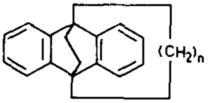
Tetrahedron Letters No. 45, pp 4317 - 4320, 1971. Pergamon Press. Printed in Great Britain.

THE SYNTHESIS OF [2.2](9,10)ANTHRACENO(2,5)FURANOPHANE AND ITS REACTION WITH DIMETHYL ACETYLENEDICARBOXYLATE.

Hans Wynberg and R. Helder
Department of Organic Chemistry, The University,
Zernikelaan, Groningen, The Netherlands.

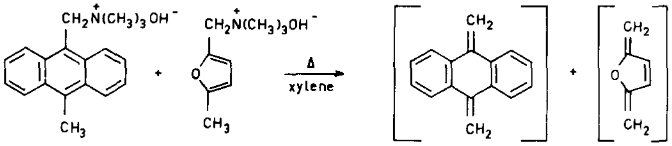
(Received in UK 14 September 1971; accepted for publication 8 October 1971)

The Diels-Alder reaction of a variety of 9,10-disubstituted anthracenes has been well studied.[1] At present we are interested in the influence which a 9,10-bridge would have on the Diels-Alder reactivity of the anthracene moiety. In addition, the adducts thus formed are of considerable theoretical interest (see for instance Wiberg[2] for a discussion of systems related to I and recent work by R. Hoffmann[3], concerning the stability of planar tetracoordinate carbon).

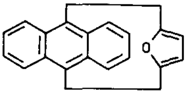


I

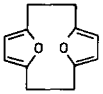
In this communication we report the synthesis of a bridged anthracene, [2.2](9,10)anthraceno(2,5)-furanophane (VI) and its reaction with dimethyl acetylenedicarboxylate. The synthesis of VI was accomplished through a 1,6 to 1,6 cycloaddition reaction.[4] Pyrolysis of an equimolar mixture of the quaternary ammonium hydroxides II and III furnished VI in 40% yield, contaminated with minor amounts of VII (up to 10% by weight). The latter was identified by comparison with an authentic sample.[4a] An initial orange colour suggested the transient presence of the unstable dimer VIII[5] in the reaction mixture.



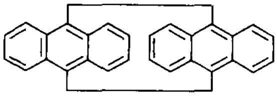
II III IV V



VI

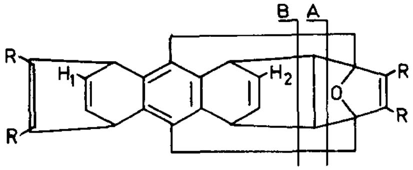


VII



VIII

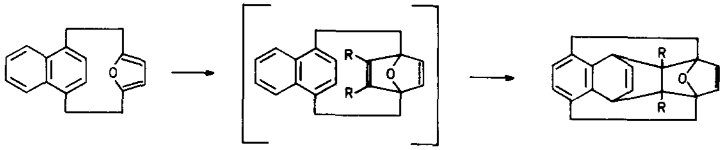
Spectra and elemental analysis of VI were in agreement with the proposed structure. Analytically pure VI was obtained by column chromatography; m.p. 170-174° with decomposition. Solutions of VI reacted with oxygen under formation of a white, flocculent precipitate (VIa). Elemental analysis of this insoluble product corresponded to addition of 1 mole of oxygen and 1 mole of water to VI. Although the structure of VIa has not been studied in detail, pyrolysis leading to anthraquinone suggests addition of the oxygen to the anthracene portion of the molecule.[6] Compound VI exhibited a λ_{max} at 420 mμ. When a solution of VI was left standing in air this λ_{max} disappeared, undoubtedly due to reaction of VI with oxygen (see above). When VI was heated with excess dimethyl acetylenedicarboxylate, a crystalline product (m.p. 212-213.5°) could be isolated (36%). Elemental analysis and molecular weight were in agreement with a structure corresponding to the addition of 2 moles of acetylenedicarboxylate to VI. The spectroscopic properties of our 1:2 adduct agreed well with structure IX.[7]



IX R = COOMe

The evidence in support of this assignment is the following: the nmr spectrum exhibited peaks at τ 3.07 (t, 2H, H_1) and τ 3.56 (t, 2H, H_2).[8] These absorptions, as well as the total absence of other absorptions in the aromatic region, are of vital importance in arriving at structure IX, clearly indicating that all of the aromatic rings containing protons (2 outer anthracene rings and the furan ring) have been involved in addition reactions. The mass spectrum showed peaks at m/e 582 (M^+), 372 (fragmentation A) and 346 (fragmentation B). IX had a λ_{max} at 315 mμ (ε 1.6x10^3) and didnot show out-of-plane C-H deformation vibrations (650-900 cm^{-1}, characteristic for aromatic hydrogens) in the ir spectrum.

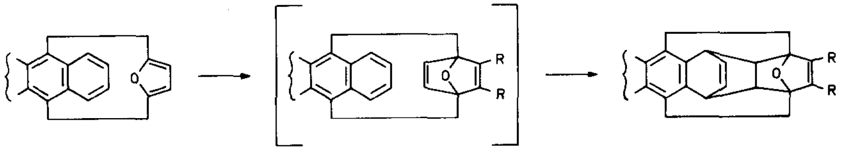
The reaction of VII with dimethyl acetylenedicarboxylate has been investigated by Cram,[4b] the same reaction of X was recently studied by Wasserman.[9] Both authors found an initial addition of dimethyl acetylenedicarboxylate to the furan ring, followed by an internal Diels-Alder reaction involving the normally activated double bound:



X

R= COOMe

In contrast to these results we found reaction of the non-activated double bound in the internal Diels-Alder reaction:



R= COOMe

IX a

The stereochemistry of our initial adduct IXa is such that the non-activated double bound can participate in the Diels-Alder reaction with the (outer) benzene ring. This work shows clearly that this rather complex bridged anthracene doesnot lend itself well to a study of the influence of the 9,10-bridge on the Diels-Alder reactivity of the anthracene system.

Simple bridged anthracenes and related systems need to be studied. We are pursuing this goal.

REFERENCES

1. (a) M.C. Kloetzel, Org. Reactions, 4, 1 (1948);
   H.L. Holmes, Org. Reactions, 4, 60 (1948).
   (b) A.S. Onishchenko, "Diene Synthesis", Chapter V, Israel Program for Scientific Translations, Jerusalem, 1964.
2. K.B. Wiberg, J.E. Hiatt and G. Burgmaier, Tetrahedron Letters, 5855 (1968).
3. R. Hoffmann, R.W. Alder and C.F. Wilcox Jr., J. Amer. Chem. Soc., 92, 4992 (1970).
4. (a) H.E. Winberg, F.S. Fawcett, W.E. Mochel and C.W. Theobald, J. Amer. Chem. Soc., 82, 1428 (1960);
   (b) D.J. Cram, C.S. Montgomery and G.R. Knox, J. Amer. Chem. Soc., 88, 515 (1966);
   (c) H.H. Wasserman and P.M. Keehn, Tetrahedron Letters, 3227 (1969).
5. J.H. Golden, J. Chem. Soc., 3741 (1961).
6. For photosensitized autoxidation of similar systems H.H. Wasserman, A.R. Doumaux and R.E. Davis, J. Amer. Chem. Soc., 88, 4517 (1966).
7. (a) Normal Diels-Alder addition to 9,10-dialkylanthracenes is known to take place to the middle ring;
   (b) No efforts were made to determine, which of the 2 possible isomers IX was present.
8. We wish to thank Dr. J. Lugtenburg for his help with the spin-decoupling experiments.
9. H.H. Wasserman and R. Kitzing, Tetrahedron Letters, 3343 (1969).