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PYROLYSIS OF syn-7,8-BENZOTRICYCLO[4 2 2 $O^{2,5}$]DECA-3,7,9-TRIENE

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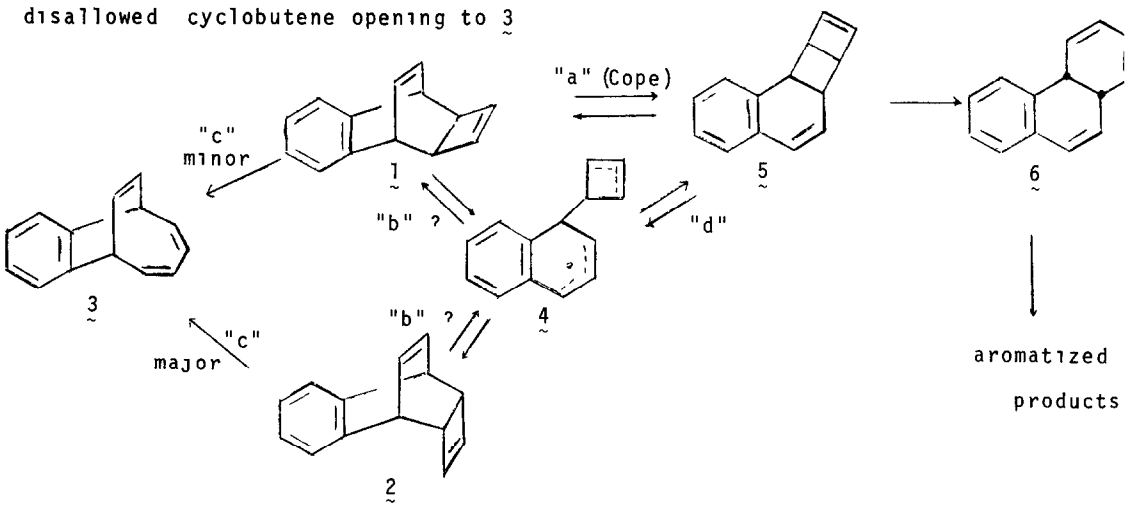
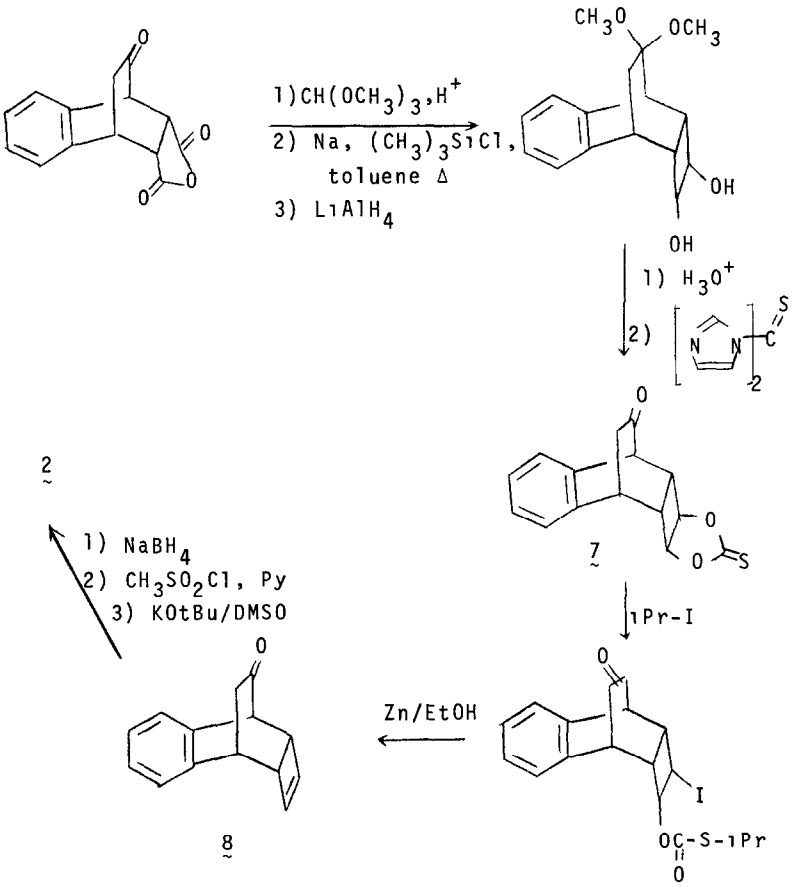
We have shown that pyrolysis of anti-7,8-benzotricyclo[4 2 2 $O^{2,5}$]deca-3,7,9-triene 1 and the parent $(CH)_{10}$ hydrocarbon can be explained by Cope rearrangement (path "a").[2] The same skeletal reorganization would be achieved by a non-concerted diradical mechanism (path "b") and a labelling study consistent with this pathway has been described.[3] In order to distinguish between concerted and diradical mechanisms, we have compared pyrolysis of the anti and syn 7,8-benzo isomers 1 and 2. If the diradical mechanism is the principal reaction pathway, there should be little difference between the two isomers in reaction rate or product distribution. On the other hand, if 1 rearranges by the Cope mechanism, 2 would have to rearrange by some other pathway since the syn benzene ring blocks the concerted mechanism. In fact, 2 is considerably less reactive than 1 and rearranges predominantly (if not exclusively) by disallowed cyclobutene opening to 3.



We have prepared 2 from the readily available endo Diels-Alder adduct of β-naphthol and maleic anhydride according to Scheme 1 This sequence avoids the tedious separation of exo and endo naphthalene Diels-Alder adducts which is inherent in the synthesis of 2 described recently by Murata, Sugihara, and Ueda[4] The crucial step in our synthesis is conversion of thionocarbonate 7 into the ketoolefin 8 Treatment of 7 with refluxing trimethylphosphite[5] results in slow destruction of starting material and formation of intractable products However, reaction with isopropyl iodide at reflux (5 hrs) followed by zinc reduction in ethanol gives 8[6] in 80% yield from 7 This method (and modifications to be described elsewhere) is general and provides a mild proce dure for conversion of thionocarbonates into olefins

Scheme 1



The syn benzo derivative 2 is thermally less reactive than 1 or 3 Pyrolysis at 380° (N_2 flow over pyrex beads, 2-3 sec contact time) results in 56% conversion of 2, >99.9% conversion of 1, and 98 4% conversion of 3 The major products from all three isomers at 380° are phenanthrene, and 1,2-, 3,4-, and 9,10-dihydrophenanthrene (identified by glpc retention times), due to extensive decomposition of 6 However, the ratio of phenanthrene derivatives 3 is 43 1 from pyrolysis of 1 and only 2 1 from 2 This difference becomes more pronounced as the temperature is lowered. At 330°, the lowest temperature which gives convenient conversion of 2, the ratio of phenanthrenes 3 is 11 1 from 1 and 1 20 from 2 (8 5% and 0 8% conversion, respectively) Thus, the calculated rate of formation of 3 is the same, within experimental error, from either 1 or 2, but the rate of rearrangement to 6 and its transformation products differs by a factor of at least 180 at 330° [7] This estimate is a conservative lower limit since it ignores rearrangement of 3 to phenanthrenes [7] Under identical conditions (330°), 3 is somewhat more reactive than 2 (1-1 5% conversion) but the precision of experiments at low conversion is insufficient to allow a more accurate calculation At 380°, 3 rearranges 5 times faster than 2 Thus, within the limits of experimental error, all of the products from 2 can be accounted for by initial rearrangement to 3 and without invoking the hypothetical process 2 → 4 → 6

It is unlikely that syn vs anti benzene ring orientation would increase the activation barrier for rearrangement of 2 compared to 1 by >6 kcal (as observed at 330°) if a diradical mechanism were involved Therefore, the Cope rearrangement remains as the most likely pathway for the process 1 → 5. However, a small but consistent amount of 2 (1-3%) is formed upon pyrolysis of 1, confirmed by Fourier Transform nmr of a 10^{-4} g sample purified by preparative glpc Conversion of 1 to 2 is conveniently explained via the diradical 4, but the available evidence is not sufficient to determine conclusively whether 4 comes from 1 or 5 Since futher transformation of 5 to 6 requires symmetry-forbidden cyclobutene opening, it is possible that diradical cleavage of the strained cyclobutane bond could compete as a minor pathway (path "d")

References

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6 Keto olefin 8 (mp 48°), IR (CCl_4) 5 77μ, nmr (CCl_4, δ) 7 24 (4H, br s), 5 82 (1H, d, J = 2 5 Hz), 5 70 (1H, d, J = 2 5 Hz), 3 98 (1 H, d, J = 3 Hz), 3 1-3 45 (3H, m), 2 10 (2H, br s)

7 The mechanism for rearrangement of 3 to phenanthrenes has not been establishe