2,4-Ethenonoradamantane by Silver(I) Ion-catalysed Rearrangement of Dehydronoriceane (Pentacyclo[5.3.1.0^{2,6}.0^{3,5}.0^{4,9}]undecane). Empirical Force-field Calculations

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Summary Treatment of dehydronoriceane with silver(I) ion afforded 2,4-ethenonoradamantane.

The recently synthesized dehydronoriceane (**1**; pentacyclo[5.3.1.0^{2,6}.0^{3,5}.0^{4,9}]undecane)[1] has the partial bicyclo[2.1.0]pentane structure constrained within a rigid cage molecule. Like bicyclo[2.1.0]pentane (**2**) itself,[2] (**1**) smoothly undergoes catalytic hydrogenation to noriceane,[1] indicating localized high strain around bond *a*.

However, we have now observed that the behaviour of (**1**) with silver(I) ion is quite different from that of (**2**). Whereas (**2**), and the even more strained spiro-compound (**3**), are inert to silver(I) ion,[3,4] (**1**) does react. Treatment of (**1**) with 3·6 mol % of AgBF$_4$ in CHCl$_3$ at room tempera-

TABLE. Molecular mechanics calculations on (**1**) and (**2**) using the Engler[6] force field

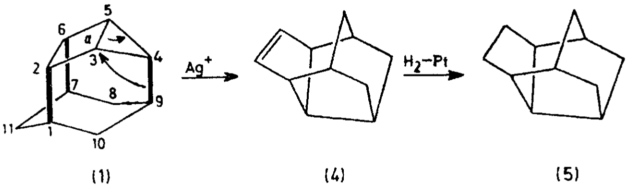
	(**1**) Calc.	(**2**) Calc.	(**2**) Exp.[a]
Bond length *a* (Å)	1·514	1·530	1·525(8) X[b] 1·536(1) M.W.[c]
Dihedral angle around *a* (deg)	115·6	124·7	112·5(3) X[b] 112·74(18) M.W.[c]
Sum of strain around bridgehead carbons (kcal mol^{-1})	88·87(C–3) 59·33(C–4)	84·45(C–1) 56·43(C–5)	
ΔH°_f (g, 25°) (kcal mol^{-1})	74·50	73·01	37·6[d]
Strain energy (kcal mol^{-1})	107·17	92·72	57·3[e]
Heat of bond *a* hydrogenolysis (kcal mol^{-1})	−81·92[f]	−91·45[f]	−55·14(36)[g]

[a] Standard deviations in parentheses. [b] *X*-Ray analysis of *exo*-5-tosylate: W. Saenger, C. H. Schwalbe, K. Fellenberger, and U. Schöllkopf, *Chem. Ber.*, 1973, **106**, 2883. [c] Microwave analysis of hydrocarbon: R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, 1972, **56**, 3837. [d] Taken from: S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279. [e] P. v. R. Schleyer, J. E. Williams, and K. Blanchard, *J. Amer. Chem. Soc.*, 1970, **92**, 2377. [f] $\Delta H^\circ_f - \Delta H^\circ_f$(noriceane) (ref. 5). [g] Ref. 2.

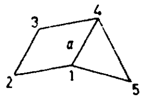
ture for 18 h gave 2,4-ethenonoradamantane (**4**; tetracyclo[5.3.1.0^{2,6}.0^{3,9}]undec-4-ene), m.p. 150—153 °C (sealed tube), in 85% yield: *m/e* 146 (M^+, 43%) and 80 (100%); ^{1}H n.m.r.: δ (CCl_4) 1·13—2·43 (9H, br. complex m), 2·67 (2H, br), 3·10 (1H, q, *J* 6 Hz), and 5·73 (2H, t, *J* 1 Hz); ^{13}C n.m.r.: δ ($CDCl_3$) 128·0 (2CH=), 59·2 (CH), 55·8 (2CH), 44·9 (2CH_2), 35·9 (CH), 35·1 (2CH), and 31·2 (CH_2); i.r. (CCl_4) 3150 and 710 cm^{-1}. The structure of (**4**) was confirmed by catalytic hydrogenation (79%) to the known 2,4-ethanononoradamantane (**5**).[5]

We first expected that the strain around bond *a* of (**1**) would be higher than that of the corresponding bond of (**2**) in order to explain the observed reactivity. Despite the acknowledged inadequacy of the presently available force-field models for cyclopropane derivatives,[6] we hoped that errors due to the force field would cancel each other when closely related molecules were compared in molecular mechanics calculations (Table). The Engler force field[6] reproduces the geometry of (**2**) well, though it overestimates the strain in (**2**) by *ca.* 30 kcal mol^{-1}. Attention should be directed to the small difference in energy terms between (**1**) and (**2**).† For (**1**) and (**2**) there appears to be no substantial difference in strain around bond *a* as well as in the whole molecule.‡ In addition, the bow-and-stern C . . . C as well as flagpole H . . . H nonbonded interactions in the boat cyclohexane ring of (**1**) amounted to only *ca.* 2 kcal mol^{-1}.

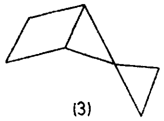
Thus, any rationalization of the observed reactivity of (**1**) toward silver(I) ion compared with (**2**) must be based on something other than strain. According to our calculation, the carbon framework structure of the bicyclopentane portion of (**1**) is similar to that of (**2**), but three C–C bonds connecting the bicyclopentane portion to the cyclohexane ring (see **1**, bold lines) are almost parallel to the plane including bond *a* and bisecting the dihedral angle between the cyclobutane and cyclopropane rings.§ We suggest that an intermediate in the rearrangement, most likely resulting from breaking of the central bond *a*, is stabilized by the hyperconjugative effect[7] of these C–C bonds. Although the nature of intermediate is not yet known, an argento carbonium ion like (**6**, R = Ag) would be unfavourable because a large dihedral angle (45°) between the vacant C(3)$^+$ orbital and the migrating C(4)–C(9) bond has been calculated for (**6**, R = H). On the other hand, if C(3) of the intermediate is *sp*^{3}-hybridized, one of its orbitals and the C(4)–C(9) bond are in an almost perfect *trans*-periplanar arrangement, as calculations on noriceane indicate. There are two possibilities for a 1,2-alkyl shift ensuing intermediate formation. Migration of the C(1)–C(2) bond to C(3) gives back the noriceane skeleton, while shift of the C(4)–C(9) bond leads to the more stable[5] 2,4-ethanonoradamantane structure.



(1) (4) (5)



(2)



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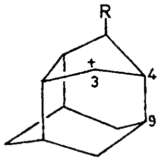

(6)

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† The Allinger 1971 force field (N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1637. gave essentially the same conclusions.

‡ Experimental determinations of heats of formation of (**1**) and noriceane[1] are in progress in Professor W. Parker's laboratory.

§ The corresponding C–C bond in the outer cyclopropane ring of (**3**) deviates from the plane by *ca.* 25°.

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[4] Compound (**2**) undergoes rapid isomerization to cyclopentene upon treatment with a rhodium complex: P. G. Gassman, T. J. Atkins, and J. T. Lumb, *J. Amer. Chem. Soc.*, 1972, **94**, 7757.

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[6] E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005.

[7] R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.