

THE REACTION OF CYCLOPROPENYL CATIONS WITH CYCLOPROPENES

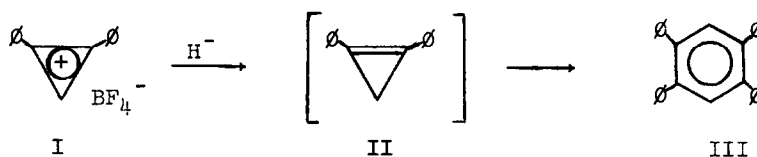
David M. Stehouwer and Daniel T. Longone

Department of Chemistry, The University of Michigan  
Ann Arbor, Michigan 48104

(Received in the USA 4 November 1969; received in the UK for publication 1 November 1969)

Cyclopropenes and biscyclopropenyl derivatives can be converted to substituted aromatic compounds by a variety of photochemical (1), thermal (1e,2), anionic (1e,3), and reductive (1e,4) processes. We now report that substituted benzenes are also produced by the reaction of cyclopropenyl cations with cyclopropenes, a reaction pathway hitherto unrecognized.

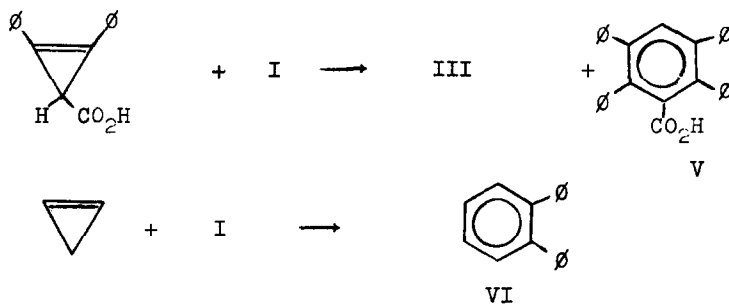
Hydride reduction of cyclopropenyl cations to cyclopropenes is well pre-  
cedented (1e,3,5). However, attempts to obtain the as yet unknown 1,2-diphenyl-  
cyclopropene (II) by this method have been singularly unsuccessful. Attempted  
reduction of 1,2-diphenylcyclopropenyl cation (I) under a variety of conditions  
gives 1,2,4,5-tetraphenylbenzene (III) as the sole characterizable product (6).  
The yields of III vary greatly (< 5% to 100%) depending upon the conditions.  
For example, addition of NaBH<sub>4</sub> in CH<sub>3</sub>CN to a solution of I in the same solvent  
affords III in quantitative yield. When the inverse addition is used, however,  
a complex mixture results and only minor amounts of III are formed (< 5%).



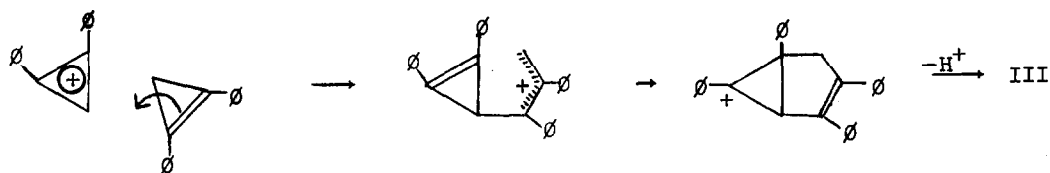
The notion that the efficient formation of III in the first reduction is due to  
reaction of I with the cyclopropene II, as generated, is amply supported by the  
experiments below.

The direct reaction of I with 1,2-diphenylcyclopropenecarboxylic acid (IV)

gives III (11%) and 2,3,5,6-tetraphenylbenzoic acid (V) in 35% yield (7). Both III and V presumably arise from a common intermediate which either decarboxylates or deprotonates to give the observed products.



The reaction of I with cyclopropene in CH<sub>3</sub>CN proceeds readily at 0° to give *o*-terphenyl, VI (44%). The formation of VI to the exclusion of the meta and para isomers indicates that adjacent phenyl groups in the cation remain ortho in the product. If this may be generalized, it follows that the adjacent phenyl groups in the cyclopropene (II or IV) also remain ortho in the product (III or V). Using the reaction of I and II as an example, the formal mechanism below describes the formation of observed products.



In contrast to I, the triphenylcyclopropenyl cation does not readily add to cyclopropenes. The reaction of 1,2,3-triphenylcyclopropenyl bromide (VII) with 1,2,3-triphenylcyclopropene (VIII) affords some hexaphenylbenzene (< 2%) but mostly 2,3-diphenylindene, the rearrangement product of VIII (8). The low yield of hexaphenylbenzene is not surprising in view of the high yield of VIII obtained in the LiAlH<sub>4</sub> reduction of the triphenylcyclopropenyl cation (3). Acid IV gives no detectable reaction with salt VII. Finally, the reaction of cyclopropene and VII yields a complex mixture containing 2,3-diphenylindene but no triphenylbenzene.

We are examining further the scope and details of the reaction of cyclopropenyl cations with cyclopropenes.

## REFERENCES

1. (a) B. M. Trost and R. Atkins, Tetrahedron Lett., 1225 (1968).  
(b) E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, J. Amer. Chem. Soc., 90, 1372 (1968).  
(c) A. W. Dow, Ph.D. Dissertation, Cornell University, 1967.  
(d) N. Obata and I. Moritani, Tetrahedron Lett., 1503 (1966).  
(e) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, J. Amer. Chem. Soc., 87, 5139 (1965).
2. D. G. Farnum and M. Burr, J. Amer. Chem. Soc., 82, 2651 (1960).
3. R. Breslow and P. Dowd, ibid., 85, 2729 (1963).
4. (a) S. Andreades, U. S. Patent 3408367; Chem. Abstr., 70, 19827 (1969).  
(b) M. A. Battiste and B. Halton, Chem. Commun., 1368 (1968).  
(c) N. Toshima, I. Moritani, and S. Nishida, Bull. Chem. Soc. Jap., 40, 1245 (1967).
5. W. J. Gensler, M. B. Floyd, R. Yanase, and K. Prober, J. Amer. Chem. Soc., 91, 2397 (1969); F. A. Carey and H. S. Tremper, ibid., 90, 2578 (1968).
6. Professor W. J. Gensler has informed us that he too isolates only III from the reaction of I (perchlorate) with  $\text{LiAlH}_4$ .
7. Acid V has been fully characterized. That it is the isomer indicated is shown by decarboxylation ( $410-420^\circ$ ) to III.
8. M. A. Battiste, B. Halton, and R. H. Grubbs, Chem. Commun., 907 (1967).