

SOME REACTIONS OF 3-ETHOXY-1,2,3-TRIPHENYLCYCLOPROPENE

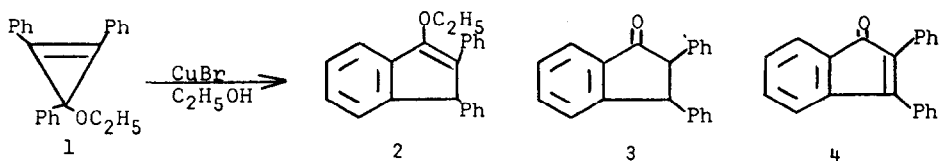
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In the past indenenes have been shown to be products of rearrangement of phenyl-substituted cyclopropenes.¹ For example, 1,2,3-triphenylcyclopropene rearranges to 1,2-diphenylindene in the presence of acid,^{1b} transition metal catalyst,^{1d} or light.^{1e} We have recently been exploring reactions of the title compound, 1, some of which show analogy to previous work.

When 1 is treated with one mole of CuBr in refluxing ethanol,² rearrangement takes place to give an 85% yield of 3-ethoxy-1,2-diphenylindene, 2;³ 10% of 2,3-diphenylindanone, 3, and a trace of 2,3-diphenylindenone, 4. Similarly,



with AgNO₃² 1 gives 40% of 2, 30% of 3, 5% of 4 and 20% of benzaldesoxybenzoin, 5.⁴ Control experiments with AgNO₃ show that 2 and 3 are interconvertible and oxidized in small amounts to 4 while 5 does not cyclize under the reaction conditions. In contrast 1 or 1 and ZnBr₂² give at the most a trace of compound 2 plus recovered starting material. Finally, irradiation of a solution of 1 in benzene under nitrogen with 3500 Å lamps using a Pyrex filter gives a 70% yield of 2.

The reaction pathway is significantly altered when 1 is treated with FeCl₃.² The products obtained are 4 (50%); 1,2,3-triphenylcyclopropene, 6, (20%) and only trace amounts of other components. The same reaction takes place when 1,2,3-triphenylcyclopropenylium tetrachloroferrate, 7,⁵ is treated with one equivalent of base under the reaction conditions. Compound 4 represents an oxidation product and 6 a reduction product. However, we feel that

this oxidation-reduction is not directly coupled since 6 but not 4 is formed in about the same amount when 7 is heated in ethanol without base. Also in the presence of FeCl_2 , 1,2,3-triphenylcyclopropenyl bromide is reduced to 6 in 40% yield. If we were to assume that (1) the usual Friedel-Crafts reaction^{1b} followed by oxidation is taking place and (2) that 1 and/or 3-hydroxy-1,2,3-triphenylcyclopropene are the initial intermediate(s), then 2 and 1-ethoxy-1,2-diphenylindene³ and/or 3 and 1,2-diphenylinden-1-ol would be considered further along the reaction route to 4. However, none of these compounds can be detected in more than trace amounts in the tlc of the crude reaction product. Furthermore, none of these compounds is oxidized to 4 in more than 25% yield by even two moles of FeCl_3 . These results leave open a number of pathways for the reaction of 1 with FeCl_3 to give 4.

Studies of the mechanisms of the reactions described, the reactions of other metal salts with cyclopropenes and relevant mass spectra are in progress.

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Footnotes

1. (a) M. A. Battiste, B. Halton and R. H. Grubbs, *Chem. Commun.*, 907 (1967); (b) R. Breslow in P. de Mayo, Ed., "Molecular Rearrangements". Interscience, New York, N. Y., 1963 pp 257-8; (c) D. M. Stehouwer and D. T. Longone, *Tetrahedron Lett.*, 5311 (1969); (d) J. A. Walker and M. Orchin, *Chem. Commun.*, 1239 (1968); (e) H. Dürr, *Ann.*, 723, 102 (1969); (f) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, 88, 1579 (1966); (g) H. Kristinsson, *Tetrahedron Lett.*, 2343 (1966); (h) J. Ciabattoni, P. J. Kocienski and G. Mellon, *Tetrahedron Lett.*, 1883 (1969); (i) A. M. Small, Ph.D. thesis, Columbia U., 1962.
2. Except for the photochemical reaction, the same conditions were always employed utilizing one mole of the metal salt; there was no attempt to run these reactions under anhydrous conditions or an inert atmosphere.
3. All new compounds have satisfactory analyses and spectra.
4. This compound has been reported as the ring-opening product of 3-hydroxy-1,2,3-triphenylcyclopropene by R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, 80, 5991 (1958).
5. This compound was reported by C. E. Coffey, *J. Am. Chem. Soc.*, 84, 118 (1962). Coffey did not fully characterize the salt but microanalysis confirms the molecular formula that he proposed. Its infrared spectrum is identical to that for 1,2,3-triphenylcyclopropenyl bromide.