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BICYCLO[3.1.0]HEX-(1,5)-ENE AND BICYCLO[4.1.0]HEPT-(1,6)-ENE

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Summary: The formation and trapping of bicyclo[3.1.0]hex-(1,5)-ene and bicyclo[4.1.0]hept-(1,6)-ene from the corresponding vicinal dibromides is described.

Small ring bicyclic alkenes have recently received considerable attention. Wagner et. al.[1] have calculated the geometries of the cyclopropene derivatives 1-4 and found all four to have a bent structure. Szeimies et.al.[2] have presented good evidence for the formation of a derivative of 1 via the elimination of hydrogen chloride from a 1-chlorobicyclo[1.1.0]butane derivative. A more complex polycyclic derivative of 2 also was obtained by the dehydrohalogention of 1-chloroquadricyclane.[3] A dimethyl derivative of 4 was obtained by Closs and Boll via the photolysis of the corresponding 3-H-pyrazole,[4] and Gassman, et. al.[5] have presented evidence that 4 is an intermediate in the reaction of 2-methylcyclohexenyl-1 chloride with n-butyllithium. All of these compounds have proven to be quite unstable and were in most cases identified via trapping as Diels-Alder adducts.


1

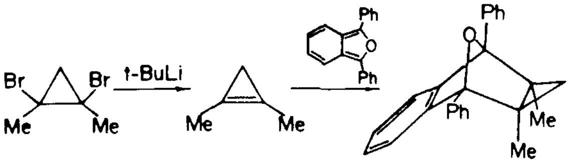

2


3

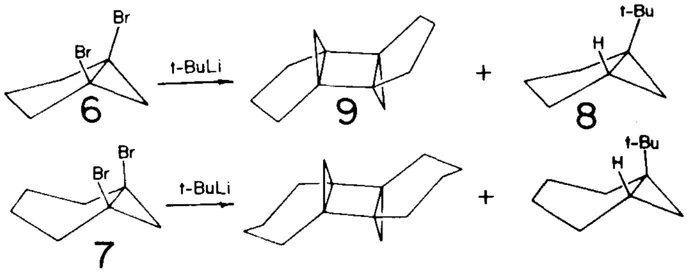

4

We wish to report some experimental results concerning the formation of 3 and 4. The most attractive route to these compounds is via an elimination reaction. In order to avoid possible ambiguities concerning the direction of elimination, we have chosen to use the reductive elimination of halogen from a vicinal dibromide. As a test of this method, 1,2-dibromo-1,2-dimethylcyclopropane (either cis or trans) was treated with t-butyllithium in tetrahydrofuran at -78° C. The reaction was quenched by the addition of methanol, and then diphenylisobenzofuran was added. An 80% yield of the Diels-Alder adduct was obtained.[6] In the nmr spectrum, one of the cyclopropyl CH_2 protons was found at relatively low field ($\delta = 2.25$)

suggesting that the CH$_2$ group was syn to the oxygen in the adduct.[7]

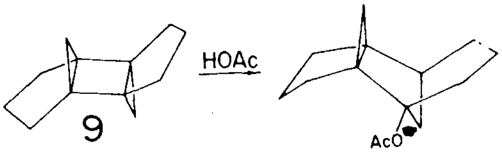


The dibromides, 6 and 7, could readily be prepared from corresponding dicarboxylic acids[8] via modified Hunsdiecker reactions.[9] When 6 was treated with t-butyllithium in THF or ether at -78°, a rapid reaction was observed. On workup, the major products were found to be a dimer and 1-*tert*-butylbicyclo[3.1.0]hexane (8). The ^{13}C nmr spectrum of the dimer indicated a relatively high symmetry which is compatable with the structures 9 or its *syn* isomer.[10] Essentially the same results were obtained in the reaction of 7 with tert-butyllithium.

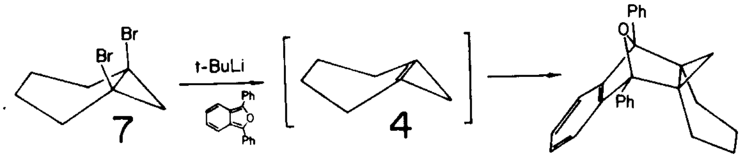


When the reaction mixtures derived from 6 or 7 were treated with carbon dioxide, 1-*tert*-butylbicyclo[3.1.0]hexane-5-carboxylic acid and 1-*tert*-butylbicyclo[4.1.0]hexane-6-carboxylic acid were obtained.

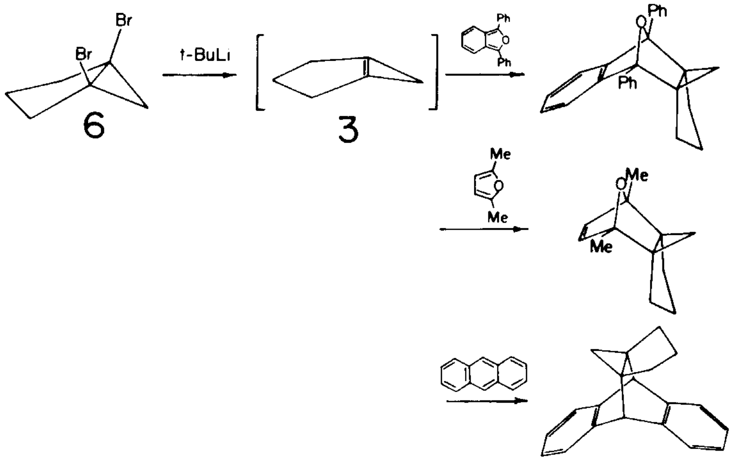
The dimer, 9, contains the [3.2.1]propellane skeleton, and therefore would be expected to react rapidly with electrophiles such as acetic acid to cleave the central bond.[11] It was found to react rapidly at room temperature to give a monoacetate which still retained a cyclopropane ring as shown by its nmr spectrum. This observation provides additional evidence for the structure of 9.



The products of the reactions of the dibromides with butyllithium strongly resemble those of the bicyclo[1.1.0]butene derivative studied by Szeimies and suggest that 3 and 4 were formed as intermediates in the reactions. When a solution of 7 and diphenylisobenzofuran in tetrahydrofuran was treated with butyllithium, a 71% yield of the Diels-Alder adduct formed from 4 was isolated. When the reaction was carried out at -120° C, and diphenylisobenzofuran was added after the butyllithium, no Diels-Alder adduct was formed. This indicates that 4 undergoes dimerization very rapidly even at -120° C. Our calculations[12] indicate that 4 has essentially the same extra strain energy as bicyclo[2.2.0]hex-(1,4)-ene 8. However, 8 does not undergo dimerization in dilute solution below 0° C. Calculations suggest that 8 is planar which should lead to steric hindrance to dimerization. The non-planar structure of 4 is probably at least in part responsible for its higher reactivity. The introduction of a *gem*-dimethyl group at the 7-position of 4 is known to reduce its reactivity,[4] and this is in accord with steric arguments.



The corresponding reaction of 6 led to the formation of 3 which could be trapped with diphenylisobenzofuran, dimethylfuran, furan or anthracene. It was, however, not possible to trap 4 with furan or dimethylfuran, presumably due to its lower reactivity.



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2. G. Szeimies, J. Harnisch and O. Baumgartl, *J.Am.Chem.Soc.* **99**, 5183 (1977); U. Szeimies-Seebach and G. Szeimies, *J.Am.Chem.Soc.* **100**, 3966 (1978).

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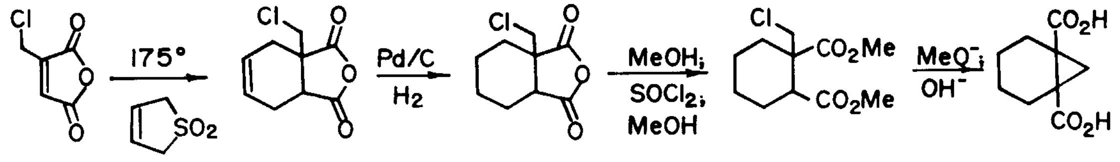
6. All new compounds had analyses, nmr and mass spectra which were consistent with the assigned structures.

7. For other examples of Diels-Alder reactions between diphenylisobenzofuran and cyclopropenes giving adducts in which the oxygen and cyclopropene methylene are *syn*, see R. Breslow, G. Ryan and J.T. Groves, *J.Am.Chem.Soc.*, **92**, 988 (1970). Also see T.H. Chan and D. Massuda, *Tet.Letts.* 3383 (1975); R.W. LaRochelle and B.M. Trost, *J.Chem.Soc.,Chem.Commun.*, 1353 (1970).

8. Bicyclo[3.1.0]hexane-1,5-dicarboxylic acid: R.N. McDonald and R.R. Reitz, *J.Org.Chem.* **35**, 2666 (1970). Bicyclo[4.1.0]heptane-1,6-dicarboxylic acid was prepared as follows:



9. S.J. Cristol and W.C. Firth, Jr., *J.Org.Chem.* **26**, 280 (1961).

10. The ^{13}H chemical shifts were: δ 31.63(t), 28.11(s), 26.89(t) and 25.82(t).

11. K.B. Wiberg, H.A. Connon and W.E. Pratt, *J.Am.Chem.Soc.* **101**, 6970 (1979).

12. K.B. Wiberg, G. Bonneville and R. Dempsey, to be published.

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