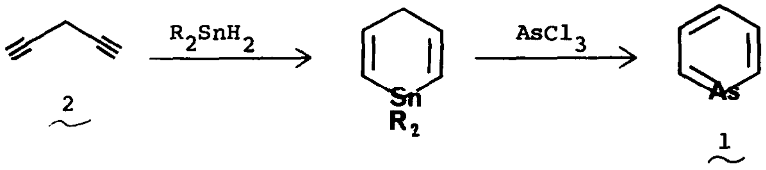
Tetrahedron Letters No. 15, pp 1283 - 1286, 1977. Pergamon Press. Printed in Great Britain.

PYROLYSIS OF 1-ARSABICYCLO[2.2.2]TRIENE DERIVATIVES

Arthur J. Ashe, III[1]* and Howard S. Friedman
Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109

(Received in USA 2 November 1976; received in UK for publication 2 March 1977)

As part of our general study of the spectral and chemical properties of the novel aromatic arsabenzene 1,[2,3] we needed methods for obtaining simple substituted arsabenzenes. Although our synthesis of 1, via hydrostannation of 1,4-diacetylenes 2 followed by exchange with $AsCl_3$,[2] has been extended to the synthesis of some 2- and 4-substituted arsabenzenes,[4,5] the synthesis necessitates that the 3-position be unsubstituted. In order to prepare 3-substituted arsabenzenes, we have examined the thermal cleavage reactions of 1,4-Diels-Alder adducts of arsabenzene.

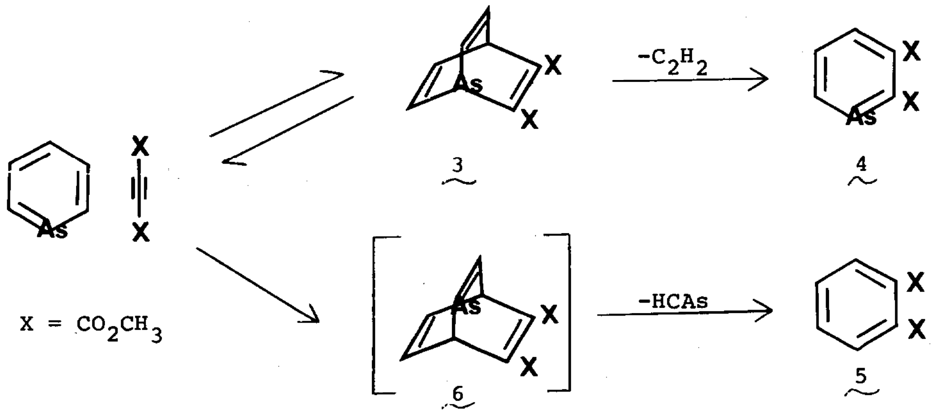


Arsabenzene will react readily with dimethyl acetylenedicarboxylate at 80° to give a good yield of the expected arsabarrelene 3.[6,7,8] H-nmr ($CDCl_3$): δ 7.0-7.4 (m, 4H), 5.6 (tt, J = 6, 2 Hz, 1H), 3.7 (s, 6H).

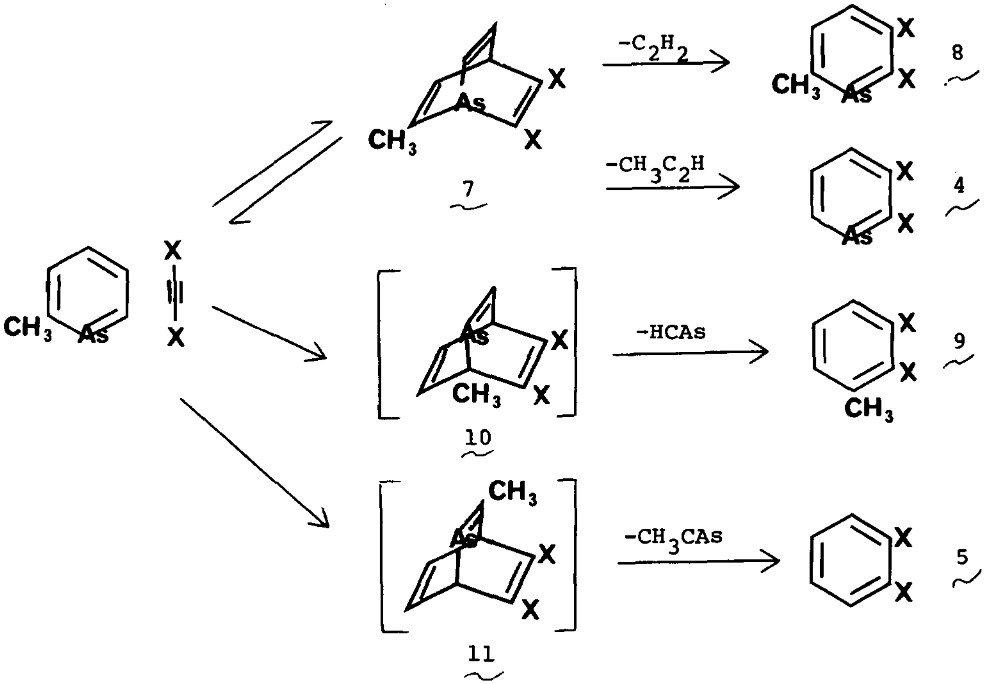
Pyrolysis of adduct 3 at 400° in the injector port of a g.l.p.c. led to Alder-Richart cleavage back to dimethyl acetylenedicarboxylate and arsabenzene as well as to 80% 2,3-dicarbomethoxyarsabenzene 4 by loss of acetylene. H-nmr (C_3D_6O): δ 10.1 (dd, J = 10, 1 Hz, 1H), 8.2 (dd, J = 10, 9 Hz, 1H), 8.0 (dd, J = 9, 1 Hz, 1H), 3.88 (s, 3H), 3.90 (s, 3H). Mass spectral m/e = 256 (M^+). The diester 4 is easily purified by g.l.p.c. and is considerably more stable towards air-oxidation than arsabenzene itself.

Very surprisingly a 5% yield of dimethyl phthalate 5 is also obtained. When the pyrolysis is run at 210° in benzene solution, the yield of dimethyl phthalate increases to 30% at the expense of 4 (32%).

Since the formation of adduct 3 is thermally reversible, it is plausible to assume that the expelled dimethyl acetylenedicarboxylate may occasionally re-add across C_2-C_5 of the arsabenzene to give transient adduct 6, which then rapidly affords dimethyl phthalate 5 on loss of the hydrocyanic acid analog, HCAs.[9] At present we have no direct evidence for the fate of the HCAs.[10] In the higher temperature gas-phase reaction, the bimolecular recombination of dimethyl acetylenedicarboxylate and arsabenzene is expected to be slow, hence the yield of dimethyl phthalate is low. The production of dimethyl phthalate, although not that of 4, can also be inhibited in the solution pyrolysis by the addition of 1,4-diphenylisobenzofuran. This reactive diene preferentially adds to the dimethyl acetylenedicarboxylate.

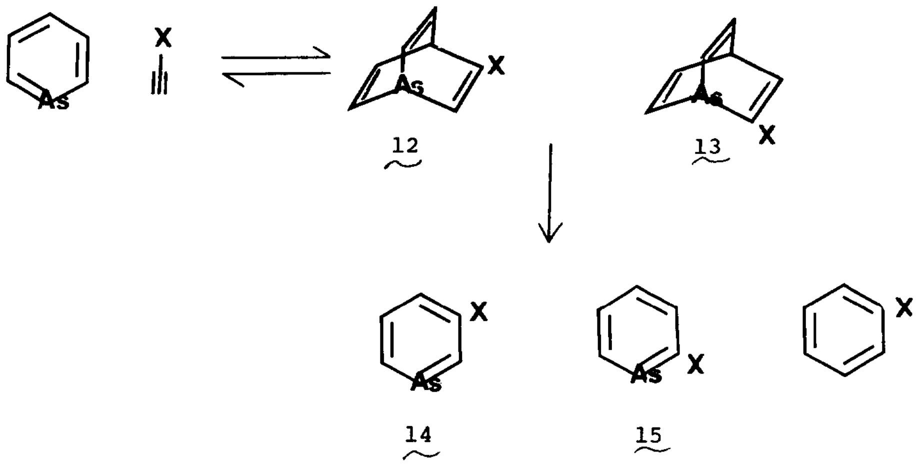


The thermal behavior of the dimethyl acetylenedicarboxylate adduct 7 of 2-methylarsabenzene is completely consistent with this mechanism. Flash pyrolysis of 7 at 400° affords 47% of 4 *via* loss of methylacetylene and 43% of 6-methyl-2,3-dicarbomethoxyarsabenzene 8 *via* loss of acetylene. Dimethyl phthalate 1% and dimethyl 3-methyl phthalate 4% are formed presumably by loss of HCAs and CH_3CAs from transient adducts 10 and 11. Higher yields of the benzocyclic products 5 - 9 are obtained when the pyrolysis is run in solution at 210°. As expected, no dimethyl 4-methyl phthalate could be detected.



Methyl propiolate reacts with arsabenzene at 100° to form two adducts in ratio of 2:3. The major product was assigned structure 12 on the basis of its H-nmr (C_3D_6O): δ 8.0 (d, J = 1.9 Hz, 1H), 7.3 (t, J = 7.2 Hz, 2H), 7.1 (dd, J = 7.2, 1.9 Hz, 2H), 5.9 (tq, J = 7.2, 1.9 Hz, 1H), 3.7 (s, 3H). Mass spectral m/e = 224 (M^+). The minor isomer was 13. H-nmr (C_3D_6O): δ 8.0 (d, J = 7.4 Hz, 1H), 7.3 (t, J = 7.4 Hz, 2H), 7.1 (dd, J = 7.4, 1.3 Hz, 2H), 5.6 (qt, J = 7.4, 1.3 Hz, 1H), 3.7 (s, 3H). Mass spectral m/e = 224 (M^+). The low regioselectivity suggests that these Diels-Alder reactions of arsabenzene are concerted. The previously proposed diradical mechamism[7] might be expected to be highly selective.

Flash pyrolysis of these adducts at 400° gave in addition to small quantities of methyl propiolate, arsabenzene and methylbenzoate a 3:2 mixture of 3-carbomethoxyarsabenzene 14: H-nmr (C_3D_6O): δ 10.6 (s, 1H), 9.8 (d, J = 9.8 Hz, 1H), 8.3 (t, J = 9.8 Hz, 1H), 8.2 (d, J = 9.8 Hz, 1H), 3.9 (s, 3H); mass spectral m/e = 198 (M^+) and 2-carbomethoxyarsabenzene 15: H-nmr (C_3D_6O): δ 10.0 (d, J = 9.8 Hz, 1H), 8.6 (d, J = 8.6 Hz, 1H), 8.1 (t, J = 9 Hz, 1H), 7.8 (t, J = 8.6 Hz, 1H), 3.9 (s, 3H); mass spectral m/e = 198 (M^+). Thus, overall the reaction consists of a simple entry into 2- and 3-monosubstituted arsabenzenes.



Acknowledgment. This work was partially supported by a grant from the USPHS (R01-GM20992).

References and Footnotes

1. A. P. Sloan Fellow, 1973-76.
2. A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 3293 (1971).
3. R. L. Kuczkowski and A. J. Ashe, III, *J. Mol. Spectrosc.*, **42**, 457 (1972); R. P. Lattimer, R. L. Kuczkowski, A. J. Ashe, III and A. L. Meinzer, *ibid.*, **57**, 428 (1975); T. C. Wong, A. J. Ashe, III and L. S. Bartell, *J. Mol. Struct.*, **25**, 65 (1975); C. Batich, E. Heilbronner, V. Hornung, A. J. Ashe, III, D. T. Clark, U. T. Cobley, D. Kilcast and I. Scanlan, *J. Am. Chem. Soc.*, **95**, 928 (1973); A. J. Ashe, III, R. R. Sharp and J. W. Tolan, *J. Am. Chem. Soc.*, **98**, 5451 (1976).
4. A. J. Ashe, III, W. T. Chan and E. Perozzi, *Tetrahedron Lett.*, 1082 (1975).
5. G. Maerkl and F. Kneidl, *Angew. Chem. Int. Ed. Engl.*, **12**, 931 (1973); *ibid.*, **13**, 667 (1974); A. J. Ashe, III and W. T. Chan, *Tetrahedron Lett.*, 2749 (1975).
6. A. J. Ashe, III and M. D. Gordon, *J. Am. Chem. Soc.*, **94**, 7596 (1972).
7. G. Maerkl, J. Advena and H. Hauptmann, *Tetrahedron Lett.*, 3961 (1972).
8. Satisfactory combustion analyses have been obtained on all new compounds.
9. This proposed mechanism is quite similar to that proposed for the thermal extrusion of HCN from dimethyl acetylenedicarboxylate adducts of azaazulenes: K. Hafner, *Lectures in Heterocyclic Chem.*, **3**, S-33 (1976).
10. Although HCAs is unknown, its phosphorus analog has been thoroughly characterized. However, the report that HCP polymerizes even at -130° suggests HCAs would be similarly labile. See T. E. Gier, *J. Am. Chem. Soc.*, **83**, 1769 (1961).