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STRAIN IN 1, 3-DIMETHYLBICYCLO[1. 1. 0]BUTANE[1]

Richard B. Turner, Peter Goebel
Department of Chemistry, Rice University, Houston, Texas
W. von E. Doering and J. F. Coburn, Jr.
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

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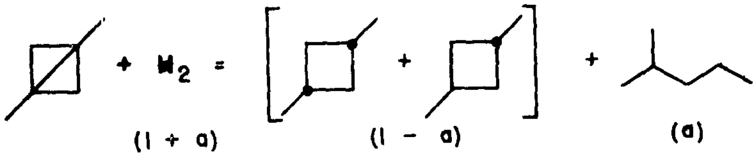
1, 3-DIMETHYLBICYCLO[1. 1. 0]BUTANE is of special interest among the several highly strained systems of recent synthesis in view of the unusual reactivity exhibited by its central 1, 3 carbon-carbon bond.[2] Thus it reacts with iodine in a facile addition to form <u>cis</u>-1, 3-diiodo-1, 3-dimethylcyclobutane, with methylene in an unprecedented manner to produce 2, 4-dimethylpenta-1, 4-diene, and is so sensitive that acetic acid suffices to transform it into 2-acetoxy-4-methyl-pent-4-ene rapidly at room temperature. Since these exceptional reactions of 1, 3-dimethylbicyclo-[1. 1. 0]butane are made accessible by a major lowering of transition state energies through relief of strain, the total strain energy becomes one of the molecule's most fundamentally significant properties.

We wish to report an estimation of this strain energy based on the heat of hydrogenation. Several difficulties have limited the experimental accuracy of the hydrogenation data. Instead of the normally ideal acetic acid solvent, the less satisfactory diethylcarbitol had to be used.[3] In this solvent the rate of hydrogenation was inconveniently slow and involved the uptake of variable amounts of hydrogen considerably in excess of one equivalent. Consequently the heat of hydrogenation of -40. 55 kcal/mole of hydrogen absorbed is probably in error by ± 1 kcal. (In two runs, 1.85 and 1.79 molar equivalents of hydrogen were absorbed with the evolution of 40.94 and 40.22 kcal/mole of hydrogen absorbed, respectively.)

Derivation of the total strain energy from this heat of hydrogenation requires, first, translation into an "experimental" heat of formation and, second, comparison with the heat of formation estimated for a strain-free model. The translation is effected on the basis of chemical equation (1) in which *cis* and *trans* 1,3-dimethylcyclobutane are stable products. Since it is assumed that the heats of formation of the two cyclobutanes are identical, no use is made of the fact that they are formed in the hydrogenation in a ratio of *ca.* 6:1.[2] The heats of formation at 25° are calculated by Franklin's method of group equivalent values[4] and corrections for strain energy are based on the heats of combustion of Kaarsemaker and Coops[5] and of Knowlton and Rossini[6], not available to Franklin in 1949. From the calculated heat of formation of dimethylcyclobutane (-6.52 kcal/mole) and the experimental heat of formation of 2-methylpentane (-41.66 kcal/mole), the "experimental" heat of formation of 1,3-dimethylbicyclo[1.1.0]butane at 25° is found to be +38.5 ± 1 kcal/mole.

(1)



The total strain in 1,3-dimethylbicyclo[1.1.0]butane can be equated with the difference between the "experimental" heat of formation (+38.5) and the heat of formation of a strain-free model (-28.5) taken as the sum of the Franklin values of the component groups [$2(CH_3)_2$: -20.24; 2 CH_2: -9.85;

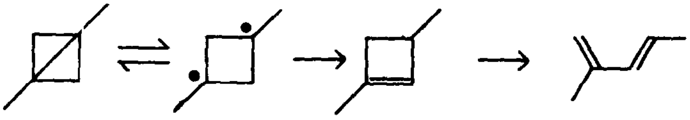
2 C: + 1.60]. The total strain is thus estimated to have the remarkably high value of 67.0 kcal/mole. It can be compared with the strain of 53.6 kcal/mole in bicyclo[2.1.0]pentane[7] which is very close to the sum of the component strain energies [cyclobutane (25.75)[5] and cyclopropane (27.15)[6]]. 1,3-Dimethylbicyclo[1.1.0]butane thus possesses the significantly incremental strain of 12.7 kcal/mole [67.0 versus 54.3 (2 x 27.15)] and thereby offers a significant exception to the hypothesis of the additivity of strains.[8] Per carbon atom the strain in the bicyclobutane is the highest found so far, 16.8 kcal/mole.

There are two possible modes of hydrogenation, the heats of which (ΔH_{H_2} = -45.1 and -47.0 kcal/mole, respectively) may be estimated by calculating the Franklin heats of formation of the two apposite products, 1,3-dimethylcyclobutane (ΔH_f^o = -6.52) and 1,1,2-trimethylcyclopropane (ΔH_f^o = -8.43). These estimated heats of hydrogenation may now be compared with those of the strain-free, similarly substituted, acyclic carbon-carbon bonds (-3.78 and -7.08, respectively). The strains relieved by hydrogenation of the 1,3 and 1,2 bonds are thus estimated to be 41.3 and 39.9 kcal/mole, respectively. Neither strain is so large as that relieved in the hydrogenation of bicyclo[2.1.0]pentane to cyclopentane (47.4).[9] Despite the fact that the bicyclobutane system possesses the greater total amount of strain, there is no one bond in bicyclobutane, the breaking of which releases quite so much strain as the breaking of the 1,3 bond in bicyclopentane.

Thermal reorganization of 1,3-dimethylbicyclo[1.1.0]butane leads

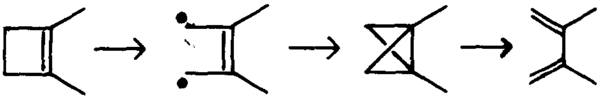
to 2,3-dimethylbutadiene in a reaction the activation energy of which has been found by Chesick to be 43.3 kcal/mole.[10] The minimum activation energy predicted for a process of two steps of which the first involves breaking the 1,2 carbon-carbon bond and the second has zero activation energy is 39.1 kcal/mole [79, estimated strength of 1°C - 3°C bond, less 39.9, relief of strain]. The difference, 4.2 kcal/mole, between this minimum value and the value actually found is smaller than the comparable difference in the cis, trans interconversions of cyclopropane [minimum 53.8 (81, estimated strength of 1°C - 1°C bond, less 27.15, strain in cyclopropane) versus 65.1 found[11]] and 2-methylbicyclo[2.1.0]pentane [minimum 29.2 (79, the estimated strength of 2°C - 2°C bond, -53.6, the strain in bicyclo[2.1.0]pentane, + 3.8, the strain in cyclopentene and, by assumption, in the cyclopenta-1,3-diyl diradical) versus 38.9 found[12]].

Neither of two possible reactions which might proceed by the breaking of the 1,3 bond of 1,3-dimethylbicyclo[1.1.0]butane has been observed so far. An N.M.R. spectrum which remains unchanged up to 180° is interpreted to indicate an activation energy for the breaking of the 1,3-bond of more than ca. 20 kcal/mole [predicted minimum is 35.7 (77, estimated strength of 3°C - 3°C bond, -41.3, relief of strain) unless lowered by 1,3 π-overlap of the 2p-2p type]. Furthermore, no 1,3-dimethylbutadiene is produced on pyrolysis. By analogy with the



rearrangement of bicyclo[2.1.0]pentane to cyclopentene, for which an activation energy of -46 kcal/mole has been found,[8, 13] rearrangement of the diradical to 1,3-dimethylcyclobutene by the migration of a hydrogen atom might ultimately have led to 1, 3-dimethylbutadiene.

In the course of making the generally significant precautionary observation that, especially of no-mechanism reactions, it is often difficult if not impossible to establish the existence of transition states which follow a higher energy, of necessity rate-determining, transition state, Professor J. A. Berson suggested to us privately and simply by way of illustration that 1, 3-dimethylbicyclo[1. 1. 0]butane might be an intermediate in the thermal reorganization of 1, 2-dimethylcyclobutene to 2, 3-dimethylbutadiene. Since thermochemical arguments coupled with the principle of microscopic reversibility will often constitute an unequivocal way of excluding hypothetical intermediates, it is perhaps instructional to point out of this specific illustration that the placing on a potential energy diagram of the heats of formation of 1, 2-dimethylcyclobutene (+22. 4)[7] and the transition state for its conversion to 2, 3 dimethylbutadiene (estimated +52. 4),[14] of 1, 3-dimethylbicyclo[1. 1. 0]-butane (+38. 5) and the transition state for its conversion to 2, 3-dimethylbutadiene (+81. 8)[10] and of 2, 3-dimethylbutadiene itself (estimated +10. 1)[4] will make it clear that 1, 3-dimethylbicyclo[1. 1. 0]-butane cannot be an intermediate in the thermal reorganization of 1, 2-dimethylcyclobutene to 2, 3-dimethylbutadiene, although the converse that 1, 2-dimethylcyclobutene be an intermediate in the rearrangement of 1, 3-dimethylbicyclo[1. 1. 0]butane, remains a possibility.



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(1) We wish to express our deep thanks to the National Science Foundation for its support of this work through Grant GP 203 to Rice University and Grant 11378 to Yale University.

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