

## Dehydrogenative Vacuum Pyrolysis: a Novel Synthetic Technique. Conversion of Cyclo-octa-1,5-diene into Styrene and Related Reactions

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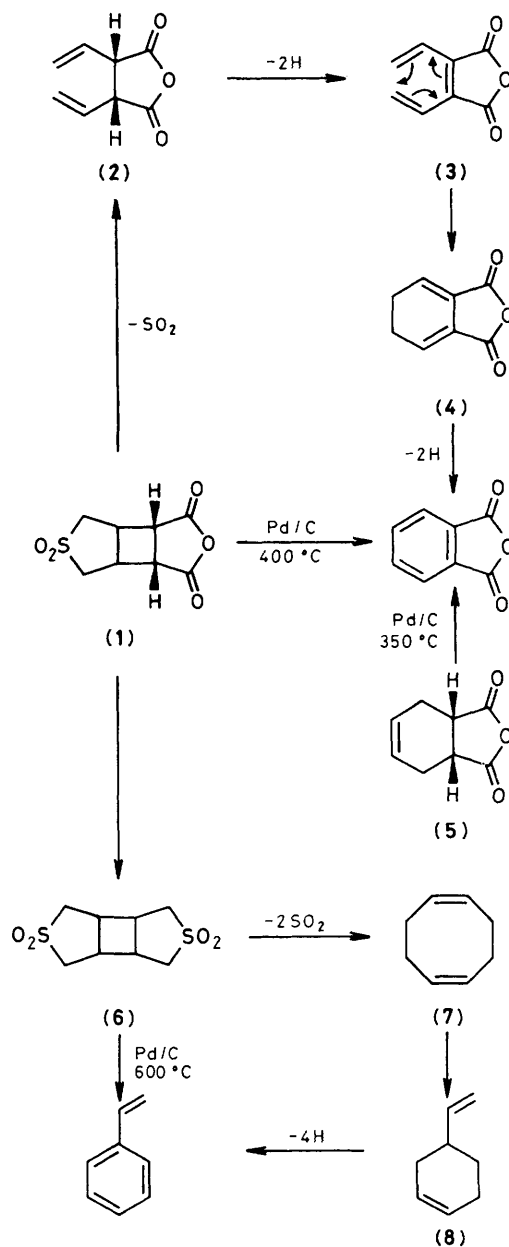
Vacuum pyrolysis in the presence of palladium on charcoal of the 3,3-dioxide (1) of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride gave, without undesirable disproportionation, phthalic anhydride, also obtained from *cis*-2,3-divinylsuccinic anhydride (2) and *cis*-1,2,3,6-tetrahydrophthalic anhydride (5), while cyclo-octa-1,5-diene (7) and the disulphone (6) each gave styrene.

Over the past decade flash vacuum pyrolysis (F.V.P.) has played an increasingly important role in preparative organic chemistry.<sup>1</sup> We now report an extension of this technique of potentially wide application based on the simultaneous use of a dehydrogenation catalyst.

The origin of our procedure lies in our earlier observation<sup>2</sup> that F.V.P. of the 3,3-dioxide (1) of 3-thiabicyclo[3.2.0]heptane-6,7-dicarboxylic anhydride, easily prepared by photolysis of equimolar amounts of butadiene sulphone and maleic anhydride, gave *cis*-2,3-divinylsuccinic anhydride (2) in 80% yield. We reasoned that removal of the ring-junction hydrogens from (2) should lead to electrocyclicisation of the resulting (3) to (4) which would afford phthalic anhydride under dehydrogenating conditions (Scheme 1). This was readily accomplished in a single step with the same apparatus<sup>3</sup> by subliming (1) at 10<sup>-3</sup> mmHg and 400 °C through a catalyst bed of 5% palladium on activated carbon.† In accord with this, similar pyrolyses of *cis*-2,3-divinylsuccinic anhydride (2) at 425 °C and of *cis*-1,2,3,6-tetrahydrophthalic anhydride (5) at 350 °C, also gave phthalic anhydride (48–52%). It is noteworthy that in none of these pyrolyses did significant and undesirable disproportionation to hydrogenated products take place. The method is therefore superior to the corresponding dehydrogenation in solution wherein, for example, *cis*-1,2,3,6-tetrahydrophthalic acid is converted into a 2:1 mixture of phthalic acid and cyclohexane-1,2-dicarboxylic acid, respectively, by palladium black in boiling tetrahydrofuran.<sup>4</sup>

We also pyrolysed the crystalline, high-melting (>320 °C) disulphone (6), prepared from (1) by successive esterification, reduction to the diol, conversion into the bistoluene-*p*-sulphonate, treatment with Na<sub>2</sub>S, and essentially quantitative oxidation of the resulting sulphide with *m*-chloroperoxybenzoic acid in methylene chloride.‡ The sparingly volatile (6) at 650 °C gave a mixture of 4-vinylcyclohexene (8) and cyclo-octa-1,5-diene (7) in the ratio *ca.* 4:1 as determined by g.l.c. (10% Pega at 100 °C). Butadiene was also detected by n.m.r., but was not quantified. Since heating of cyclo-octa-1,5-diene in the gas phase causes a rearrangement to 4-vinylcyclohexene as well as giving minor amounts of butadiene,<sup>5</sup> it is reasonable to conclude that this compound is an intermediate in the thermal decomposition of (6), although its mode of formation is not certain.

When we subjected (6) to pyrolysis over 5% palladium on activated carbon catalyst at 600 °C, both rearrangement and dehydrogenation occurred simultaneously. As a result, styrene



Scheme 1

† The catalyst, available from Alpha Division in 6–8 mesh pellets, is packed into the horizontal pyrolysis tube (35 × 2.3 cm, i.d.) between a coarse silica frit 12 cm from the exit end and a loose plug of quartz wool. Prior to each pyrolysis, it is conditioned by baking at 700 °C until a pressure of 10<sup>-3</sup> mmHg is obtained.

‡ Satisfactory elemental analytical data were obtained for compound (6).

was obtained as the major product, albeit in low yield (12%), together with benzene (4%), toluene (2%), xylenes (2%), and ethylbenzene (2%). Much better yields of styrene at 45%

conversion were obtained by direct pyrolysis of cyclo-octa-1,5-diene (7) under dehydrogenating conditions. At 650 °C with 5% palladium on activated carbon catalyst, the crude pyrolysis product consisted of styrene (62%), xylenes (3%), toluene (9%), and benzene (26%). No ethylbenzene was detected.

Received, 8th April 1983; Com. 450

### References

- 1 For a review explaining the technique of F.V.P. with a description of apparatus and a survey of applications, see: R. F. C. Brown, 'Pyrolytic Methods in Organic Chemistry,' Academic Press, London, 1980.
  - 2 J. I. G. Cadogan, I. Gosney, L. M. McLaughlin, and B. J. Hamill, *J. Chem. Soc., Chem. Commun.*, 1980, 1242.
  - 3 For full details of the construction and operation of the type of F.V.P. apparatus used, see: W. D. Crow and R. K. Solly, *Aust. J. Chem.*, 1966, **19**, 2119.
  - 4 R. P. Linstead, E. A. Braude, P. W. D. Mitchell, K. R. H. Wooldridge, and L. M. Jackman, *Nature (London)*, 1952, **169**, 100.
  - 5 R. Srinivasan and A. A. Levi, *J. Am. Chem. Soc.*, 1964, **86**, 3756.
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