

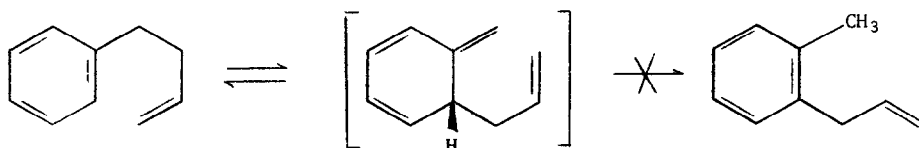
THE COPE REARRANGEMENT OF *CIS*-2-PHENYLVINYLCYCLOPROPANE

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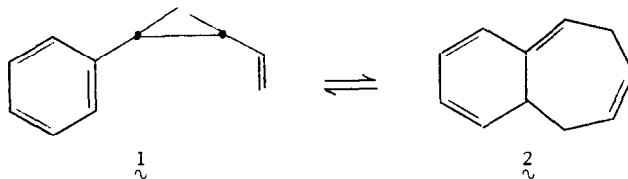
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The Cope rearrangement proceeds readily where an appropriately arranged 1,5-hexadiene moiety is present and neither double bond is part of an aromatic ring, but the rearrangement generally fails when one of the double bonds is part of an aromatic ring.<sup>1</sup> Doering<sup>2</sup> has suggested that the Cope rearrangement of 4-phenyl-1-butene is invisible because the initial



product reverts to the reactant rather than undergoing the 1,3-hydrogen shift which would reveal its presence. In fact heating 4-phenyl-1-butene with *t*-butoxide gave *o*-allyltoluene along with several other products, which permits the interpretation that the Cope rearrangement is followed by a base catalyzed prototropy. Since other rationalizations are also possible, further study of the problem appeared in order.

Assuming that Prof. Doering's very reasonable explanation is correct, an attractive substrate for further study is *cis*-2-phenylvinylcyclopropane (1). It is an analog of

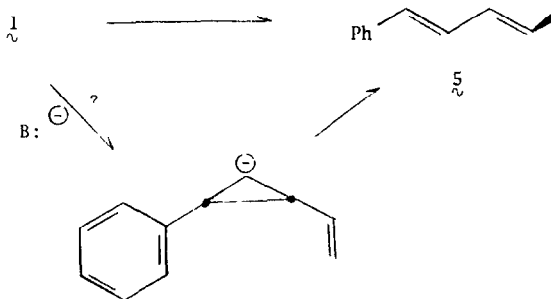


*cis*-1,2-divinylcyclopropane which undergoes Cope rearrangement even at  $-40^\circ$ .<sup>3</sup> Also the equilibrium content of the direct Cope rearrangement product would be much higher than with 4-phenyl-1-butene. Thus it would seem reasonable to expect that rearrangement should occur at moderate temperatures and that the intermediate  $\underset{\sim}{2}$  might be trapped by rather specific reagents.

Both  $\underset{\sim}{1}$  and the *trans* isomer ( $\underset{\sim}{3}$ ) were prepared by the procedure of Closs.<sup>4</sup> The two isomers were separated by glc on a 5% DEGS column at  $100^\circ$ , and pure samples of each were obtained. Examination revealed that  $\underset{\sim}{1}$  undergoes two expected thermal reactions which limit the temperature range useful for study of the Cope rearrangement. At  $150^\circ$   $\underset{\sim}{1}$  and  $\underset{\sim}{3}$  interconvert without apparent formation of other products. In the range  $175$ - $200^\circ$   $\underset{\sim}{1}$  and  $\underset{\sim}{3}$  are slowly converted to 4-phenylcyclopentene ( $\underset{\sim}{4}$ ).

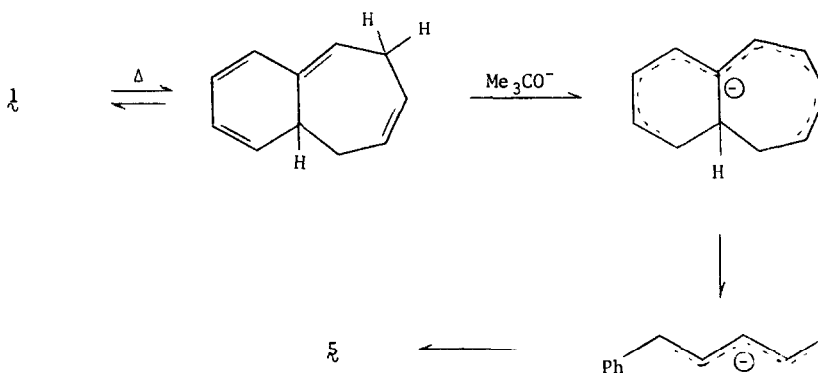
Attempts to trap  $\underset{\sim}{2}$  by a Diels-Alder reaction were unsuccessful. When  $\underset{\sim}{1}$  was heated with dimethyl acetylenedicarboxylate for 5 hrs at  $225^\circ$ , only polymer was obtained. A mixture of  $\underset{\sim}{1}$  and maleic anhydride was heated in xylene at temperatures from  $96$ - $200^\circ$  and at times varying from 5 to 24 hrs without formation of an adduct. Heating a cyclohexane solution of excess *N*-phenylmaleimide with  $\underset{\sim}{1}$  at  $100^\circ$  for 10 days gave only polymer.

When  $\underset{\sim}{1}$  was heated at  $150^\circ$  for 35 hrs with 0.5 M *t*-butoxide/*t*-butyl alcohol, the main product was 1-phenyl-1,3-pentadiene ( $\underset{\sim}{5}$ ), which could arise via electrocyclic ring-opening of a cyclopropyl carbanion. Such a mechanism would require that anion formation at the benzylic



and/or allylic positions occur reversibly and be unproductive of cleavage product. Treatment of a mixture containing 80%  $\overset{1}{\sim}$  and 20%  $\overset{3}{\sim}$  with butyl lithium in THF at 0° followed by a D<sub>2</sub>O quench showed interconversion of  $\overset{1}{\sim}$  and  $\overset{3}{\sim}$ , solely via removal of the benzylic proton. After standing 100 hrs at 25° the deep red solution gave no  $\overset{5}{\sim}$ . More significantly a solution of  $\overset{1}{\sim}$  in 0.54 M t-butoxide in t-butyl alcohol (OD) gave  $\overset{5}{\sim}$  heavily deuterated in the olefinic chain, but recovered  $\overset{1}{\sim}$  and  $\overset{3}{\sim}$  were totally free from deuterium! Clearly  $\overset{5}{\sim}$  is not formed via the route suggested above.

A reasonable alternative is that  $\overset{1}{\sim}$  forms  $\overset{2}{\sim}$  which loses a proton giving an anion which undergoes electrocyclic ring opening. Recent work<sup>5</sup> has shown that a heptatrienide ion cyclizes



while a nonatetraenide ion does not. In the present case ring opening would be favored by regeneration of the aromatic ring. One consequence is that  $\overset{5}{\sim}$  can be formed solely from  $\overset{1}{\sim}$  and not from  $\overset{3}{\sim}$ . When a mixture of 80.5%  $\overset{1}{\sim}$  and 19.5%  $\overset{3}{\sim}$  was heated at 95° for 14 days with 0.43 M t-butoxide/t-butyl alcohol, the product contained 56.9%  $\overset{1}{\sim}$ , 18.9%  $\overset{3}{\sim}$  and 24.2%  $\overset{5}{\sim}$ . A control sample heated in the absence of the base gave a final mixture containing 77.5%  $\overset{1}{\sim}$  and 22.5%  $\overset{3}{\sim}$ . These results provide reasonable evidence that the Cope rearrangement of  $\overset{1}{\sim}$  is a reality, and that rearrangement proceeds slowly at 100°.

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*References*

1. A. C. Cope, L. Field, D. W. H. MacDowell and M. E. Wright, *J. Amer. Chem. Soc.*, 78, 2547 (1956); A. C. Cope, J. E. Meili and D. W. H. MacDowell, *ibid.*, 78, 2551 (1956).
2. W. von E. Doering and R. A. Bragole, *Tetrahedron*, 22, 385 (1966).
3. W. von E. Doering and W. R. Roth, *ibid.*, 19, 715 (1963).
4. S. H. Goh, L. E. Closs and G. L. Closs, *J. Org. Chem.*, 34, 25 (1969).
5. R. B. Bates, W. H. Deines, D. A. McCombs and D. E. Potter, *J. Amer. Chem. Soc.*, 91, 4608 (1969); R. B. Bates, S. Brenner and B. I. Mayall, *ibid.*, 94, 4765 (1972).