

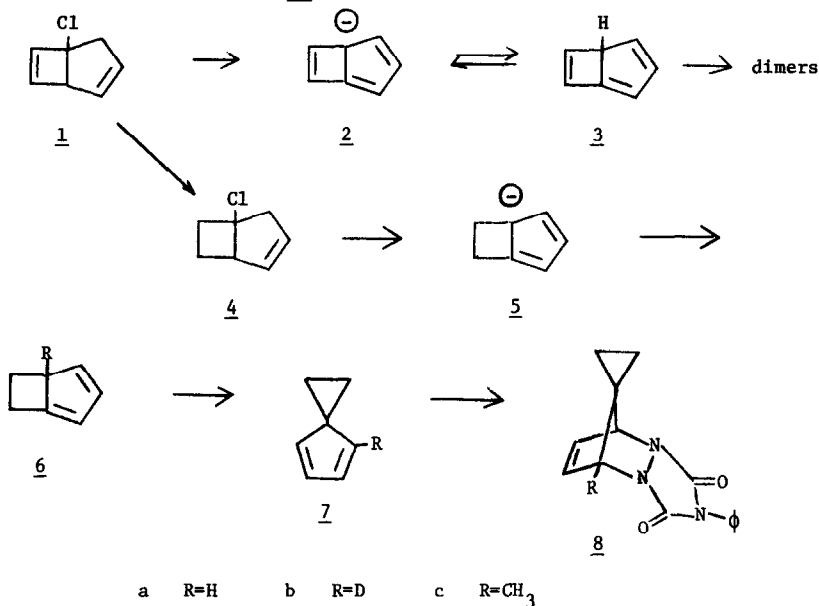
A FACILE 1,5 ALKYL SHIFT CONVERTING
 BICYCLO[3.2.0]HEPTA-1,3-DIENE INTO SPIRO[2,4]HEPTA-4,6-DIENE

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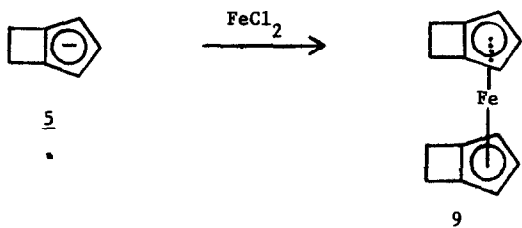
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We have reported¹ that the bicycloheptatrienyl anion 2 can be prepared from chlorodiene 1 by treatment with strong base. Although the corresponding neutralized triene 3 undergoes rapid dimerization, we were able to estimate the pK_a of 3 relative to its anion 2 and used this estimate in a discussion of the antiaromaticity of cyclobutadiene. As a model for some of the angle strain involved in these species, we wished to prepare the corresponding dihydroanion 5 and to determine the pK_a of a corresponding hydrocarbon such as 6a. Remarkably, we find that 6a undergoes a very fast isomerization to 7a under extremely mild conditions.



Partial hydrogenation of chlorodiene 1 in pentane over Pd-C at 0°C gave the chlorobicycloheptene 4 in more than 90% yield. Treatment of 4 with an excess of lithium diethylamide in tetrahydrofuran at -20°C afforded the anion 5 (accompanied by varying amounts of hydrocarbon 7a) whose nmr spectrum showed the expected vinyl protons at δ 5.49 (t, J=2.8, 1 H) and 5.19 (d, J=2.8, 2 H). The anion solution could be treated with FeCl₂ to afford the ferrocene derivative 9 in 65% yield as deep yellow prisms, mp 60-61°C; the nmr spectrum of 9 had signals at δ 3.90 (d, J=2.0, 4 H), 3.74 (t, J=2.0, 2 H), and 3.3-2.6 (A₂B₂, 8 H).



Quenching of the solution of anion 5 with methanol, water, or acetic acid below 0°C afforded hydrocarbon ²7a as the only distillable product in 44-49% yield. If the quenched reaction mixture was treated with N-phenyltriazolinedione the adduct 8 could be isolated in 50-60% yield. Quenching of the anion solution with D₂O or AcOD affords a mixture of 7a and the deuterio derivative 7b. If instead the anion solution is treated with an excess of CH₃I it is converted to a volatile diene fraction consisting of 73% of the known methyl derivative 7c along with 27% of 7a. The substitution position is clear from the nmr spectra ⁴ of the dienes 7 and also of the adducts 8.

It is thus apparent that the formation of the spirodienes 7a, b, and c must occur by protonation (deuteration, methylation) of anion 5 at the ring junction to afford 6a, b, or c. Under the reaction conditions these compounds undergo a 1,5 alkyl migration (ring contraction) to afford 7. An indication of the facility with which this rearrangement occurs was obtained by nmr spectral studies. A solution of the anion 5 accompanied by some hydrocarbon 7a was prepared and cooled to -50°C. Addition of methanol to this mixture at -50° caused complete disappearance of 5 while the signals corresponding to 7a markedly increased. No other new signals could be detected. Thus, 6a is rapidly rearranging to 7a even under these conditions of low temperature and fast observation. The predominant protonation (and alkylation) of anion 5 at the ring junction is consistent with the behavior we observed earlier¹ for the triene anion 2,

which protonates to afford 3. Apparently, steric rather than special electronic factors are involved.

The striking observation in these studies is the extremely rapid 1,5 alkyl shift by which 6a is converted to 7a. Activation energies for 1,5 alkyl shifts in cyclopentadienes are normally⁵ of the order of 36-48 kcal/mole, while 1,5 hydrogen shifts are considerably easier with activation energies⁵ of 19-24 kcal/mole. Apparently in 6a the ring-contracting 1,5 alkyl shift has been so lowered in energy that it proceeds faster than a 1,5 hydrogen shift, which would convert 6a to an isomeric diene. Interestingly, on the basis of nmr chemical shifts it has been suggested⁶ that spirodiene 7a is somewhat aromatic, its cyclopropane ring electrons being partially delocalized in the cyclopentadiene ring. Similar stabilization in the transition state for our rearrangement, coupled with relief of strain⁷, may explain the facility of the 6 to 7 rearrangement.

Finally, it should be mentioned that Hamer and Stubbs have recently reported⁸ the formation of 7a from a base catalyzed elimination designed to proceed through 6a, and they have commented on the remarkable ease of this rearrangement. Reversibility of the rearrangement is suggested by the report of Kloosterzeil and coworkers⁹ that pyrolysis of 7a affords a dimethylenecyclopentene via the intermediacy of 6a. However, the activation energy of 38 kcal/mole for that reaction is consistent with our observation that the rearrangement of 7 to 6 is an endothermic process. Unfortunately, the very facile rearrangement we have observed makes it impossible to equilibrate anion 5 with a corresponding hydrocarbon, and thus to determine the pK_a of interest with respect to anion 2.¹⁰

References

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10. Support of the work by the National Institutes of Health is gratefully acknowledged