

THE SILVER ION ASSISTED METHANOLYSIS OF 7-PHENYL-7-CHLORONORCARANE

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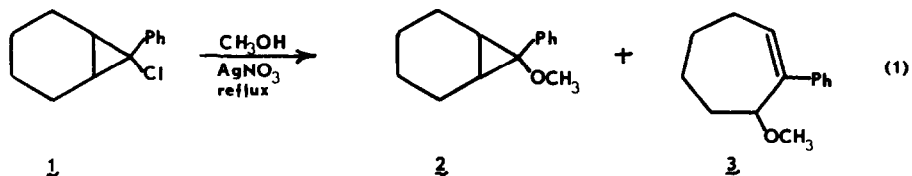
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The recent work of both Landgrebe (1), and Schleyer and Schollkopf (2) prompts us to report

another example of a cyclopropyl cation which is intercepted by a nucleophile before disrotatory ring opening can occur (3).

A solution of 7-phenyl-7-chloronorcarane (1) (a 2:1 mixture of the epimers as determined by gas chromatography) in methanolic silver nitrate was stirred at reflux until all starting material had been consumed. The crude product was analyzed by gas chromatography and showed two major volatile components (2 and 3) to be present in yields of 24% and 19% respectively (eqn. 1). Both components exhibit molecular ion peaks at  $m/e = 202$  in the mass spectra and analyze correctly for  $C_{14}H_{18}O$ .



The nmr of 2 exhibits two singlets at 2.96 ppm and 3.10 ppm (relative to tetramethylsilane) in a 3:1 ratio which together integrate for 3 protons, indicating a mixture of the two epimeric 7-phenyl-7-methoxynorcaranes (2a and 2b). We tentively assign the configuration of the major



isomer as 2a. We base our assignment on the nmr line position of the methoxyl protons in the major isomer which are at higher field. This is in agreement with the known shielding property of the cyclopropyl ring system which because of steric factors can only effect the methoxyl protons in epimer 2a (4,5). Compound 2 also exhibits complex absorption between 0.50 and 2.21 ppm (10 protons).

The nmr of 3 exhibits absorption at 7.21 ppm (5 protons, singlet), 6.08 ppm (1 proton, triplet,  $J=7.5$  Hz), 4.20 ppm (1 proton, doublet,  $J=6.0$  Hz), 3.21 ppm (3 protons, singlet), 2.84-1.84 ppm (8 protons, multiplet).

It is interesting to note that when 1 is stirred at room temperature in methanol with 0.4 eq. of silver nitrate, compounds 2 and 3 are obtained in a 3.6:1 ratio. The unreacted starting material recovered in a 48% yield from the reaction when analyzed by gas chromatography is > 97% pure. When this material, 1a, is reacted with silver nitrate in refluxing methanol 2 and 3 are obtained in a 1:12 ratio (51% yield). Compound 1a shows no appreciable reaction on treatment with silver nitrate at room temperature.

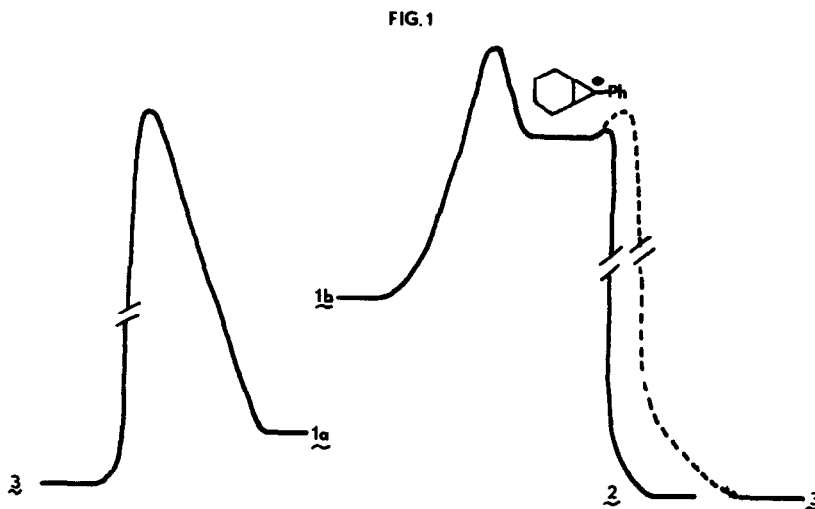
We assign the stereochemistry of the two epimeric 7-phenyl-7-chloronorcaradienes (1a and 1b where  $1a:1b = 2:1$ ) as depicted below.



The justification of our assignments lies in the known mode of addition of phenylchlorocarbene to cis-olefins (6); the broad phenyl absorption observed in the nmr of 1a (6); and, most importantly, the predominant formation of the olefin 3 from 1a. Based on Woodward-Hoffmann considerations we feel that the stereochemistry assigned to 1a is correct, and that 3 must arise, in this case, from a concerted ring opening (3).

The predominant formation of 2 from the mixture of epimers 1 at room temperature implies that it arises via a nonconcerted process, and that its precursor must be 1b since 1a is unreactive at this temperature. Here then is an example of a nonconcerted process taking precedence over a concerted one. This is undoubtedly due to the higher ground state energy of 1b relative

to 1a (7). The energy of activation for the nonconcerted reaction in the case of 1b must, therefore, be less than that for the concerted reaction observed in the case of 1a. Thus in considering the rate of solvolysis of various epimeric cyclopropyl derivatives one must take into account not only the stereochemistry of the leaving group (3) but also the relative ground state energies of the reactants. Our arguments with respect to this system are summarized in figure 1.



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