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THE STEREOCHEMISTRY OF DECOMPOSITION OF 1-DIAZO-2-PHENYL-5-t-BUTYLCYCLOHEXANES

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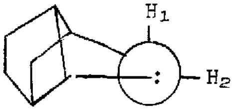
There is little information as to the detailed stereochemistry of 1,2-rearrangements of carbenes. Thermolysis of 1-diazo-*cis*-decalin (**1**) gives *cis*-Δ^1-octalin (**2**, 73%) rather than $\Delta^{1,9}$-octalin (**3**, 27%), the more stable isomer.[1] The limited conversion of **1** to **3** has been rationalized on the supposition that rearrangement of α-methyne hydrogen is repressed because it can not migrate perpendicular to departing nitrogen in one of the conformationally likely transition states for decomposition.[1] 5-Diazobrexane, a system in which its presumed carbene (**4**) is locked in a strained boat conformation, undergoes rearrangement of *exo* (H_1, near perpendicular) rather than *endo* (H_2, antiplanar) α-hydrogen.[2] Calculations indicate further that (1) ethylidene isomerizes to ethylene via perpendicular-like migration of hydrogen (H_2, **5**) gauche to the methylene proton (H_1)[3a-d] and (2) less rigorously, cyclohexylidene in chair conformation undergoes preferential axial hydrogen migration.[3] A study is now reported of carbenic decompositions of 1-diazo-2-phenyl-*cis*-5-t-butylcyclohexane (**6**) and 1-diazo-2-phenyl-*trans*-5-t-butylcyclohexane (**7**) as generated by pyrolyses of sodium salts[4] (**8** and **9**, respectively) of *p*-tosylhydrazones[4,5] (**10** and **11**, respectively) of *cis* (**12**)[6] and *trans* (**13**) -2-phenyl-5-t-butylcyclohexanones.[6] The investigation reveals that for cyclohexylidenes **14** and **15** in apparent restricted chair conformations, migrations of hydrogen and of phenyl groups occur preferentially by axial processes.



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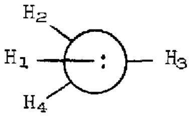

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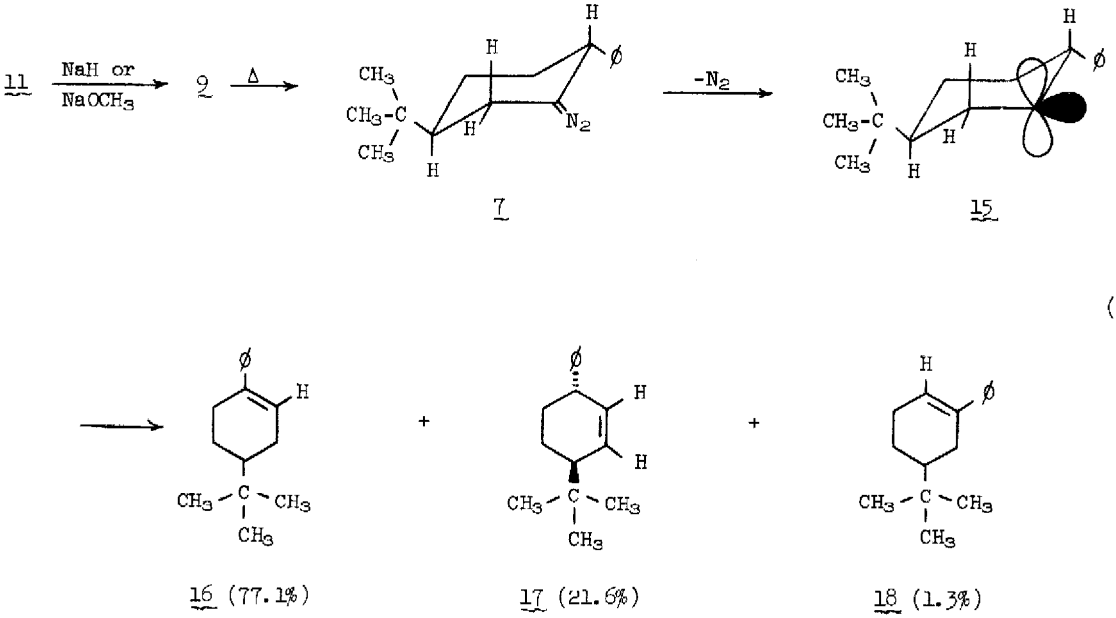
Decomposition of **11** in diglyme in the presence of sodium hydride (1.3-2.3 equiv) or sodium methoxide (5 equiv) occurs at 160° *via* **9** and **7** to yield 1-phenyl-4-t-butylcyclohexene

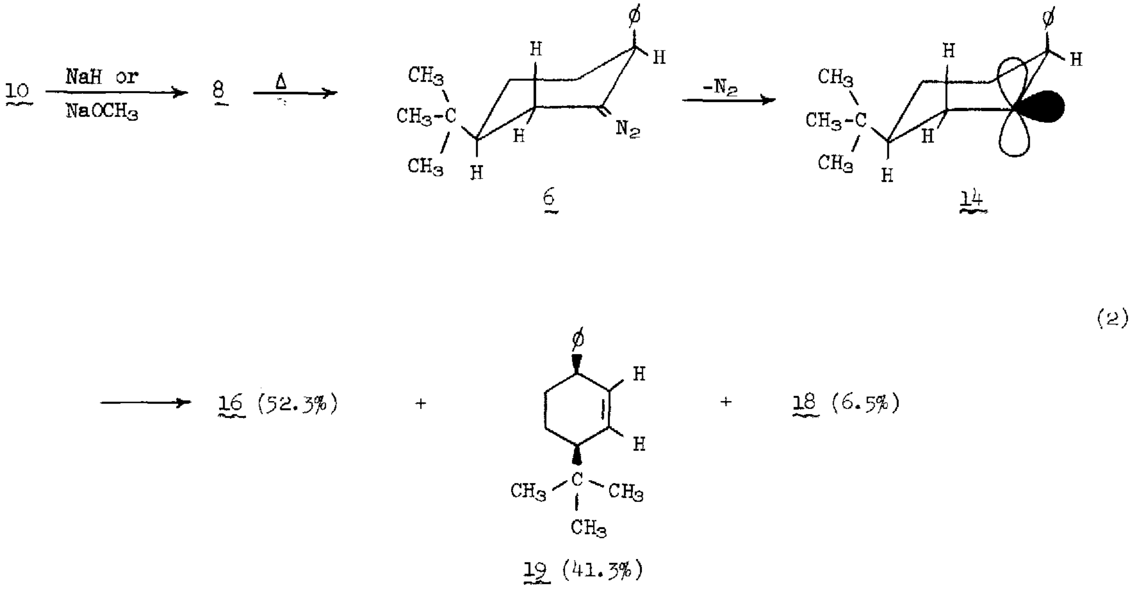
(16, 77.1%) and 3-t-butyl-*trans*-6-phenylcyclohexene (17, 21.6%) by hydrogen rearrangement and 2-phenyl-4-t-butylcyclohexene (18, 1.3%) by phenyl migration.[7] Similar results were obtained for vacuum pyrolyses (160-200°) of dry 9 containing excess sodium hydride (1.4-3.7 equiv). The principal carbenic reaction in thermolysis of 7 thus involves migration of α-methyne rather than α-methylene hydrogen (the ratio of 16 to 17 is 3.6:1) and rearrangement of phenyl



(1)

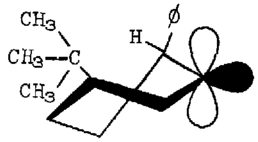
to give 18 is extremely minor. On the basis of equatorial conformational preferences of the 2-phenyl and the 5-t-butyl groups, it is apparent that migration of α-methyne hydrogen in decomposition of 7 occurs axially. The results also imply that rearrangement of α-methylene hydrogen in 15 *via* an axial path is likely and raises the question that migration of phenyl is inhibited because of its equatorial (antiplanar) stereochemistry. Of further note is that decomposition of sodium 2-phenylcyclohexanone *p*-tosylhydrazonate at 160° yields 1-phenylcyclohexene (77%) and 3-phenylcyclohexene (22%) in proportions almost identical to 16 and 17 as obtained from 7 and thus the steric requirements for rearrangements in thermolyses of 1-diazo-2-phenylcyclohexane and 7 would appear to be quite similar.

Thermolysis (160°) of 6, as generated from solid 8 or in diglyme from 10 and sodium hydride (1.2-1.9 equiv) or sodium methoxide (5 equiv), results in 16 (52.3%) and 3-t-butyl-*cis*-6-phenylcyclohexene (19, 41.3%) by migration of hydrogen and 18 (6.5%) by rearrangement



(2)

of phenyl.[7] As compared to 7, 6 decomposes with less rearrangement of α-methyne hydrogen and with greater migration of its α-methylene hydrogen and its phenyl group. The fact that the ratio of 16:19 produced from 6 is significantly less (1.3:1) than of 16:17 (3.6:1) from 7 indicates that the transition state leading to 16 is of greater energy when the phenyl group is axial rather than equatorial. It is not yet clear whether 16 is formed by antiplanar (equatorial) migration of α-methyne hydrogen in 14 or/and conformational change to twist boat or inverted chair forms and rearrangement of the hydrogen from pseudo-axial or axial positions in transition states structurally similar to 20 and 21.



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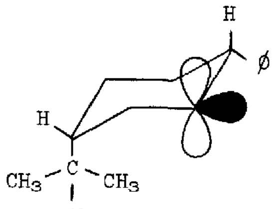

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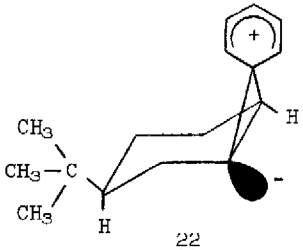
The ratio for phenyl migration in decomposition of 6 and 7 is 5:1. These results provide the first example of conformational preference for carbenic rearrangement of a group other than hydrogen and, along with the observation that 2-phenyl-1-propene is not formed upon thermolysis of 2-diazo-1-phenylpropane,[8] indicate that axial migration of phenyl is favored *stereoelectronically* via a transition state having structural character as in 22.[9] A factor



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contributing to the greater migration of phenyl in decomposition of 6 than in 7 may be greater relief of strain in 14 and/or 20 than in 15. The extent to which such effects may be operative is being investigated.

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References

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4. All new compounds gave satisfactory analyses and appropriate ir, uv, nmr, and mass spectra.

5. *p*-Tosylhydrazones 10 and 11 were prepared from 12 and 13 by reaction with p-tosylhydrazine and ethanol at 25° and converted by sodium hydride in ethyl ether to 8 and 9 without epimerization of the 2-phenyl groups.

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7. Cyclohexenes 16 and 18 were identified by glc comparison with authentic samples, the structure of 17 was established from its nmr and upon its hydrogenation to 1-t-butyl-*trans*-4-phenylcyclohexane, and 19 was identified by mass spectral and nmr methods.

8. Decomposition of sodium 1-phenyl-2-propanone *p*-tosylhydrazonate at 160° yields *cis* (17%) and *trans* (69%) -1-phenylpropenes and allylbenzene (14%); G. Kaufmann, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1967.

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