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TRANSITION METAL PROMOTED REARRANGEMENT OF 1-PHENYLBICYCLO [2.1.0]PENTANE[1]

Michael A. McKinney and S.K. Chou

Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233

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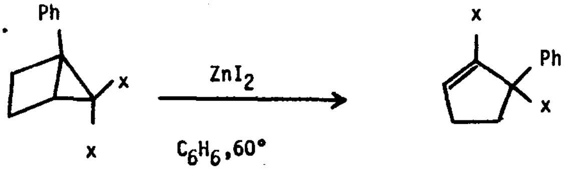
We wish to report the first example of a zinc-catalyzed rearrangement of the bicyclo [2.1.0]pentane ring system. Namely, the rearrangement of 1-Phenylbicyclo[2.1.0]pentane(**1a**) with a catalytic amount of zinc iodide in benzene (2 hr, 60°) to give as the sole product 3-phenylcyclopentene(**2a**).

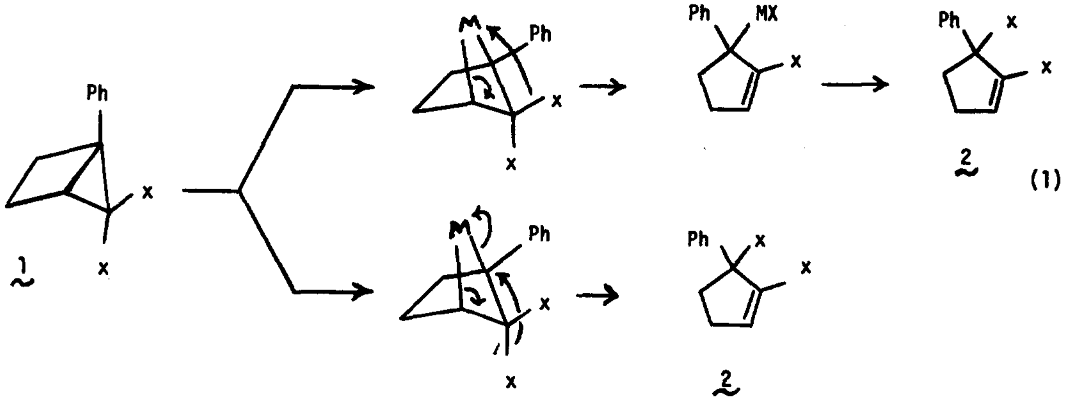


1a, x = H
1b, x = D

2a, x = H
2b, x = D

1-Phenylbicyclo[2.1.0]pentane[2](**1a**) was prepared by treatment of 1-phenylcyclobutene[3] with diazomethane catalyzed by cuprous chloride[4] and purified by preparative glpc (15% diethylene glycol succinate on 80-100 mesh base washed Chromosorb W). The assignment of structure followed from spectral data [$\lambda_{max}^{H_2O}$ 230nm ($\epsilon \sim 9{,}000$)[5]; $\delta_{TMS}^{CDCl_3}$ 7.25 (m, 5, aromatic), 1.72-2.72 (br m, 4, cyclobutyl), 1.12-1.67 (br m, 3, cyclopropyl); mass spectrum (70eV m/e 144]. The product of rearrangement (**2a**) was purified by glpc and identified by comparison of its spectral properties (ir, nmr and mass spectra) with those of an authentic sample.[6]

In order to gain some insight into the mechanism of this zinc-catalyzed rearrangement, we studied the isomerization of the 5,5-dideuterio compound **1b**. The results obtained are consistent with a mechanism involving metalocyclic intermediates[7] (eq. 1) or a metal assisted concerted [$\sigma^2_s + \sigma^2_s$] pericyclic reaction.[8] The results are inconsistent with a mechanism involving the type of metal hydride intermediates observed in the rhodium catalyzed rearrangement of bicyclo[2.1.0]pentane and its 5-carboethoxy, 2 and 5-methyl derivatives.[9]



(1)

The deuterated substrate was prepared as described above using deuterated diazomethane.[10] The 5,5-dideuterio compound, 1b, was glpc purified and rearranged with zinc iodide (27 mol%) in benzene (25 min, 60°) to give labeled 3-phenylcyclopentene (2b), which was purified by glpc and analyzed by proton nmr and mass spectroscopy.[11] The data obtained for two runs on separately prepared starting materials of different deuterium composition are given in Table I.

Table I

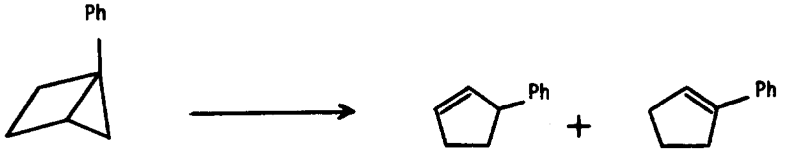
Deuterium Distribution in 3-Phenylcyclopentene, 2b

	Position	
Sample	Vinyl ^{c}	benzyl ^{c}
1^a	0.30±0.06d	0.33 ± 0.06d
2^b	0.42±0.07d	0.47 ± 0.05d

a. By mass spectra the starting material (1b) contained 0.68 deuteriums and the product (2b) 0.64 deuteriums.
b. By mass spectra the starting material (1b) contained 0.90 deuteriums and the product 0.86 deuteriums.
c. Based on nmr integration using the phenyl integration as 5.00 protons. The integrals were corrected running a pure sample of 2a at the same instrument settings. The errors given are the standard deviations over seven integrations.

The data indicate that within experimental error equal amounts of deuterium result in the benzylic and vinylic positions of the 3-phenylcyclopentene product. The rearrangement, therefore, involves hydrogen or deuterium migration from C(5) of the labeled phenylbicyclopentane without scrambling of the label by intervention of metal hydride intermediates.

The rearrangement of 1 is also catalyzed by other transition metals. However, the rearrangement of 1 promoted by rhodium and silver is much less regiospecific than the zinc-catalyzed rearrangement. In these cases mixtures of 2a and 1-phenylcyclopentene are obtained as products (eq. 2).



(2)

1	$[Rh(CO)_2Cl]_2$	56	44
	$AgBF_4$	28	72

The mechanism of these latter transformations is presently under investigation.

References

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5. Phenylcyclopropane shows ultraviolet absorption at 220nm ($\varepsilon \sim 8{,}800$).

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11. The zinc iodide was dried under vacuum for 25 hrs before use and the solution of **1** in benzene was dried over molecular sieves. If wet zinc iodide was used the only product obtained was 1-phenylcyclopentene. This probably represents the outcome of a proton[12] (HI) induced rearrangement of **1a**. A thermally induced rearrangement of 1a occurs in the absence of ZnI_2 but this reaction proceeds considerably slower than the metal catalyzed reaction at 60°. The sole product of the thermal rearrangement carried out in benzene solution was 1-phenylcyclopentene.

12. We have extensively studied the perchloric acid catalyzed cleavage of 1. These results will be reported in a full paper.