Tetrahedron Letters No.22, pp. 1863-1864, 1970. Pergamon Press. Printed in Great Britain.

SILVER ION CATALYSIS IN THE ADDITION OF BENZYNE TO CYCLOOCTATETRANENE

E. Vedejs and R. A. Shepherd

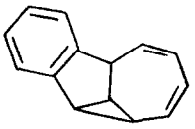
Chemistry Department, University of Wisconsin,
Madison, Wisconsin 53706

(Received in USA 27 February 1970; received in UK for publication 13 April 1970)

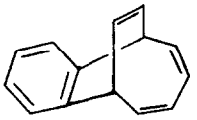
We have previously shown that decomposition of benzenediazonium-2-carboxylate (I) in cyclooctatetraene (COT) affords the monoadducts II, III, an isomer IV which was not characterized, and phenanthrene[1]. We now report that the product ratio is remarkably affected by silver ion catalysis. In the absence of catalyst (apparatus scrupulosuly cleaned after soaking in conc. $HCl-HNO_3$ to remove trace metals) the reaction between I and COT produces IV as a major product. Apparently, our original results were influenced by traces of unknown catalysts, since II predominated and relatively little IV was formed. The structure of IV (mp 54.5°-55.5°; NMR δ $CDCl_3$, 2 H; 3.78 multiplet, 2 H; 6.07 singlet, 2 H; 6.23 four lines, 2 H; 7.13 A_2B_2, 4 H; decoupling at 3.78 δ causes collapse of all other nonaromatic hydrogens to singlets) is deduced from the characteristic NMR spectrum and the absence of significant absorption ($\varepsilon < 600$) beyond 235 mμ in the ultraviolet spectrum.[2] Further evidence for the carbon skeleton of IV is available from its partial conversion to III[3] upon pyrolysis in a flow system at 400°. The stereochemistry assigned to IV follows from the expected addition of benzyne to the least hindered face of bicyclo[4.2.0]-octatriene. Thus, the uncatalyzed benzyne reaction is analogous to the addition of 4-phenyl-1,2,4-triazoline-3,5-dione to COT.[4] On the other hand, addition of 0.5 mole % (based on I) of silver acetate or silver fluoborate to the reaction mixture causes a drastic reduction in the relative yields of IV, phenanthrene, and biphenylene, while II becomes the major hydrocarbon product.[5]

Friedman has proposed that Ag^+ catalyzed addition of benzyne to benzene may involve a benzyne-Ag^+ complex with enhanced electrophilic tendencies.[6] Our results support this rationale since polar addition of the benzyne-Ag^+ complex to COT may

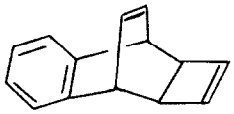
lead to the homotropylium ion V which is a likely precursor of II. Experiments are planned to investigate the nature of σ and π bonding between silver and carbon orbitals in the intermediate V.



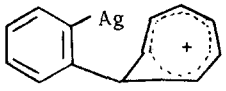
II



III



IV



V

Products From Catalyzed and Uncatalyzed Benzyne Reactions with COT in CH_2Cl_2 at 35°.

Catalyst	GLPC (Carbowax, 170°) Determined Relative Yields of Volatile Hydrocarbon Products				
	II	III	IV	Phenanthrene	Biphenylene
None	12%	31%	28%	14%	14%
$AgBF_4$	80%	8%	6%	1%	trace
AgOAc	82%	10%	4%	1%	1%
Unknown[1]	62%	10%	8%	12%	8%

References

1) E. Vedejs, Tetrahedron Letters 1968, 2633.

2) Compound IV has been synthesized independently by Prof. L. Friedman, to be published. We thank Prof. Friedman for informing us of his work.

3) The major product of thermolysis of IV is an isomeric hydrocarbon which is also a pyrolysis product of III. This subject will be considered in more detail elsewhere.

4) A. B. Evnin, R. D. Miller and C. R. Evanega, Tetrahedron Letters 1968, 5863.

5) The yields of the 2:1 adduct 9-phenyl-9,10-dihydrophenanthrene were determined by preparative TLC. The ratio of the 2:1 adduct to II is 26:1 for the uncatalyzed reaction, and 1:11 for the reaction catalyzed by silver fluoborate. In our initial study[1], this ratio was 3.5:1.

6) L. Friedman, J. Amer. Chem. Soc., 89, 3071 (1967).