Enthalpies of Formation of *cis*- and *trans*-1,2-Diethylcyclopropane and *cis*- and *trans*-Bicyclo[6.1.0]nonane. Structural Effects on Energies of Cyclopropane Rings

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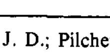
Abstract: The enthalpies of formation of *cis*- and *trans*-1,2-diethylcyclopropane were determined by oxygen bomb calorimetry. The *cis*-diethyl isomer was 1.1 kcal/mol less stable than the trans isomer. Alkyl groups were found to stabilize a cyclopropane ring by the same amount as for a carbon–carbon double bond. The enthalpies of formation *cis*- and *trans*-bicyclo[6.1.0]nonane also were determined by oxygen bomb calorimetry. The two bicyclo[6.1.0]nonanes have essentially the same enthalpies of formation, in contrast to *cis*- and *trans*-cyclooctene. The introduction of a trigonal center makes the *trans*-bicyclononane 3 kcal/mol less stable than the cis isomer. Molecular mechanics calculations are reported for a series of *cis*- and *trans*-bicyclo[*n*.1.0]alkanes. In order to better estimate the strain energy of *trans*-bicyclo[4.1.0]heptane, the difference in energy between it and its cis isomer was calculated via ab initio molecular orbital theory.

Although the difference in energy between cis- and trans-substituted alkenes is fairly well-known,[1,2] there is relatively little information concerning the difference in energy between cis- and trans-substituted cyclopropanes.[3,4] It has been assumed to be on the order of 1 kcal/mol, and the difference is believed to be important in determining the rates of solvolyis of epimeric 3-substituted cyclobutyl derivatives that rearrange stereospecifically to cis- or trans-substituted cyclopropylcarbinyl cations.[5]

In order to gain information on the energy differences, we have examined two pairs of cyclopropyl derivatives: *cis*- and *trans*-1,2-diethylcyclopropanes (**1** and **2**) and *cis*- and *trans*-bicyclo[6.1.0]nonanes (**3** and **4**). The enthalpies of combustion of the four compounds were determined by oxygen bomb calorimetry. The values are summarized in Table I. The enthalpies of vaporization for **1** and **2** were estimated,[6] providing values of $\Delta H_f(g)$. The enthalpy of vaporization for **3** is known,[7] and it was assumed to have the same value for **4**.[6] The enthalpies of formation derived from these data are given in Table II.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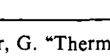
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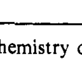
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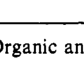
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Table I. Enthalpies of Combustion of Cyclopropanes

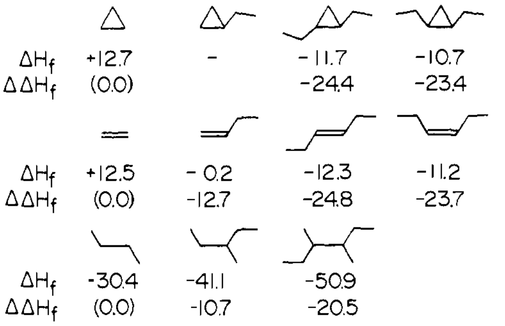
compd	ΔH_c, kcal/mol	av
cis-1,2-diethylcyclopropane	−1117.41	
	−1117.76	
	−1117.25	−1117.47 ± 0.30[a]
trans-1,2-diethylcyclopropane	−1116.90	
	−1116.77	
	−1116.30	−1116.66 ± 0.36
cis-bicyclo[6.1.0]nonane	−1376.30	
	−1376.04	
	−1376.43	−1376.25 ± 0.22
trans-bicyclo[6.1.0]nonane	−1376.52	
	−1376.61	
	−1376.71	
	−1377.00	−1376.71 ± 0.21 (−1376.75 ± 0.22)[b]

[a] Uncertainties are given as 2 times the standard deviation from the mean ($2\bar{s}$).[35] [b] Corrected for 8% cis.

Table II. Enthalpies of Formation of Cyclopropanes

compd	$\Delta H_f(l)$, kcal/mol	ΔH_v, kcal/mol	$\Delta H_f(g)$, kcal/mol
cis-1,2-diethylcyclopropane	−19.12 ± 0.33	8.46 ± 0.20	−10.66 ± 0.39
trans-1,2-diethylcyclopropane	−19.93 ± 0.38	8.19 ± 0.20	−11.74 ± 0.43
cis-bicyclo[6.1.0]nonane	−16.76 ± 0.25	11.80 ± 0.10	−4.96 ± 0.27
trans-bicyclo[6.1.0]nonane	−16.30 ± 0.24	11.80 ± 0.10	−4.50 ± 0.26

Chart I



One of the principal quantities of interest is the difference in enthalpy between **1** and **2**. It was found to be 1.1 kcal/mol.

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(1) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970. Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analyzed Thermochemical Data; Organic and Organometallic Compounds"; University of Sussex: 1977.

(2) Wiberg, K. B.; Wasserman, D. J. *J. Am. Chem. Soc.* **1981**, *103*, 6563.

(3) Rodewald, L. B.; DePuy, C. H. *Tetrahedron Lett.* **1964**, 2951.

(4) Flowers, M. V.; Frey, H. M. *Proc. R. Soc. London, Ser. A* **1960**, *A257*, 122.

(5) Wiberg, K. B.; Nelson, G. L. *Tetrahedron Lett.* **1969**, 4385.

(6) The ΔH_v were estimated from the boiling points of *cis*- and *trans*-diethylcyclopropane (93.5 and 89.5 °C, respectively)[8] and the Fishtine equation[9] along with the Watson correlation.[9] The enthalpy of vaporization of **3** was reported to be 11.80 ± 0.10 kcal/mol[7] and 11.90 ± 0.19 kcal/mol[10] and that of **4** was reported to be 10.21 ± 0.14 kcal/mol with no experimental data given.[10] We have found that **3** and **4** cannot readily be separated by distillation, nor are they readily separated by gas chromatography. Thus, the reported difference in ΔH_v appears much too large. On the basis of the apparently very similar boiling points, we assume that they have essentially the same ΔH_v.

(7) Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J Am. Chem. Soc.* **1970**, *92*, 3109.

(8) Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256.

(9) Reid, R. C.; Sherwood, T. K. "Properties of Gases and Liquids: Their Estimation and Correlation"; McGraw-Hill: New York, 1966; pp 151–153.

(10) Corbally, R. P.; Perkins, M. J.; Carson, A. S.; Laye, P. G.; Steele, W. V. *J. Chem. Soc., Chem. Commun.* **1978**, 778. No experimental details were given. In the case of **4** (liquid) they reported ΔH_f = −19.7 ± 0.8 kcal/mol using a micro bomb calorimeter and −21.9 ± 1.1 kcal/mol with a conventional oxygen bomb calorimeter.

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Table III. Molecular Mechanics Calculations[a]

compd	ΔH_f(calcd)	ΔH_f(obsd)[b]	strain energy[c]
cis-bicyclo[4.1.0]heptane (**5a**)	4.5		
cis-bicyclo[4.1.0]heptane (**5b**)	1.3	0.4	27.2
trans-bicyclo[4.1.0]heptane (**6**)	27.3[d]		54.1 (calcd)[d]
cis-bicyclo[5.1.0]octane (**7**)	−3.0	−4.0	27.7
trans-bicyclo[5.1.0]octane (**8**)	8.1		39.8 (calcd)
cis-bicyclo[6.1.0]nonane (**3**)	−5.8	−5.0	31.6
trans-bicyclo[6.1.0]nonane (**4a**)	−3.1	−4.5	32.1
trans-bicyclo[6.1.0]nonane (**4b**)	0.8		
cis-1,2-diethylcyclopropane (**1**)	−11.4	−10.7	26.9
trans-1,2-diethylcyclopropane (**2**)	−12.3	−11.7	25.5

[a] All values are given in kcal/mol. [b] Data were taken from ref 1. [c] Based on experimental values except when marked calcd. [d] See text for ab initio values: $\Delta H_f = 41.5$ kcal/mol, strain energy 68 kcal/mol.

Similar cis/trans energy differences have been found for other cyclopropanes. Rodewald and DePuy[3] found $\Delta G = 2.1$ kcal/mol for the equilibration of *cis*- and *trans*-1,2-diphenylcyclopropane and Flowers and Frey[4] found $\Delta G = 1.2$ kcal/mol for the 1,2-dimethylcyclopropanes. The entropy difference would be expected to be small, and so $\Delta H \sim \Delta G$. It may at first seem surprising that the difference in energy in the case of cyclopropane is the same as that for alkenes, even though the latter have a shorter C–C distance. However, the C–C–C angle is considerably smaller for the cyclopropane than for the alkene, and would place the alkyl groups at about the same distance if they could not relieve the interaction by bond angle bending.

It is known that a cyclopropane ring exhibits many of the characteristics of alkenes. We have therefore compared the changes in enthalpy of formation with alkyl substitution in the saturated, unsaturated, and cyclopropane series (Chart I). In the case of the saturated series, butane was chosen as the base so that methylene hydrogens would be replaced by ethyl groups in each case. The data are taken from reference 1, except for the *n*-hexenes which are based on enthalpies of hydration.[2] It can be seen that the changes in ΔH_f are essentially the same for the alkene and cyclopropane series but considerably larger than those of alkane series. Thus, alkyl groups stabilize cyclopropane and ethylene equally well.[11]

Our main interest has been with the bridged cyclopropanes, and therefore we also wished to determine the effects of cis vs. trans fusion in at least one case. The *cis*- and *trans*-bicyclo[6.1.0]nonanes were chosen since *trans*-cyclooctane is known to be 11.4 kcal/mol less stable than *cis*-cyclooctene,[12] and the difference in energy rises rapidly as the rings become smaller.[13] The

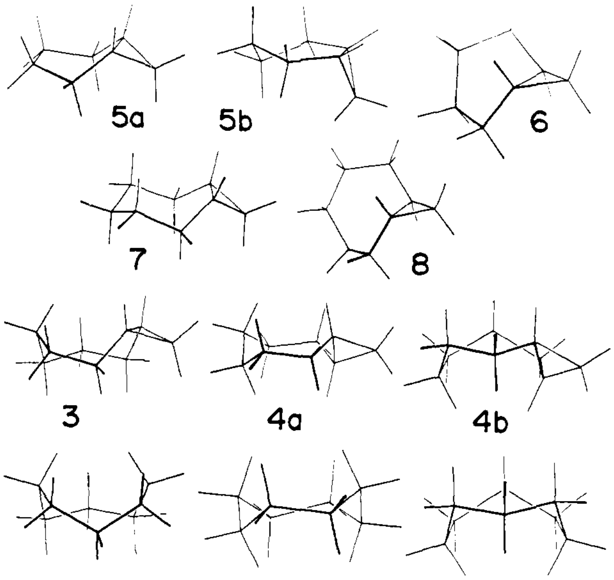

Figure 1. Conformations of bicyclo[*n*.1.0]alkanes as calculated by molecular mechanics. In the case of the bicyclo[6.1.0]nonanes (**3** and **4**), the corresponding cyclooctane conformers are drawn below each structure.

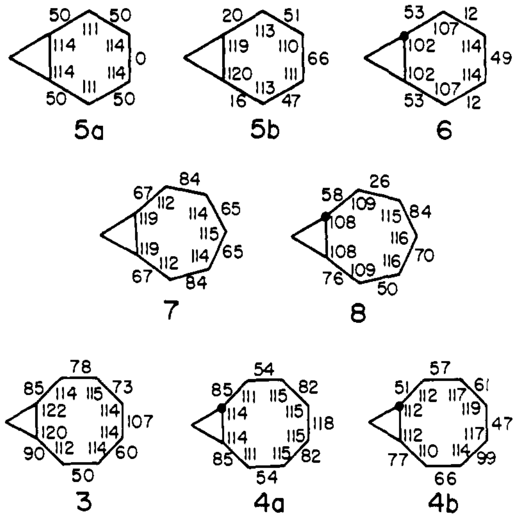

Figure 2. Geometrical parameters for the bicyclo[*n*.1.0]alkanes as calculated by molecular mechanics. The bond angles are given inside the figures, and the torsional angles are given on the outside.

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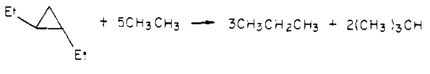
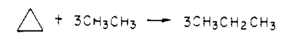
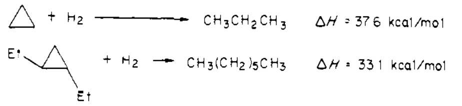
(11) A referee suggested that a better way to examine alkyl group substitution is via group separation isodesmic reactions (Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814. George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317) such as:



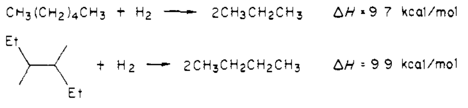
which is one definition of the strain energy. Here, $\Delta H = -26.4$ kcal/mol as compared to



for which $\Delta H = -26.5$ kcal/mol. This suggests that alkyl groups have no effect on the energy of a cyclopropane ring. A more conventional view would be to examine the hydrogenation energies:



Here, the stabilization effect is seen. This may be contrasted with the corresponding acyclic cases:



Here, there is essentially no effect of substitution. This points out the difficulty in defining some of the common concepts in organic chemistry.

(12) Rogers, D. W.; v. Voithenberg, H.; Allinger, N. L. *J. Org. Chem.* **1978**, *43*, 360.

Table IV. Enthalpy of Combustion of *cis*-Bicyclo[6.1.0]nonane

sample, g	Mylar, g	CO_2 ratio	ΔR, Ω	ΔE_s, J/Ω	$q_i + q_n$, J	q_w, J	R_{fin}, Ω	ΔH, kcal/mol
0.456939	0.053991	0.999736	0.189784	25.17	6.88	6.88	0.27101	−1376.30
0.361343	0.053001	0.99996	0.152116	22.95	6.80	5.46	0.25188	−1376.04
0.447162	0.061660	0.999682	0.187443	24.39	6.88	6.88	0.26606	−1376.42
								av = −1376.25 ± 0.22

[a] Mylar was used to contain the sample; ΔE_s is the difference from the standard system; q_i is the ignition energy; q_n is the energy of forming nitric acid; q_w is the Washburn correction; R_{fin} is the final resistance. $E_s = 117984.24 \pm 10.2$ J/Ω. ΔH_{comb} for Mylar was −22977.3 ± 10.1 J/Ω.

effect of cis vs. trans fusion on a cyclopropane ring would be expected to be somewhat smaller because the torsional angle between trans hydrogens is only 140–150° for cyclopropane whereas it is 180° for a double bond.

The enthalpies of combustion of **3** and **4** were determined, giving the data shown in Tables I and II. The enthalpy of formation of **3** also has been determined by Boyd et al.[7] and by Steele et al.,[10] who reported $\Delta H_f = -19.4 \pm 0.8$ kcal/mol and -19.2 ± 0.9 kcal/mol, respectively. The latter workers also reported $\Delta H_f = -19.7 \pm 0.8$ kcal/mol for **4**. The difference between these values and those reported herein are larger than would be expected on the basis of two uncertainty intervals. The present values have the smaller uncertainty, and the study made use of both succinic acid and *n*-nonane as secondary standards in order to ensure that there were no large systematic errors. Since both **3** and **4** were included in this study, the difference in enthalpy between them should not be subject to systematic errors. The enthalpies of formation of **3** and **4** are the same within experimental error. Using the Franklin group equivalents[14] for the estimation of the energy of the unstrained model, strain energies were found to be 31.6 kcal/mol for the cis and 32.1 kcal/mol for the trans isomer. Even correcting for the difference in energy for cis- vs. trans-fused cyclopropanes, the trans isomer has only 1 kcal/mol greater strain than the cis isomer.

The results may be accommodated when one considers the conformations of cyclooctane.[15] The relatively low-energy conformer is well suited to either cis or trans fusion of a cyclopropane ring (Figure 1). One might roughly estimate the strain as the sum of the strain energies of cyclooctane (9.2) and cyclopropane (27.5) less one torsional interaction (3.0) which is common to the two rings, or 33.7 kcal/mol. This is in reasonable agreement with the observed value.

In order to put this estimate on a more quantitative basis, a series of molecular mechanics calculations were carried out using the parameters of Boyd.[7] The results are summarized in Table III. In the cis-fused series, **3** and **7** were found to have only one low-energy conformation (Figures 1 and 2). Two conformations were found for **5**, having a boat and a twist-boat cyclohexane ring, respectively. The latter (**5b**) was found to have the lower energy. The enthalpies of formation of all three compounds are known, and the calculated enthalpies agree with the observed values to within 1 kcal/mol.

Two conformations were found for *trans*-bicyclo[6.1.0]nonane (**4a** and **4b**). The former had the lower calculated energy, and gave a value that agreed with the observed enthalpy of formation. The calculated differences in ΔH_f between **3** and **4** is somewhat larger than the observed difference. The trans isomer has external angles at the cyclopropane ring of 123° which is a major contributor to the angle strain. It is known that the strain associated with large angular deformation is overestimated by a simple harmonic bending function.[16] Thus, the larger calculated difference is expected.

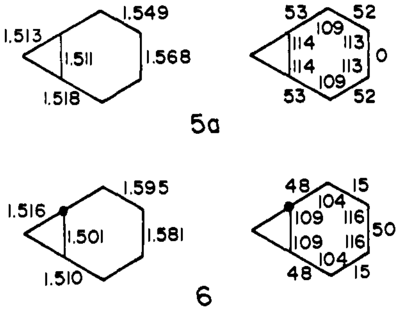


Figure 3. Geometrical parameters for the bicyclo[4.1.0]heptanes, as calculated by ab initio MO theory.

Thermochemical data for the other *trans*-bicyclo[*n*.1.0]alkanes are not as yet available. However, the calculated enthalpies appear to be quite reasonable. The strain energy increases by 8 kcal/mol on going from **4** to **8**, and there is a further increase in strain of 14 kcal/mol on going from **8** to **6**. Again, it was possible that these strain energies are somewhat overestimated because of the large external angles at the cyclopropane rings.

Allinger's MMI force field has received considerable use.[16] In order to see if these parameters would lead to different estimates, the molecular mechanics calculations were repeated by using MMI and gave essentially the same calculated heats of formation[17] as obtained with Boyd's parameters. The one exception was **6**, for which MMI gave $\Delta H_f = 14.9$ kcal/mol. This is much lower than the estimate given in Table IV, and would lead to a strain energy equal to that of **8**. Thus, the result seems unreasonable.

In order to obtain a more definitive estimate of the energy and geometry, we have carried out a geometry optimization for **5a** and **6** using the 3-21G[18] basis set. It is known that ab initio calculations using split valence basis sets lead to very good bond angles and bond lengths that are only slightly shorter than the observed lengths.[19] The symmetrical conformer, **5a**, was chosen for study rather than **5b** because with a seven-carbon system, some element of symmetry was needed in order to complete the calculation in a practical length of time. The optimized structure of **5a** (Figure 3) was quite similar to the molecular mechanics structure. However, this agreement was not found with **6**. The molecular mechanics calculation places the small six-membered-ring angle adjacent to the cyclopropane ring whereas the ab initio calculation places it one carbon removed from the cyclopropane ring. The latter method also leads to larger variations in bond lengths than the former, and this may represent rehybridization effects and C–C bond stretching anharmonicity which are not presently incorporated into molecular mechanics.

The calculated energies for **5a** and **6** were −270.51890 and −270.45849 hartrees, respectively (1 hartree = 627.5 kcal/mol), giving an energy difference of 37.9 kcal/mol for the nonvibrating molecules at 0 K. This should be a rather good estimate since

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(13) Inoue et al. found *trans*-cycloheptene to have a half-life of only 23 min at −10 °C whereas *trans*-cyclooctene is reasonably stable at room temperature (Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1635).

(14) Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.

(15) Anet, F. L. *Fortsch. Chem. Forsch.* **1974**, *45*, 169.

(16) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

(17) The ΔH_f calculated with MMI were 5.2 (**5a**), 2.0 (**5b**), 14.9 (**6**), −2.1 (**7**), 9.0 (**8**), −5.4 (**3**), −4.0 (**4a**), and −1.6 (**4b**) kcal/mol.

(18) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(19) Pople, J. A. *Mod. Theor. Chem.* **1977**, *4*, 1. DeFrees, D. J.; Raghavachari, K.; Schlegel, H. B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5576. The latter paper shows that whereas inclusion of electron correlation affects bond lengths, it has little affect on bond angles.

it is known that the correlation energy cancellation is particularly good when two structurally similar compounds are compared.[20] The molecular mechanics calculation gave estimates of the zero-point energies and $(H^\circ - H^\circ_0)/T$ that were essentially the same for the two compounds. Therefore, the difference in energy at 25 °C should also be 37.9 kcal/mol. The difference in energy between **5a** and **5b** was estimated as 3.2 kcal/mol by both molecular mechanics calculations. Combining these data with the enthalpy of formation of **5b** leads to $\Delta H_f = 41.5$ kcal/mol for **6**, considerably larger than obtained with either molecular mechanics calculation. This illustrates the limits of the latter method when applied to highly strained compounds. The strain energy of **6** is now raised to 68 kcal/mol.

Two derivatives of **6** have been reported,[21,22] and both were found to undergo a facile thermal rearrangement to the cis isomer. Cyclopropane undergoes a thermal cis–trans isomerization with $E_a = 65$ kcal/mol.[23] If **6** has 40 kcal/mol more strain than cyclopropane, then its activation energy for isomerization could be reduced to as low as 25 kcal/mol if most of the strain could be relieved in the activated complex. It is interesting to note that Gassman and Bonser[22] observed $E_a = 26$ kcal/mol for the rearrangement of *trans*-bicyclo[4.1.0]hept-3-ene.

One would expect that the introduction of a trigonal center into one of the rings would increase the difference in energy between cis- and trans-fused isomers since the latter can less well accommodate an increased bond angle. This was examined in the case of the bicyclo[6.1.0]nonanes by allowing the 2-ketones (**9** and **10**) to equilibrate in the presence of base.[24] The equilibrium was approached from both sides and gave $K = 0.007 \pm 0.003$ at 25 °C, or $\Delta G = 3.1 \pm 0.4$ kcal/mol. We would anticipate only a small entropy difference, leading to $\Delta G \sim \Delta H$. Thus, the introduction of a trigonal center destabilizes the trans-fused isomer by about 3 kcal/mol.

Experimental Section

Preparation and Purification of Compounds. *cis*-Bicyclo[6.1.0]nonane was prepared by the cuprous chloride catalyzed reaction between cyclooctane and diazomethane.[25] It was purified by preparative gas chromatography on a 20 ft × $^3/_8$ in. 20% DC 710 on Anaprep 50/60 column at 130 °C. Injections of 0.5 mL were made. The flow rate was 200–250 mL/min, and it had a retention time of about 20 min. The compound was bulb-to-bulb distilled just before the combustion runs were initiated. Analysis of the compound by GC using a 5-μL sample showed no impurities. The presence of 0.2% of an impurity could easily be detected.

trans-Bicyclo[6.1.0]nonane was prepared by treating 11 g (0.1 mol) of *trans*-cyclooctene with excess diazomethane in ether to give, after removal of solvent, 15.8 g of the pyrazoline. The latter was dissolved in 650 mL of pentane and irradiated for 20 h with a 450-W Hanovia lamp using a Corex filter. Distillation gave 10.8 g (87%) of the bicyclononane with bp 42–44 °C at 10 mm. Purification was carried out as described above. The column would not separate the cis and trans isomers. Analysis using a 40-ft 20% Carbowax 20M on Anakrom ABS 70/80 column at 150 °C and a flame ionization detector showed that the product consisted of 92% trans and 8% cis. No other compounds were found.

cis-1,2-Diethylcyclopropane was prepared via a modified Simmons–Smith reaction[8] using *cis*-3-hexene. It was purified as described above. By use of a 20-ft column, a flow rate of 30 mL/min, and a column temperature of 50 °C, *cis*-3-hexene appeared after 23 min and the product appeared after 37 min. It was necessary to cool the collector in liquid nitrogen in order to obtain efficient collection. The purity of the product was checked by GC and by the NMR spectrum (270 MHz, δ −0.33 (1 H, m), 0.6 (3 H, m), 0.99 (6 H, t), 1.2 (2 H, m), and 1.4 (2 H, m)). No impurities could be detected.

trans-1,2-Diethylcyclopropane was prepared in the same fashion by using *trans*-3-hexene and was purified as described above. Analysis by GC and NMR indicated no detectable impurities. The NMR spectrum (270 MHz, $CDCl_3$) had bands at δ 0.15 (2 H, t), 0.36 (2 H, m), 0.95 (6 H, t), 1.1 (2 H, m), and 1.3 (2 H, m).

Combustions. The enthalpies of combustion were determined by oxygen bomb calorimetry using a standard Parr bomb and calorimeter and a platinum resistance thermometer as the temperature sensor. Benzoic acid (NBS sample 39i) was used to standardize the apparatus. Standarization runs were made both before and after each set of combustion runs. Succinic acid was used as a secondary standard. We observed $\Delta H_c = -356.45 \pm 0.08$ kcal/mol whereas the more recent literature values are -356.34 ± 0.06[26] and -356.28 ± 0.10 kcal/mol.[27] Our value is in good agreement with these results. Since succinic acid is quite different than the compounds we planned to study, we also determined the enthalpy of combustion of nonane. We observed -1464.47 ± 0.23 kcal/mol whereas the literature values are -1463.89 ± 0.27[28] and -1463.67 ± 0.45[29] kcal/mol. Again, these numbers are in satisfactory agreement.

The liquid samples have a significant vapor pressure, and therefore they were contained in Mylar bags. The enthalpy of combustion of Mylar was found to be −5497 ± 2 cal/g (50% relative humidity). The literature value is −5463 cal/g.[30] Since the enthalpy of combustion is so small, the use of a Mylar bag will not significantly increase the error in the combustion experiments.

The samples were ignited with a 36-gauge platinum fuse wire. Power was supplied from a 22 000-μF capacitor initially charged to 27 V. The energy involved was calculated from the change in voltage. In all cases 1.00 g of water was added to the bomb before it was sealed.

In the analysis of the data from the combustion runs, the resistance data for the fore and after periods were separately fit to an equation of the form

$$R = b_1 + b_2 t + b_3 t^2$$

using the method of least squares. Here, t is the time. The rms error was on the order of $2\text{–}7 \times 10^{-6}$ Ω ($(2\text{–}7) \times 10^{-5}$ deg). From the equations, the resistance at the end of the fore period (20 min) and at the beginning of the after period (36 min) could be determined. The stirring and heating constants for the calorimeter were determined by analyzing the fore and after periods together via the equation

$$\mathrm{d}R/\mathrm{d}t = c_1 + c_2 t$$

Having the constants c_1 and c_2, it is then possible to determine the resistance correction due to stirring and heat transfer from the external bath for the reaction period via

$$\Delta R = \int_{t=20}^{t=36} c_1 \,\mathrm{d}t + c_2 t \,\mathrm{d}t$$

The integration was performed numerically. The Washburn corrections were made by using the method of Prosen and were calculated by a subroutine that was supplied by the Thermochemistry Section of the NBS.[31] The other corrections (such as the change in ΔH from 28 °C (the final temperature) to 25 °C were made in the standard fashion.[32] The results of typical combustion runs are summarized in Table IV.

Equilibration of Bicyclo[6.1.0]nonan-2-ones. The base-catalyzed isomerization of *trans*-bicyclo[6.1.0]nonan-2-one to the cis isomer has been observed by DePuy and Marshall.[24] The equilibration was carried out in the dry ether with sodium methoxide as the catalyst. The trans isomer gave after 7 days at 25 °C a mixture consisting of 97.7% of the cis ketone, 1.1% of the trans ketone, and 1.2% of an unidentified ketone which was not present in the starting material. When the cis ketone was treated under the same conditions for 2 days, 0.3% of the trans ketone and 0.3% of the unidentified ketone was found. In both cases, the product

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composition was determined by GC using a 12-ft, 10% Carbowax 20M column at 150 °C.

Calculations. The molecular mechanics calculations were carried out with the parameters of Boyd[7] and also with MMI.[16] The ab initio calculations were carried out by using the program GAMESS[33] which is derived from HONDO.[34] The optimization was continued until the largest gradient was less than 0.001 hartree/bohr.

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Registry No. 1, 71032-67-2; **2**, 71032-66-1; **3**, 13757-43-2; **4a**, 39124-79-3; **5a**, 286-08-8; **6**, 54376-67-9; **7**, 16526-90-2; **8**, 21370-66-1.

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π-Complexes as Intermediates in Reactions. Biomimetic Cyclization[1]

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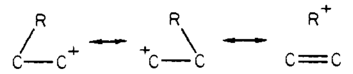
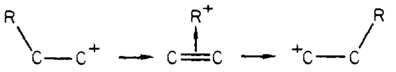
Abstract: The advantages of the π-complex representation of "nonclassical carbocations" are pointed out, with special reference to the electrophilic additions of carbocations to CC multiple bonds involved in biomimetic cyclizations. Studies of the cyclizations of *cis*- and *trans*-2-undeca-6,10-dienyl cations to decalin derivatives, using MINDO/3, indicate them to take place stepwise via intermediate olefin–carbenium ion π-complexes.

When the π-complex theory[2-9] was introduced[2] nearly forty years ago, one of the first applications[2,3] was to the intermediates in the Wagner–Meerwein rearrangement of carbenium ions. At that time there was no rational explanation of the extreme ease with which these rearrangements take place in contrast to the difficulty of analogous rearrangements of radicals or anions. The transition states for all three reactions are equivalent in terms of resonance theory, being represented as hybrids of three contributing structures:


(1)

This problem was immediately solved by the recognition that the intermediate in the rearrangement of a carbenium ion can be represented as an olefin π-complex:


(2)

The bond linking the apical and basal groups in the π-complex is effectively a two-center dative bond, differing from ordinary two-center bonds only in that one of the contributing orbitals is a π MO rather than an AO. This analogy shows that only two electrons can be accommodated in it, any additional electrons having to go into an antibonding MO. The π-complexes derived from radicals or cations as apical groups are therefore much less stable than those from cations. Rearrangements of alkyl radicals or carbanions should therefore be much less facile than those of carbenium ions, as indeed they are.

The π-complex representation also makes it immediately clear that a π-complex isomer of a classical carbenium ion may well be more stable than the latter. Since the bond energy of a C=C double bond is less than twice that of a C—C single bond by only ca. 20 kcal/mol, the π-complex should be more stable than the isomeric carbenium ion (see eq 2) if the bond energy of the bond between the basal (olefin) and apical groups is greater than this difference. Since there is no essential difference between this bond and a normal two-center bond and since even the weakest covalent two-center bond (F–F) has a bond energy >30 kcal/mol, it is very likely that this condition will usually be met. Indeed, high-level ab initio calculations[10] and calculations[11] by MINDO/3[12] suggest that carbenium ions are generally less stable, in the gas phase, than isomeric π-complexes.

These arguments were given[4] at a conference at Montpelier in 1949, together with the representation of metal–olefin complexes as π-complexes stabilized by back-coordination and a discussion of the relationship between the classical and π-complex representations of species containing three-membered rings (see ref 9).

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