

THE REACTION OF PHENALENYL ANION WITH METHYLENE CHLORIDE AND BUTYLLITHIUM - A NEW METHOD OF PREPARING 1,8-NAPHTHO(C₄H₄)HYDROCARBONS.¹

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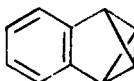
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Katz and coworkers have recently prepared benzvalene(I) on a large scale by reacting lithium cyclopentadienide with CH₂Cl₂ and methyl lithium at -45°. ² Similar treatment of the indenyl anion and the cyclononatetraene anion with CH₂Cl₂ and alkyl lithium afforded benzo-benzvalene(II)² and isobullvalene(III),^{3,4} respectively.



I

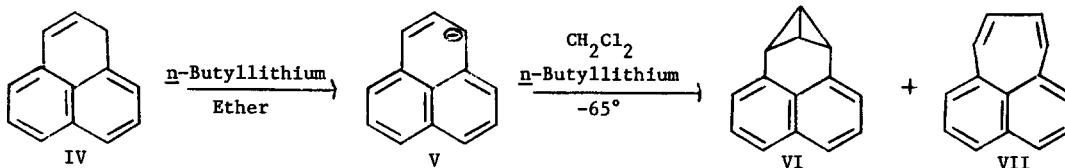


II



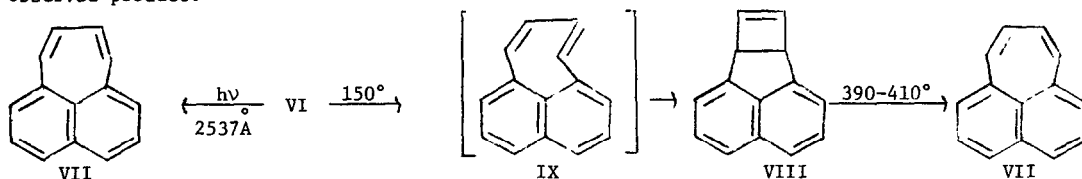
III

We wish to report that this reaction can be applied to the phenalenyl anion (V) as well. Thus, when 38.7 mmol of phenalene (IV)⁵ in 500 ml of ether was treated with 45.6 mmol of *n*-butyllithium at room temperature followed by 237 mmol of CH₂Cl₂ and 91.7 mmol of *n*-butyllithium at -65°, there was obtained, after chromatography on alumina, 4.15 g of a mixture comprising two components: naphthobicyclobutane(VI) (80%) and pleiadiene (VII) (20%). Several recrystallizations from ligroine gave analytically pure VI: m.p. 76.5-77°; nmr (CCl₄): τ 2.50-3.17 mult (6H, arom), 7.07 tr (2H, benzylic methine, J = 2.5 Hz), 7.80 tr (2H, central methine, J = 2.5 Hz).

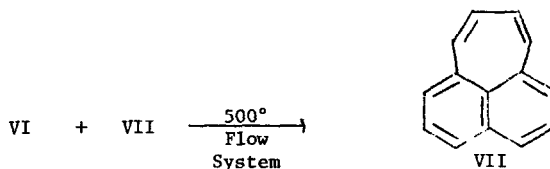


The new compound VI proved to be quite stable, because refluxing in CCl₄ for 16 hr or heating a cyclohexane solution at 125° for 30 min produced no visible changes in the NMR. However, heating a solution of VI in cyclohexane at 150° yielded the known naphthocyclobutene

(VIII)^{6,7} in 75% yield. There were no other components visible in the NMR during the course of the isomerization. This reaction can be pictured as proceeding by a symmetry-allowed ring opening to give cis,trans-pleiadiene (IX), which undergoes conrotatory ring closure to give the observed product.



Photolysis of a cyclohexane solution of VI, on the other hand, gave only pleiadiene (VII). Potentially, this represents a new method of preparing this interesting hydrocarbon. However, Meinwald has observed⁶ that VIII is isomerized to pleiadiene at 390-410°. Thus, we found that the best way of making pleiadiene was to pass the original mixture of VI and VII through a helix-packed column at 500°. An 80% yield of pleiadiene was obtained under these conditions.



In conclusion, application of the Katz technique to the phenaleny system has now made the valence isomers, VI, VII, and VIII, readily available for other investigations.

Footnotes and References

1. The authors wish to thank the Petroleum Research Fund of the American Chemical Society and the Research Corporation for generous support of this work.
2. T. J. Katz, E. J. Wang, N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971).
3. (a) T. J. Katz and J. J. Cheung, *ibid.*, **91**, 7772 (1969); (b) T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970).
4. K. Hojo, R. T. Seidner, and S. Masumune, *ibid.*, **92**, 6641 (1970).
5. Phenalene was prepared in 50% yield by the reduction of phenalene with a 1/1 mixture of LiAlH_4 and AlCl_3 in ether.
6. J. Meinwald, G. E. Samuelson, and M. Ikeda, *ibid.*, **92**, 7604 (1971).
7. W. Hartmann and H-G. Heine, *Angew. Chem.*, **83**, 291 (1971).