Tetrahedron Letters No. 2, pp 163 - 166, 1977. Pergamon Press. Printed in Great Britain.

THE REACTION OF BENZ(de)ANTHRACENYL ANION WITH METHYLENE CHLORIDE/n-BUTYLLITHIUM

Richard M. Pagni* and Michael Burnett

Department of Chemistry, University of Tennessee,
Knoxville, Tennessee 37916

Alan C. Hazell*
Department of Inorganic Chemistry, Aarhus University
DK-8000 Aarhus C. Denmark

(Received in USA 13 August 1976; received in UK for publication 30 November 1976)

The addition of chlorocarbene[1] to cyclic π anions has become a reaction of synthetic utility in recent years.[2-5] Perhaps the best known reaction of this type is Katz's preparation of benzvalene from the addition of chlorocarbene to the cyclopentadienyl anion (1).[2] In all of the anions which have been studied (1 through 5), the addition of the carbene appears to be completely regiospecific either because of the high intrinsic symmetry of anion (1,[2] 3,[3] and 4[4]), where only one site of attack is possible, or, when the anion lacks high symmetry as with 2[2] and 5[5], attack on the benzene ring is precluded because aromaticity would be destroyed in the process.[6] We decided to investigate the reaction of chlorocarbene with benz(de)anthracenyl anion (6), because of the expectation that more than one site of this unsymmetrical anion might be attacked by chlorocarbene. This expectation was realized.

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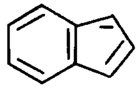

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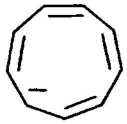

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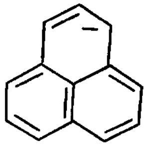

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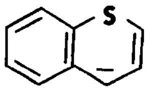

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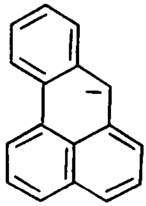

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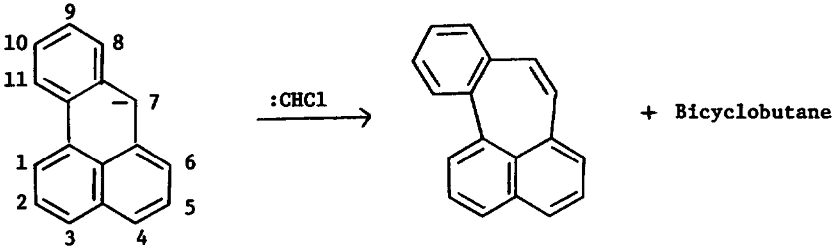
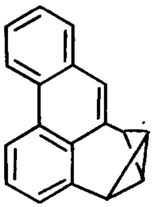
Treatment of 6 (prepared by the reaction of 7H-benz(de)anthracene[7] with n-butyllithium) in ether at -78° first with methylene chloride and then with n-butyllithium afforded two major products.[8] After separation on a MgO column[9,10] and recrystallization, the first component eluted from the column was identified as the known[11] 4,5-benzocyclohepta(1,2,3-de)naphthalene (7)[12,13] (12% yield). The second and major component (23% yield) was a crystalline compound which was isomeric with 7, and possessed a bicyclobutane structure based on its nmr spectrum.[13,14]



6 7

Only two structures seemed reasonable for the unknown bicyclobutane and these were 1,10-phenanthrotricyclo[4.1.0.0^{2,7}]heptene (8), which has the phenanthrene ring system, and 1,9-anthrotricyclo[4.1.0.0^{2,7}]heptene (9), which has the anthracene one. The present compound had a signal in its nmr spectrum[14] at δ8.27-8.72 (2H) which is a characteristic of numerous phenanthrene derivatives.[15] This strongly suggests that 8 is the correct structure, and this has recently been confirmed by a single crystal X-Ray determination.[16]



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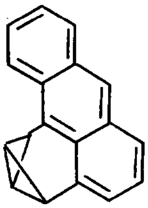

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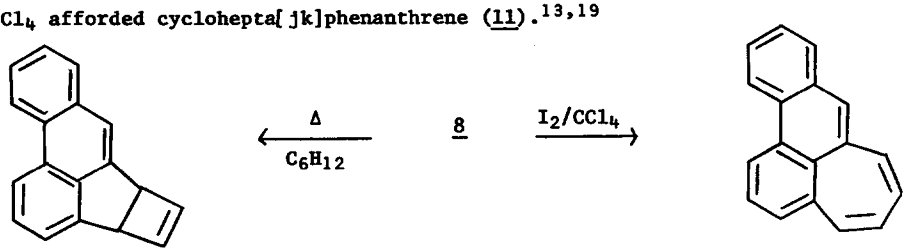
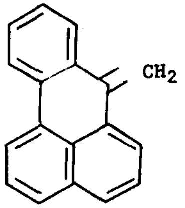
The bicyclobutane (8) proved to be a versatile precursor to other isomeric phenanthrenes. For example, heating a sample of 8 in cyclohexane at 150° resulted in the formation of 1,10-phenanthrobicyclo[3.2.0]hepta-2,6-diene (10),[13,17] while treating 8 with a catalytic amount of I_2[18] in CCl_4 afforded cyclohepta[jk]phenanthrene (11).[13,19]



10 11

As can be seen, some selectivity has been observed in the addition of chlorocarbene to 6. Unfortunately, the regioselectivity cannot be put on a quantitative basis because the observed products are not formed in 100% yield. The missing material probably arises from the decomposition of initially-formed, unstable exocyclic methylene compounds, such as 12. Attempts to trap these compounds by the addition of N-phenyltriazolinedione and dimethyl acetylenedicarboxylate to the reaction mixture immediately after all the n-butyllithium had been added have so far failed.



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In conclusion, it is interesting to note that the observed products, 7 and 8, arise by attack of the carbene on C-7 and C-6 (and/or C-4) of 6, the carbons which possess the most negative charge in 6.[20] This could be a useful guide in predicting the course of similar reactions.[21]

References and Notes

1. Chlorocarbene refers to the reagent formed in the reaction between an alkyllithium and CH_2Cl_2. The reagent could be either free :CHCl or dichloromethyllithium, $LiCHCl_2$.

2. T. J. Katz, E. J. Wang, and N. Acton, J. Am.Chem. Soc., 93, 3782 (1971).

3. (a) T. J. Katz and J. J. Cheung, J. Am. Chem. Soc., 91, 7772 (1969). (b) T. J. Katz, J. J. Cheung, and N. Acton, ibid., 92, 6643 (1970).

4. (a) R. M. Pagni and C. R. Watson, Jr., Tetrahedron Lett., 59 (1973); (b) I. Murata and K. Nakasuji, ibid., 53 (1973).

5. I. Murata, T. Tatsuoka, and Y. Sugihara, Tetrahedron Lett., 4261 (1973).

6. 5 clearly has two nonaromatic sites which might be attacked by the carbene.

7. A. Streitwieser, Jr., J. H. Hommons, E. Ciuffarin, and J. I. Brauman, J. Am. Chem. Soc., 89, 59 (1967).

8. TLC on 7% MgO/Celite showed 4 spots when the plate was eluted with ligroine. Two of these products were very minor and could not be isolated.

9. MgO and MgO/Celite are excellent adsorbents for molecules with double bonds and/or aromatic rings. See L. R. Snyder, J. Chromatog., 28, 300 (1967). In the present case, 100% MgO in a very tightly packed column was used. Because the flow was so slow, both vacuum and pressure assists were used to speed the column flow.

10. Our initial endeavors to separate the compounds on alumina were successful, but more recent batches of alumina resulted in the isomerization of 8 into another compound. Very active silica gel also worked, but not as well. Any trace of H_2O in the silica gel resulted in complete destruction of 8.

11. (a) J. F. Muller, D. Cagniant, and P. Cagniant, Bull. Soc. Chim. Fr., 4364 (1972); (b) J. T. Craig, M. A. Pitt, K. W. Wan, and A. D. Woolhouse, Aust. J. Chem., 25, 837 (1972).

12. Compound 7 had: mp 66.0-66.5° (lit 65°^{11a}, 64-65°^{11b}); nmr (CCl_4): δ6.98-7.70 (m, 10H, benzo- and naphthoaromatic) and 6.45 (s, 2H, vinyl); mass spec: parent peak at m/e 228.

13. The compound gave a satisfactory C,H analysis.

14. Compound 8 had: m.p. 99-100°; nmr (CCl_4): δ8.28-8.72 (m, 2H, H-4 and H-5 of thephenanthrene ring), 7.18-7.95 (m, 6H, remaining phenanthrene protons), 2.10-3.38 (two overlapping t, 2H, bicyclobutane benzylic) and 2.45-2.58 (t, 2H, bicyclobutane central methine, J=3.0 Hz); mass spec: parent peak at m/e 228.

15. A quite extensive compilation of mono-and disubstituted phenanthrene nmr's can be found in K. D. Bartle and J. A. S. Smith, Spectrochimica Acta, 23A, 1689, 1715 (1967).

16. The details of the X-Ray structure proof will be published elsewhere.

17. Compound 10 had: m.p. 133°; nmr ($CDCl_3$); δ8.17-8.70 (m, 2H, H-4 and H-5 of phenanthrene ring), 7.26-7.93 (m, 6H, remaining arom), 6.30 (s, 2H, vinyl), and 4.63 (s, 2H, benzylic); mass spec: parent ion at m/e 228.

18. The ring opening of a bicyclobutane with I_2 has precedent. See C. R. Watson, Jr., R. M. Pagni, J. R. Dodd, and J. E. Bloor, J. Am. Chem. Soc., 98, 2551 (1976).

19. Compound 11 had: m.p. 108°; nmr (CCl_4): δ8.00-8.33 (m, 2H, H-4 and H-5 of phenanthrene ring), 6.67-7.48 (m, 6H, remaining arom), 5.87-6.32 (m, 2H, vinyl adjacent to phenanthrene ring), and 5.18-5.62 (m, 2H, remaining vinyl); mass spec: parent ion at m/e 228.

20. The negative charges for the odd alternant anion (6) were computed by hand. See M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry," Plenum Publishing Co., New York, N. Y., 1975.

21. The authors wish to thank the Research Corporation, the National Institutes of Health, through a Biomedical Support Grant, and the University of Tennessee, for a summer fellowship to RMP, for support of this work. We would also like to thank Jared Butcher for technical assistance.