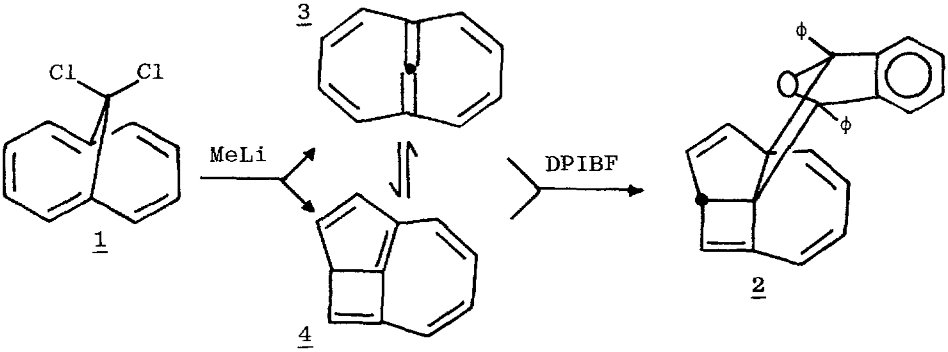
Tetrahedron Letters No. 42, pp 3761 - 3764, 1976. Pergamon Press. Printed in Great Britain.

THE CARBENOID REACTIONS OF 11,11-DICHLOROTRICYCLO[4.4.1.$0^{1,6}$]-UNDECA-2,4,8-TRIENE (7).

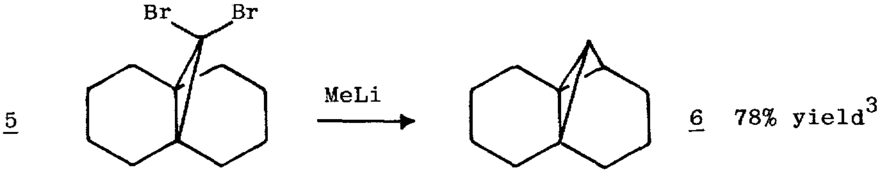
Jane B. Carlton[1] and Ronald H. Levin*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138, U.S.A.

(Received in USA 24 June 1976; received in UK for publication 7 September 1976)

In a previous study we found that when 11,11-dichloro-1,6-methano[10]annulene (1) was treated with methyllithium in the presence of 1,3-diphenylisobenzofuran (DPIBF), only one carbenoid derived product was obtained.[2] The structure of this 1:1 adduct was determined by X-ray crystallography to be that shown below for 2, and a mechanistic rationale involving allene 3 and/or bicycloheptatriene 4 was advanced.



In contrast to this result, an earlier report on the carbenoid chemistry of 11,11-dibromotricyclo[4.4.1.$0^{1,6}$]undecane (5), a saturated analogue of 1, revealed intramolecular carbon-hydrogen insertion to be the major reaction pathway.[3] No allene formation or dimers were reported in this study.



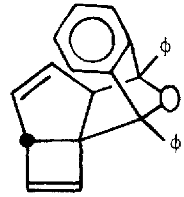
It therefore became of interest to investigate another derivative of 1 in order to probe the generality of our observations. 11,11-Dichlorotricyclo-[4.4.1.$0^{1,6}$]undeca-2,4,8-triene (7) was selected for this purpose. Triene 7 is a synthetic precursor to 1 and readily prepared by the method of Nelson and Untch.[4] This molecule contains a number of structural features which serve to make it an appropriate substrate for further investigation. The carbon framework is, in essence, the same as that in 1 and 5. However, unlike 1, it contains two methylene units located α to the bridgehead carbons. In fact, Dreiding molecular models suggest that these carbon-hydrogen bonds in 7 can occupy the same spatial volume element relative to the ultimate carbenoid center as do the analogous bonds in 5. Hence, the C-H insertion reaction is a distinct possibility for 7. In addition, this molecule contains a norcaradiene-cycloheptatriene moiety, further establishing its similarity to 1.[5] Should such a unit be required for ready electronic reorganization and allene formation, then the chemistry of 7 might parallel that of 1.

When 7 was treated with a slight excess of methyllithium at 15°C, four products were obtained; of these, only 8 was found to be carbenoid derived.[6] This substance, isolated in 6% yield, was shown to be a mixture of $C_{22}H_{20}$ hydrocarbons. The similarity between certain regions of the pmr spectrum of this dimer mixture and the dimer mixture obtained from 1 suggested that allene and/or bicycloheptatriene formation was occurring. A careful search of the reaction crude by combination vpc-ms failed to detect any material which might conceivably be the bicyclobutane or a bicyclobutane-derived product.

Generation of the carbenoid in the presence of DPIBF led to the complete suppression of dimer formation, the 1:1 adducts 9 (4.4%) and 10 (1.6%) being formed instead.[7] The relative stereochemistry in 9 and 10 is assigned on the basis of the pmr data contained below in Table I. As can be seen, the comparable centers in 2 and 9 have strikingly similar line shapes and coupling constants. The pmr signals of H-2 through H-8 of 9 have, however, been shifted upfield relative to the corresponding signals of 2. The aromatic protons from the DPIBF derived residue of 9 absorb in the region from δ 7.00 to 7.80, and the signals are very similar in appearance to those of 2.

In 10, H-2 now resonates at higher field than H-3, just as in 11.[8d] Additionally, the pmr spectrum of the aromatic protons of 10 (a multiplet from δ 7.23 to 7.77 and a broad singlet at δ 7.03) is similar to that of 11 and unlike that of either 2 or 9.

These observations are again consistent with a mechanism based on allene and/or bicycloheptatriene intermediates. Furthermore, these results establish that the carbenoid derived from 1 is not unique in its ability to undergo the electronic reorganizations discussed above. Indeed, the carbenoid derived from 7 reacts by a similar pathway despite the attractive[9] alternative of intramolecular carbon-hydrogen insertion. A comparison of 1, 5 and 7 suggests that allene

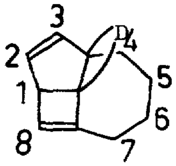


11

Table I. 100 MHz PMR Data for DPIBF Adducts[a,b,c,d]

	2	9	10	11[8c]
H-1	3.00(dd:2.4,2.4)	3.07(br.s.)	3.14(dd:3,3)	3.27(quintet)
H-2	6.04(dd:2.4.5.9)	5.56(dd:2.5,5.9)	5.31(dd:3,6)	5.53(dd)
H-3	5.32(d:5.9)	5.18(d:5.9)	5.65(d:6)	5.76(dt)
H-4	5.92(m)	2.47(m-2 proton)	2.87(br.s); 2.68(br.s)	
H-5	5.34*(m)	4.45(m)	5.19(m)	
H-6	5.28*(m)	4.45(m)	5.19(m)	
H-7	6.16 (m)	2.87(br.s-2 proton)	2.09(m-2 proton)	
H-8	6.38 (br.s)	5.87(br.s)	5.72(d:3)	6.24,6.05(ABq-2 proton)

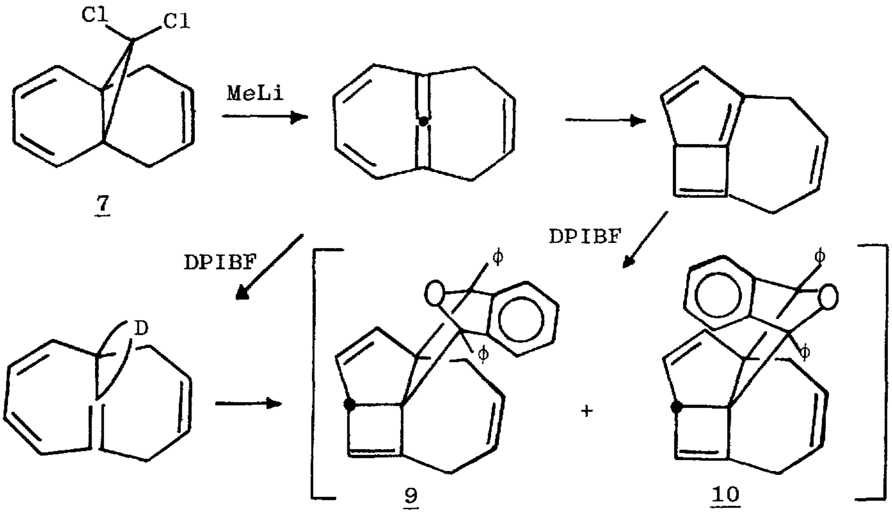
[a] Spectra were recorded on a Varian XL-100-15 spectrometer operated in the FT mode using CDCl$_3$ as solvent; [b] starred values within a column may be interchanged; [c] coupling constants are reported in Hertz; [d] the numbering is based on the following diagram:



D = DPIBF derived moiety

formation will occur from carbenoids with a weakened (i.e., via incorporation into a norcaradiene framework) or nonexistent (i.e., cycloheptatriene) internal cyclopropane bond. Further experiments designed to test these ideas and distinguish between allene and bicycloheptatriene intermediates are in progress.

Acknowledgement is made to the Research Corporation and the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. R. H. L. is also grateful to the E. I. duPont deNemours Company for a Young Faculty Grant.



References

1. National Institutes of Health Trainee, 1974 - present.
2. J. B. Carlton, R. H. Levin and J. Clardy, J. Amer. Chem. Soc., **98**, 0000 (1974).
3. R. Vaidyanathaswamy and D. Devaprabhakara, Chemistry and Industry, 515 (1968).
4. P. H. Nelson and K. G. Untch, Tetrahedron Lett., 4475 (1969).
5. The pmr spectrum of 7 reveals the equilibrium to lie, within the limits of detection, entirely on the norcaradiene side. This, of course, does not mean that reactions of 7 cannot utilize the minor cycloheptatriene component.
6. The three remaining products (obtained in ca. 65% yield) are of considerable interest as they allow for meaningful comment upon the initial metallation process. These results will be described in another article.
7. 9: High resolution mass observed: 412.18135, calcd. 412.18271.
   10: High resolution mass observed: 412.18233, calcd. 412.18271.
8. a) R. Breslow, W. Washburn and R. C. Bergman, J. Amer. Chem. Soc., **91**, 196 (1969); b) N. L. Bauld, C. E. Dahl and Y. S. Rim, ibid, **91**, 2787 (1969); c) C. E. Dahl, Ph.D. Thesis, The University of Texas at Austin, 1971: Diss. Abstracts, **32**, 5685-B (1972); d) W. Washburn, Ph.D. Thesis, Columbia University, 1971: Diss. Abstracts, **32**, 3866-B (1972).
9. In tetrasubstituted cyclopropylidenoids, intramolecular carbon-hydrogen insertion generally occurs to the exclusion of allene formation. See, for example, W. R. Moore and J. B. Hill, Tetrahedron Lett., 4343 (1970).