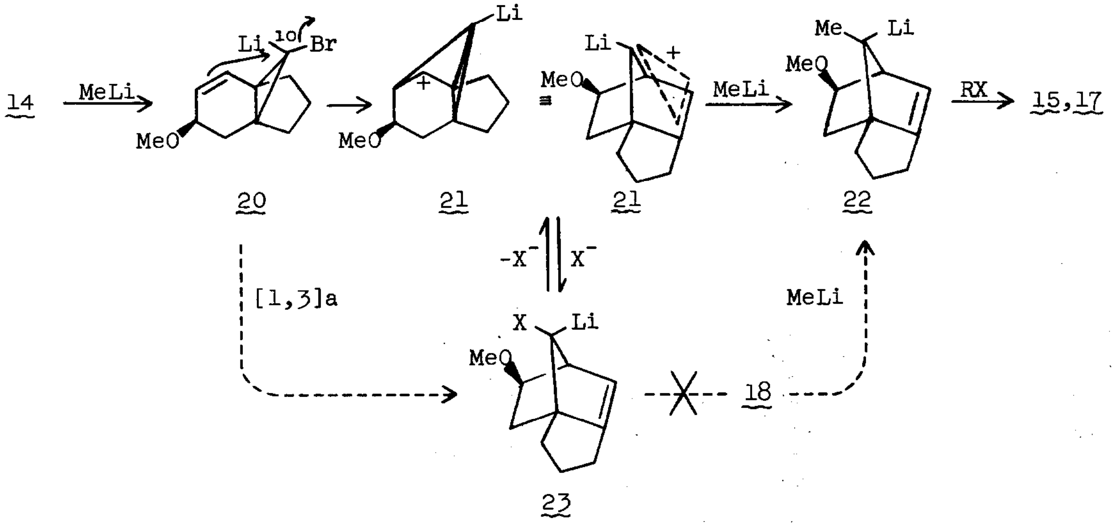


18



19

completely stable to MeLi (in or out of MeI) means that both halogens must be removed from 14 prior to product (17) formation. Also, if carbenoids such as 20 or 23 undergo halogen exchange, it is meaningless in terms of product formation, since no 17 is formed in the presence of I^-. A scheme which accounts for the stereochemistry of 15(17), as well as the other facts, is shown below. We prefer the precedented[20] cationic-type conversion of 20 to 21, rather than the antarafacial shift to 23, because it is difficult to



understand why the C_{10}-epimeric carbenoid wouldn't undergo the same shift.[21] We strongly doubt that 22 could be formed directly from 18, for precedent[7] makes it apparent that 18 would rearrange prior to intermolecular trapping. Indeed, when the reaction was carried out in 2-butene or isobutylene, no olefin trapping resulted. Furthermore, it is doubtful that insertion of 18 into MeLi would result in only, or even mainly 22; rather the epimer, where Li could coordinate to oxygen, should be favored. The stereoretentive conversion of 22 to 15(17) is very reasonable,[22] although we have not yet been able to verify it. All attempts at generation of 22 (*e.g.*, from 15 and *n*BuLi) have led to replacement of X by H.

Experiments aimed at elucidating the pathway for formation of 16 will soon be reported.

Acknowledgements. We thank Professor Robert Moss for very helpful discussions This work was partly supported by the National Science Foundation.

References and Footnotes

1. This is Propellanes 21.
2. Alfred P. Sloan Fellow, 1976-78.
3. W. M. Jones, *Accts. Chem. Res.*, 10, 353 (1977).
4. K. H. Holm and L. Skattebol, *Tetrahedron Lett.*, 2347 (1977).
5. See, however, cautions regarding the mode of formation of allenes: (a) L. Skattebol, *J. Org. Chem.*, 31, 2789 (1966); (b) W. R. Moore and B. King, *ibid.*, 36, 1877 (1971).
6. L. Skattebol, *Tetrahedron*, 23, 1107 (1967).
7. (a) R. A. Moss, U-H. Dolling and J. R. Whittle, *Tetrahedron Lett.*, 931 (1971); (b) R. A. Moss and U-H. Dolling, *ibid.*, 5117 (1972).

8. (a) The MeLi induced rearrangements[8b] of 8,8-dibromobicyclo[5.1.0]oct-2-ene and 8,8-dibromobicyclo[5.1.0]octa-2,4-diene are more difficult to assess, since some, but not all, of the bona fide carbene rearrangement products[8c] were observed; (b) M. S. Baird and C. B. Reese, Tetrahedron Lett., 2895 (1976); (c) K. Okumura and S-I. Murahashi, ibid., 3281 (1977).
9. These include, we propose, the cases reported by (a) M. S. Baird and C. B. Reese, Chem. Comm., 523 (1972); (b) M. Christl and M. Lechner, Ang. Chem. Int. Ed., 14, 765 (1975); (c) L. A. Paquette and R. Taylor, Tetrahedron Lett., 2745 (1976).
10. (a) The recently reported[10b] rearrangement involving 7-diazobicyclo[4.1.0]hept-2-ene may be a real carbene rearrangement; (b) K. H. Holm and L. Skattebol, J. Am. Chem. Soc., 99, 5480 (1977).
11. (a) The carbenoid mechanism outlined by Paquette for the 5 to 8 conversion is apparently flawed;[11b] (b) L. A. Paquette and R. Taylor, J. Am. Chem. Soc., 99, 5708 (1977).
12. P. Warner, S. Lu, E. Myers, P. DeHaven and R. A. Jacobson, ibid., 99, 5102 (1977), and references therein.
13. (a) J. Carlton, R. H. Levin and J. Clardy, ibid., 98, 6068 (1976); (b) J. Carlton and R. H. Levin, Tetrahedron Lett., 3761 (1976).
14. P. Warner and S-C. Chang, submitted for publication.
15. The stereochemistry of 14 is based on work with the corresponding alcohol, from which 14 can be made (NaH, MeI); details will be published soon.
16. E. Vogel, et al., Annalen, 759, 1 (1972).
17. The structures of 15 and 17 are supported by elemental analysis, pmr decoupling experiments and Eu shift reagent pmr studies of 15, 17 and the corresponding alcohols.
18. The quantitative aspects of these dependencies are still under investigation.
19. This crown ether, available from Aldrich, is competitively destroyed by MeLi.
20. X. Creary, J. Am. Chem Soc., 98, 6608 (1976).
21. Of course we aren't yet sure that the rearrangement is dependent upon the stereochemistry of 20, yet the fact that the C-4 epimer of 14 affords less product analogous to 15 and more analogous to 16, suggests that is the case. Stereospecific carbenoid generation experiments are underway.
22. The identity of RX may be MeI, or, quite likely, 14.[23]
23. D. Seyferth, R. Lambert, Jr. and M. Massol, J. Organometal. Chem., 88, 255 (1975).

Table I. Yields[a] of 15 and 16 in the Presence of Various Substances.

Salt[b] or Ether	% 15	% 16	Total Yield
None	34	62	96
LiI	48	56	104
$LiClO_4$	47	49	96
$NaClO_4$	29	62	91
KI	32	65	97
Et_4NBr	26	74	100
12-C-4 (10 eq.)	3	72	75
12-C-4 (20 eq.)	0	59	59

(a) For reactions run at room temperature to completion; yields determined by pmr and/or glc; (b) 4 eq. salt were used each time, but dissolution was incomplete for the last 3 salts.

(Received in USA 11 July 1978; received in UK for publication 22 August 1978)