Hetero-π-systems From 2 + 2 Cycloreversion, Part 2.[1] Ab Initio Thermochemical Study of Heterocyclobutanes 2 + 2 Cycloreversion to Form Heteroethenes H$_2$C=X (X=NH, O, SiH$_2$, PH, S)

Leonid E. Gusel'nikov,[1] Vitaly G. Avakyan,[1,2] and Stephan L. Guselnikov[1]

[1]Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Prospect, 117912 GSP, Moscow, Russia

[2]Photochemistry Center, Russian Academy of Sciences, 7a Novatorov St., 117421 Moscow, Russia

ABSTRACT: Ab initio and DFT thermochemical study of diradical mechanism of 2 + 2 cycloreversion of parent heterocyclobutanes and 1,3-diheterocyclobutanes, cyclo-(CH$_2$CH$_2$CH$_2$X), and cyclo-(CH$_2$XCH$_2$X), where X = NH, O, SiH$_2$, PH, S, was undertaken by calculating closed-shell singlet molecules at three levels of theory: MP4/6-311G(d)// MP2/6-31G(d)+ZPE, MP4/6-311G(d,p)//MP2/6-31G (d,p)+ZPE, and B3LYP/6-311+G(d,p)+ZPE. The enthalpies of 2 + 2 cycloreversion decrease on going from group 14 to group 16 elements, being substantially higher for the second row elements. Normally endothermic 2 + 2 cycloreversion is predicted to be exothermic for 1,3-diazetidine and 1,3-dioxtane. Strain energies of the four-membered rings were calculated via the appropriate homodesmic reactions. The enthalpies of ring opening via the every possible one-bond homolysis that results in the formation of the corresponding 1,4-diradical were found by subtracting the strain energies from the central bond dissociation energies of the heterobutanes CH$_3$CH$_2$—CH$_2$XH, CH$_3$CH$_2$—XCH$_3$, and HXCH$_2$—XCH$_3$. The latter energies were determined via the enthalpies of the appropriate dehydrocondensation reactions, using C—H and X—H bond energies in CH$_3$XH calculated at G2 level of theory. Except 1,3-disiletane, in which ring-opening enthalpy attains 69.7 kcal/mol, the enthalpies of the most economical ring openings do not exceed 60.7 kcal/mol. The 1,4-diradical decomposition enthalpies found as differences between 2 + 2 cycloreversion and ring-opening enthalpies were negative, the least exothermicity was calculated for ·CH$_2$SiH$_2$CH$_2$CH$_2$. The only exception was 1,3-disiletane, which being diradical, CH$_2$SiH$_2$CH$_2$SiH$_2$, decomposed endothermically. Since decomposition of the diradical containing two silicon atoms required extra energy, raising the enthalpy of the overall reaction to 78.9 kcal/mol, 1,3-disiletane was predicted to be highly resisting

INTRODUCTION

Recently, $2 + 2$ cycloreversion has been reviewed as a route to the doubly bonded hetero-π-systems [1]. The direction and even possibility of the four-membered rings to cyclorevert is strongly affected by the nature, number, and position of heteroatoms; in some cases making the mechanism of the process rather tentative. This prompted us to undertake an ab initio thermochemical study of the diradical mechanism of $2 + 2$ cycloreversion of parent 1-heterocyclobutanes (**1**) and 1,3-diheterocyclobutanes (**2**) on the basis of the calculations of the closed-shell singlet molecules at three levels of theory: MP4/6-311G(d)//MP2/6-31G(d)+ ZPE, MP4/6-311G(d,p)//MP2/6-31G(d,p)+ZPE, and B3LYP/6-311+G(d,p)+ZPE. To predict the enthalpies of heterocyclobutanes ring opening via a one-bond homolysis resulting in the formation of the corresponding 1,4-diradical, $\Delta H_{\text{r.o.}}$ (A—B), we used an approach (Fig. 1) formulated by Conlin et al. [2] (CNCW) consisting in subtraction of the strain energy of the four-membered ring, E_s, from the central bond dissociation energy (CBDE) of the corresponding unstrained structures, D(A—B). In fact,

CNCW approach for dimethylsiletane [2] resulted in quite convincing value of the ring-opening enthalpy that closely parallels the experimental activation energy. The values obtained by CNCW approach even better matched the experimental ring-opening enthalpies than those derived from the energies of the four-membered cycles and diradicals calculated, using the second-order multireference perturbation theory for multiconfigurational self-consistent-field (8,8)/6-31G(d) geometries [3]. For example, the ring-opening activation energy of siletane via a C—C bond cleavage was predicted to be 51.5 kcal/mol [3], being by ~11 kcal/mol lower than that obtained from the kinetics [4]. The 1,4-diradical decomposition enthalpies, $\Delta H_{\text{r.d.}}$ (D—C), were found as a gap between $2 + 2$ cycloreversion and ring-opening enthalpies, $\Delta H_{\text{cyclorev.}}$ and $\Delta H_{\text{r.o.}}$ (A—B), respectively (see Fig. 1). Their negative or positive values indicated, correspondingly, the exothermicity or endothermicity of the diradical decomposition. Of course, in the latter case, the ring opening may lose its prerogative of being a limiting step of $2 + 2$ cycloreversion.

There are two apparent diradical routes that may lead 1-heterocyclobutanes to $2 + 2$ cycloreversion products, that is, ethene and/or heteroethene(s), CH_2=X: (i) a two-step process via a consecutive C—X and C—C bonds cleavage, and (ii) a two-step process via a consecutive C—C and C—X bonds cleavage (Scheme 1). The enthalpies of the ring opening, 1,4-diradicals decomposition, and the overall reaction of $2 + 2$ cycloreversion are correspondingly denoted by $\Delta H_{\text{r.o.}}$ (**1**, C—X) and $\Delta H_{\text{r.o.}}$ (**1**, C—C), $\Delta H_{\text{r.d.}}$ (**1**, C—C) and $\Delta H_{\text{r.d.}}$ (**1**, C—X), and ΔH_1.
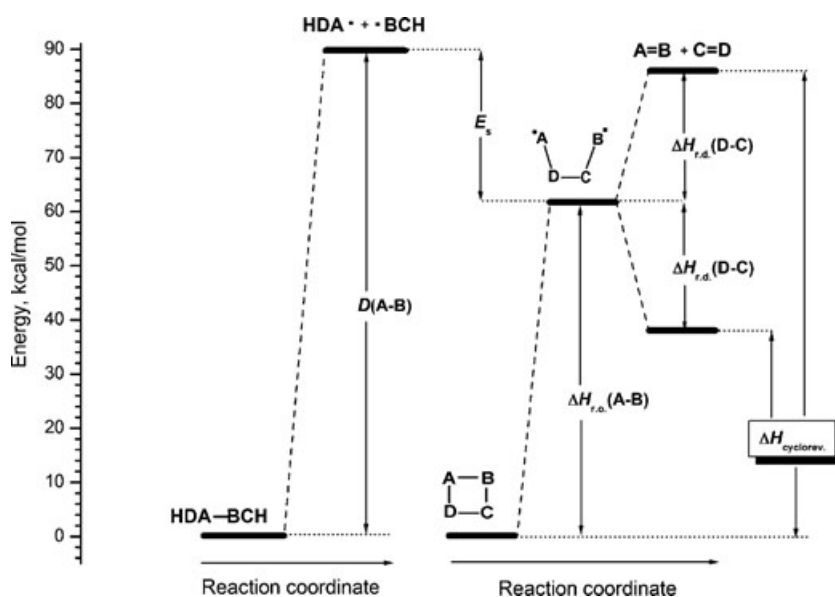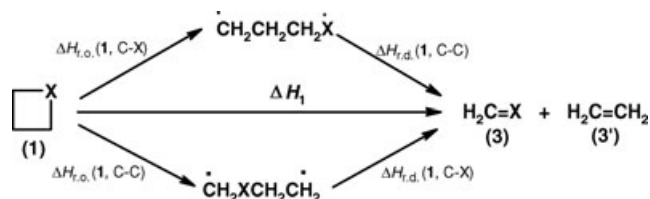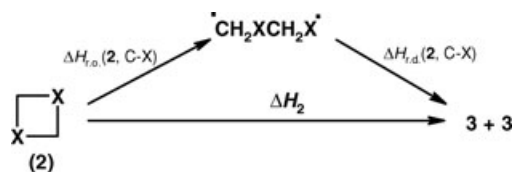

FIGURE 1 A schematic energy level diagram for $2 + 2$ cycloreversion.

SCHEME 1 Two routes of ring-opening and 1,4-diradical decompositions in the course of 2 + 2 cycloreversion of heterocyclobutanes **1**.

SCHEME 2 Ring-opening and 1,4-diradical decompositions in the course of 2 + 2 cycloreversion of heterocyclobutanes **2**.

There is the only diradical route leading 1,3-diheterocyclobutanes to 2 + 2 cycloreversion products, that is, heteroethene(s) $CH_2=X$. It involves the ring opening and decomposition of the resulting 1,4-diradical via a consecutive cleavage of two C—X bonds. Their enthalpies are referred to as $\Delta H_{r.o.}$ (**2**, C—X) and $\Delta H_{r.d.}$ (**2**, C—X), whereas the enthalpy of 2 + 2 cycloreversion is denoted by ΔH_2 (Scheme 2).

In particular, we were interested in (i) predicting the enthalpies of ring opening via an every possible one-bond homolysis route that results in the formation of the corresponding 1,4-diradical and verifying whether the most economical of them parallel the available experimental activation energy, and (ii) estimating both the 1,4-diradical decomposition and 2 + 2 cycloreversion enthalpies. To determine the enthalpies of various ring openings of **1** and **2** via the differences between the CBDE of heterobutanes, $CH_3CH_2—CH_2XH$, $CH_3CH_2—XCH_3$, and $HXCH_2—XCH_3$, and heterocyclobutane strain energies (Eqs. (1)–(3)), it was vital to find their values that had been mostly unknown.

$$\Delta H_{r.o.}(\mathbf{1}, C—X) = D(CH_3CH_2—XCH_3) - E_s(\mathbf{1}) \quad (1)$$

$$\Delta H_{r.o.}(\mathbf{1}, C—C) = D(CH_3CH_2—CH_2XH) - E_s(\mathbf{1}) \quad (2)$$

$$\Delta H_{r.o.}(\mathbf{2}, C—X) = D(CH_3X—CH_2XH) - E_s(\mathbf{2}) \quad (3)$$

The central bond energies in heterobutanes were evaluated from the enthalpies of the following dehydrogenation reactions:
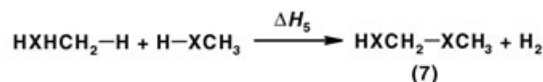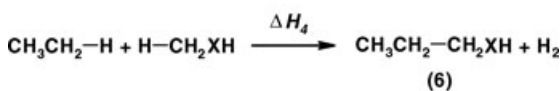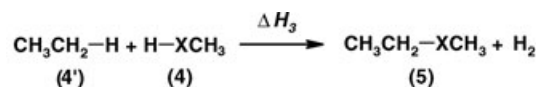
Their enthalpies in terms of the breaking and forming bond energies could be expressed by Eqs. (4)–(6).

$$\Delta H_3 = D(CH_3CH_2—H) + D(H—XCH_3)$$
$$- D(CH_3CH_2—XCH_3) - D(H—H) \quad (4)$$

$$\Delta H_4 = D(CH_3CH_2—H) + D(H—CH_2XH)$$
$$- D(CH_3CH_2—CH_2XH) - D(H—H) \quad (5)$$

$$\Delta H_5 = D(CH_3X—H) + D(H—CH_2XH)$$
$$- D(CH_3X—CH_2XH) - D(H—H) \quad (6)$$

Notice, the dissociation energies of C—H bond in ethane and H—H in hydrogen were the accurate reference data, whereas $D(C—H)$ and $D(X—H)$ in heteroethanes CH_3XH were subjected to calculation at G2 level of theory. As expected, the CBDE values obtained from Eqs. (4)–(5) appeared to be quite reliable, as they matched the literature data available to us. The strain energies, $E_s(\mathbf{1})$ and $E_s(\mathbf{2})$, were determined as the reversed sign enthalpies, ΔH_6 and ΔH_7, of the homodesmic reactions:
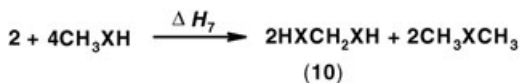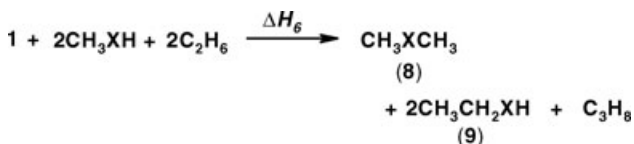
Therefore, to obtain the cycloreversion enthalpies, ΔH_1 and ΔH_2, the optimization of geometries and calculations of the total energies of **1–3** were required. The same procedure for **4–7** made it possible to evaluate $\Delta H_{r.o.}$ (**1**, C—X), $\Delta H_{r.o.}$ (**1**, C—C), and $\Delta H_{r.o.}$ (**2**, C—X), and for **8–10,** it enabled us to estimate the strain energies of heterocyclobutanes **1** and **2**.

COMPUTATIONAL METHODS

Full geometry optimization of the above series of molecules was performed by an ab initio method using two standard basis sets 6-31G(d) and 6-31G(d,p)

with the account of electron correlation at the second order of Möller-Plesset perturbation theory MP2 [5,6]. Zero-point vibrational energies (ZPEs) were also determined at the both MP2/6-31G(d) and MP2/6-31G(d,p) levels of theory. The hydrogen atomic mass of 1.088 [7] linearizing $\Delta v = v_{\text{theor}} - v_{\text{exp}}$ and the scale factor 0.96 were used for ZPE calculations. Final energies of all molecules were computed using the fourth-order perturbation theory MP4 in 6-311G(d) basis set for the both MP2/6-31G(d) and MP2/6-31G(d,p) geometries. All of the MP2 and MP4 calculations were executed in the GAMESS suite of program [8] (PC GAMESS, version adapted by A. A. Granovsky, Moscow State University). We also checked whether a lower theoretical level, that is, B3LYP/6-311+G(d,p) would reproduce the data of ab initio calculations (GAUSSIAN 98 suite of program) [9].

Total energies of **1** to **10** along with the available data on heats of formation picked up mainly from NIST Web server as well as from Stewart's article [10] are given in Table 1.

Total energies of the molecules and related radicals calculated using Gaussian-2 (G2) method (Gaussian 98 suite of programs [9]) are given in Table 2.

RESULTS

Structures of Heterocyclobutanes

The structural parameters for the completely optimized four-membered cycles are listed in Tables 3 and 4, in which the numerals before and after the slash are referred to as the parameters calculated at the MP2/6-31G(d) and MP2/6-31G(d,p) levels of theory, respectively. To our knowledge, an account of electron correlation in terms of the second order of Möller-Plesset perturbation theory for the calculation of heterocyclobutane structures was applied in this article for the first time. When available, the experimental data are listed in parenthesis. It is noteworthy that all the four-membered cycles studied have a bent skeleton. Herein, we do not discuss the effect of number and position of heteroatoms X on the geometries of hetrocyclobutanes. The geometric parameters (Tables 3 and 4) are given as the reference data to convince the reader in the reliability of structural data for which the thermochemical calculations have been performed.

Structure of Heteroethenes

Schematics of heteroethenes are shown in Fig. 2, the structural parameters for the completely op-

timized structures are listed in Table 5. Like in Tables 3 and 4, the numerals before and after the slash are referred to as the parameters calculated at the MP2/6-31G(d) and MP2/6-31G(d,p) levels of theory, respectively.

It is worthy noticing that both theoretical levels somewhat overestimate the experimental C=X bond lengths, particularly for X = NH, O, SiH$_2$.

Reaction Enthalpies, C—C and C—X Bond Dissociation Energies

The reaction enthalpies calculated at MP4/6-311G(d)//MP2/6-31G(d), MP4/6-311G(d,p)//MP2/6-31G(d,p), and B3LYP/6-31+G(d,p) levels of theory are given in Tables 6–10.

The derived central C—C and C—X bond energies in heterobutanes are given in Tables 7–9. The latter were obtained from Eqs. (4)–(6) using C—H and X—H bond dissociation energies in CH$_3$XH (Table 11) calculated at G2 level of theory and appeared to be in a good agreement with the reference data [70a] and Wiberg's calculations [11].

To estimate the accuracy of the enthalpies obtained via the MP4/6-311G(d)//MP2/6-31G(d), MP4/6-311G(d,p)//MP2/6-31G(d,p), and B3LYP/6-31+G(d,p) calculations, they were compared with those obtained via the reference data on the standard heats of formation, when available. The smallest difference between the values compared, $|\Delta H(\Delta_f H) - \Delta H|$, served as a criterion for choosing the most appropriate level of theory [here $\Delta H(\Delta_f H)$ is the reaction enthalpy calculated from the standard heats of formation and ΔH is the one obtained by our theoretical calculations]. Obviously, the reaction enthalpies derived from the standard heats of formation are better matched by those obtained by ab initio, rather than by B3LYP/6-311+G(d,p) calculations (see Tables 7, 8, and 10). Therefore, in further discussion, only ab initio data are taken into account.

DISCUSSION

Central Bond Energies in CH$_3$CH$_2$—CH$_2$XH, CH$_3$CH$_2$—XCH$_3$, and CH$_3$X—CH$_2$XH

Calculations by both theoretical levels give close values of the most central C—C bonds energies in CH$_3$CH$_2$-CH$_2$XH (Table 8). Except for one point, the values calculated at the level 2 are lower than those obtained at the level 1 by 0.3–0.9 kcal/mol only, depending on X. The largest deviation, 1.6 kcal/mol, was noticed for propanethiol. In general, the values obtained at the levels 1 and 2 are in a reasonable agreement with the available reference data

TABLE 1 Total Energies and Zero-point Energies, ZPE (in hartree) and Standard Heats of Formation, $\Delta_f H$ (in kcal/mol)

Molecule	X	MP2/6-31G(d) MP2/6-31G(d,p)	ZPE	MP4/6-311G(d)//MP2/6-31G(d)[a] MP4/6-311G(d,p)//MP2/6-31G(d,p)[b] B3LYP/6-311+G(d,p)[c]	$\Delta_f H^d$
1	CH$_2$	−156.67582	0.106167	−156.7281032	**6.8** [12]
		−156.682786	0.106579	−156.788236	
		−	0.110357	−157.256582	
	NH	−172.6294746	0.095419	−172.742276	−
		−172.687595	0.09583	−172.796459	
		−	0.099339	−173.287426	
	O	−192.4715527	0.083183	−192.595165	**−19.25**[13]
		−192.519496	0.083461	−192.640955	
		−	0.086803	−193.159220	
	SiH$_2$	−407.62055	0.094789	−407.7446855	**9.3** [14]
		−407.685379	0.095196	−407.812547	
		−	0.098711	−408.665450	
	PH	−458.859886	0.088773	−458.986531	−
		−458.917881	0.089094	−459.044761	
		−	0.092215	−459.916204	
	S	−515.0928284	0.081004	−515.219369	**14.6** [12],**14.60** $\pm$ 0.30 [15]
		−515.141072	0.081245	−515.26469	
		−	0.084158	−516.154927	
2	NH (*cis*)	−188.6398268	0.08439	−188.7554037	−
		−188.691513	0.084785	−188.804382	
		−	0.088052	−189.3173229	
	NH (*trans*)	−188.6411717	0.084649	−188.7565595	−
		−188.69261	0.08502	−188.805358	
		−	0.088198	−189.319170	
	O	−228.333871	0.060427	−228.471211	−
		−228.365454	0.06061	−228.50231	
		−	0.062786	−229.066206	
	SiH$_2$	−658.64031	0.083367	−658.7769337	−
		−658.705104	0.083757	−658.852348	
		−	0.086864	−660.089815	
	PH (*cis*)	−761.100949	0.071056	−761.243653	−
		−761.151981	0.071291	−761.299579	
		−	0.073906	−762.5742064	
	PH (*trans*)	−761.104155	0.071078	−761.247035	−
		−761.15535	0.071311	−761.303015	
		−	0.073818	−762.574268	
	S	−873.556558	0.055419	−873.699366	−
		−873.588584	0.055534	−873.729817	
		−	0.057253	−875.041886	
3	CH$_2$	−78.28503	0.04839	−78.3440051	12.4 [12], **12.54** [16]
		−78.317282	0.048672	−78.374125	
		−	0.050807	−78.6139783	
	NH	−94.3152071	0.037881	−94.374883	**16** $\pm$ 2 [17], 26 $\pm$ 2 [18], 26.4 $\pm$ 3.2 [20]
		−94.340912	0.038038	−94.399482	
		−	0.039794	−94.65818694	
	O	−114.1677476	0.02546	−114.238144	**−26.0**[12]
		−114.183498	0.025556	−114.253644	
		−	0.026485	−114.5363414	
	SiH$_2$	−329.25119	0.037977	−329.3223969	44.7 $\pm$ 1.4 [14], 37 $\pm$ 4.8 [20], 43 $\pm$ 4.8 [21], 40.6 $\pm$ 2.4 [22], **46.4** [23], 45.4 [24a]
		−329.2831803	0.038241	−329.359678	
		−	0.040007	−329.983196	
	PH	−380.5208959	0.032167	−380.593987	26.47 [24b]
		−380.5463701	0.032363	−380.621719	
		−	0.03354	−381.2610309	

(*Continued*)

TABLE 1 Continued

Molecule	X	MP2/6-31G(d) MP2/6-31G(d,p)	ZPE	MP4/6-311G(d)//MP2/6-31G(d)[a] MP4/6-311G(d,p)//MP2/6-31G(d,p)[b] B3LYP/6-311+G(d,p)[c]	$\Delta_f H^d$
	S	−436.7551131	0.02372	−436.827512	**28.3** ± 2.0 [25], 22 ± 2 [26]
		−436.770963	0.023832	−436.842462	
		–	0.024697	−437.5019815	
4	CH₂	−79.49474	0.07163	−79.56184	−20.2 [12], **−20.04** ± 0.07
		−79.5434	0.071898	−79.60743	[27], −20.24 ± 0.12 [28]
		–	0.074377	−79.856260	
	NH	−95.5065309	0.0612530	−95.5767087	**−5.5** [12]
		−95.550275	0.061468	−95.618173	
		–	0.063808	−95.888439	
	O	−115.3461356	0.0488520	−115.4252532	**−48.0** [29],
					−48.07 ± 0.05 [30]
		−115.382009	0.04917	−115.462861	
		–	0.051111	−115.757393	
	SiH₂	−329.25119	0.058276	−330.5641261	**−6.96** [14], −7.3 [22], −7.8
					[31], −6.96 ± 0.96 [32],
					−6.8 [33], −6.4 [34]
		−330.533632	0.058706	−330.621049	
		–	0.060940	−331.253258	
	PH	−381.7211972	0.0523530	−381.8026155	–
		−381.763796	0.052654	−381.850842	
		–	0.054304	−382.501220	
	S	−437.9526684	0.0443250	−438.0348085	**−5.46** ± 0.14 [35]
		−437.987785	0.044588	−438.072176	
		–	0.045931	−438.742623	
5	CH₂	−157.82604	0.126466	−157.948371	**−30.03** ± 0.16 [36],
					−30.37 ± 0.16 [36]
		−157.907453	0.126849	−158.023774	
		–	0.131415	−158.504978	
	NH	−173.8340226	0.115748	−173.958082	–
		−173.908696	0.116139	−174.028316	
		–	0.120430	−174.532999	
	O	−193.674539	0.103656	−193.809504	**−51.73** ± 0.16 [37]
		−193.739155	0.103988	−193.870667	
		–	0.107700	−194.402141	
	SiH₂	−408.8253158	0.114001	−408.962534	**−26.7** [38] (additivity),
					−25.4 [38] (ab initio)
		−408.906836	0.114411	−409.046114	
		–	0.118692	−409.912635	
	PH	−460.0581451	0.10812	−460.1971864	–
		−460.132652	0.108438	−460.270705	
		–	0.112276	−461.154318	
	S	−516.2879424	0.10036	−516.426084	**−14.42** ± 0.27 [39]
		−516.3526007	0.100642	−516.486526	
		–	0.104077	−517.390989	
6	NH	−173.8406715	0.116047	−173.966244	**−16.8**[b] [12], −16.7 ± 0.2
					[40], −16.77 ± 0.13 [41]
		−173.917102	0.117248	−174.037552	
		–	0.120906	−174.540626	
	O	−193.6822944	0.103624	−193.817109	**−61.2** [12], −61.09 ± 0.31
					[41], −60.9 ± 1.1 [42],
					−61.85 ± 0.26 [44]
		−193.751143	0.104234	−193.884937	
		–	0.108260	−194.412433	
	SiH₂	−408.8135024	0.113358	−408.947092	**−15.97** [38] (additivity),
					−14.7 [38] (ab initio)
		−408.89453	0.113848	−409.033894	
		–	0.118086	−409.898174	

(*Continued*)

TABLE 1 Continued

Molecule	X	MP2/6-31G(d) MP2/6-31G(d,p)	ZPE	MP4/6-311G(d)//MP2/6-31G(d)[a] MP4/6-311G(d,p)//MP2/6-31G(d,p)[b] B3LYP/6-311+G(d,p)[c]	$\Delta_f H^d$
	PH	−460.0520358	0.107337	−460.188623	−
		−460.12752	0.107702	−460.266893	
		−	0.111447	−461.148640	
	S	−516.2856241	0.099267	−516.422978	−**16.2** [12], −16.39 ± 0.15 [38]
		−516.354733	0.099652	−516.491614	
		−	0.102988	−517.392338	
7	NH	−189.852192	0.105469	−189.979572	−
		−189.921937	0.105903	−190.045458	
		−	0.109866	−190.5722179	
	O	−229.5373804	0.081171	−229.684361	−
		−229.589202	0.081489	−229.737413	
		−	0.084649	−230.3148518	
	SiH$_2$	−659.8218306	0.100977	−659.969722	−
		−659.902929	0.101468	−660.064654	
		−	0.105722	−661.3137006	
	PH	−762.2844592	0.088817	−762.437479	−
		−762.353017	0.089082	−762.513787	
		−	0.092186	−763.7983607	
	S	−874.7440578	0.073065	−874.897368	−
		−874.795404	0.073281	−874.949728	
		−	0.075324	−876.27521	
8	CH$_2$	−118.660343	0.09901	−118.75516	−**25.02** ± 0.12 [35], −24.82 ± 0.14 [45]
		−118.725384	0.09933	−118.815661	
		−	0.102985	−119.180686	
	NH	−134.6652983	0.08856	−134.7618042	−6.6 [12], −**4.7** ± 0.5 [43]
		−134.723623	0.088685	−134.817011	
		−	0.091976	−135.205417	
	O	−154.5034553	0.076346	−154.6109034	−**43.99** ± 0.12 [37]
		−154.5518258	0.076762	−154.657249	
		−	0.079285	−155.071921	
	SiH$_2$	−369.66357	0.086345	−369.773493	−**22.6** [14], −23.2 [22], −20.0 [31], −**22.6** ± 0.96 **[32]**−**22.6** [33], −23.0 [34]
		−369.728688	0.086729	−369.842097	
		−	0.089976	−370.592523	
	PH	−420.8936099	0.080369	−421.0052946	−**15.0** [44]
		−420.951644	0.080575	−421.063703	
		−	0.083632	−421.831593	
	S	−477.1211081	0.072679	−477.2318782	− **8.9** [12], −**8.96** ± 0.48 [45], −8.98 ± 0.14 [46]
		−477.16935	0.07281	−477.277236	
		−	0.075429	−478.065845	
9	NH	−134.6751781	0.088601	−134.773122	−**11.4** [12]
		−134.73525	0.0889	−134.829514	
		−	0.092404	−135.216340	
	O	−154.5169699	0.076429	−154.624060	−**56.23** ± 0.12 [44]
		−154.569211	0.076663	−154.676782	
		−	0.079732	−155.088116	
	SiH$_2$	−369.64707	0.086071	−369.753226	−8.2 [34], −**11.0** [38] (additivity), −9.0 [38] (ab initio), −15.0 [47], −34.18 [48]
		−369.711684	0.08637	−369.825126	
		−	0.089770	−370.573539	
	PH	−420.8857466	0.079995	−420.994797	−**12.0** [12]
		−420.944804	0.080252	−421.058103	
		−	0.083054	−421.824158	

(*Continued*)

TABLE 1 Continued

Molecule	X	MP2/6-31G(d)
		MP2/6-31G(d,p)
			ZPE	MP4/6-311G(d)//MP2/6-31G(d)[a]
				MP4/6-311G(d,p)//MP2/6-31G(d,p)[b]
				B3LYP/6-311+G(d,p)[c]
					$\Delta_f H^d$

	S	−477.17104	0.071959	−477.229330	−**11.03** [46]
		−477.171974	0.072171	−477.282793	
		−	0.074581	−478.068030	
10	NH	−150.6954286	0.078430	−150.796535	−
		−150.750416	0.078852	−150.848466	
		−	0.08195	−151.2574153	
	O	−190.3876961	0.054328	−190.506614	−
		−190.426628	0.054807	−190.550077	
		−	0.057352	−191.0077838	
	SiH$_2$	−620.64305	0.073143	−620.759865	−
		−620.707276	0.073767	−620.843139	
		−	0.076573	−621.9741067	
	PH	−723.1113644	0.060872	−723.234404	−
		−723.164471	0.061157	−723.300492	
		−	0.06289	−724.4690882	
	S	−835.5770046	0.044829	−835.701794	−
		−835.612846	0.04476	−835.744057	
		−	0.046172	−836.9540298	

[a]Level of theory 1 ("level 1").
[b]Level of theory 2 ("level 2").
[c]Level of theory 3 ("level 3").
[d]Values used in thermochemical calculations are given in boldface.

(see Table 8). It inspires hope that the central C—C bond energies first reported here for propylsilane and propylphosphine are fairly accurate. The values of the central C—X bond energies in CH_3CH_2—XCH_3 (Table 7) and $HXCH_2$—XCH_3 (Table 9) calculated at the level 2 are substantially lower (by 1.1–4.7 kcal/mol depending on X) than those obtained at the level 1 and the former better fits the available reference data. Plots of the central bond energies in CH_3CH_2—CH_2XH, CH_3CH_2—XCH_3, and CH_3X—CH_2XH versus X calculated by the more sophisticated theoretical level are shown in Fig. 3.

It is seen that the replacement of one methyl group in butane by hydroxyl, silyl, phosphine, or mercapto group gradually decreases the central C—C bond energy in CH_3CH_2—CH_2XH from 87.7/87.3 to 81.8/80.2 kcal/mol. Exception is propylamine whose C—C CBDE is practically as low as for propanethiol. C—X bond energy in CH_3CH_2—XCH_3 series is naturally dependent on the nature of X. The dependence is quite pronounced for C—N CBDE that is substantially (by 5.1 kcal/mol) lower than C—C CBDE, and especially manifests itself for C—P and C—S CBDEs whose values are as low as 68.7 and 70.6 kcal/mol, respectively. An appearance of the second heteroatom in CH_3X—CH_2XH series weakens C—N, C—P, and C—S as well as strengthens C—O and C—Si central C—X bonds.

Strain Energies

Plots of the strain energies of **1** and **2** versus X calculated at the theoretical levels 1 and 2 are shown in Fig. 4.

The calculated values of strain energies are mostly independent from the level of theory. The exceptions are thietane, 1,3-dioxetane, and 1,3-dithietane. For thietane, higher strain energy, 19.0/20.3 kcal/mol, was obtained at the level 2, whereas for 1,3-dioxetane and 1,3-dithietane calculations at the level 1 gave higher values, 36.0/34.5 and 16.6/14.3 kcal/mol, respectively. Depending on X, the strain energies of heterocyclobutanes vary between 14.3 and 34.5 kcal/mol. The highest strain energy is

TABLE 2 G2 Total Energies of Molecules and Related Radicals (in hartree)

Molecule	G2 (0 K) Energy	Radicals	G2 (0 K) Energy
CH_3CH_3	−79.63088	•CH_2CH_3	−78.97016
CH_3NH_2	−95.66691	•CH_2NH_2	−95.01857
		CH_3N•H	−95.00887
CH_3OH	−115.53460	•CH_2OH	−114.88157
		CH_3O•	−114.86756
SiH_3CH_3	−330.65783	$CH_3SiH_2^•$	−330.01063
		•CH_2SiH_3	−329.99662
CH_3PH_2	−381.90604	•CH_2PH_2	−381.24977
		CH_3PH•	−381.27773
CH_3SH	−438.14847	•CH_2SH	−437.49692
		CH_3S•	−437.51126
H_2	−1.16635	H•	−0.5

TABLE 3 Optimized Structural Parameters for Heterocyclobutanes **1** (in angstroms and degrees)[a]

| X	Dihedral angle, γ	r XC	r CC	∠CXC	∠CCX	∠CCC
CH$_2$	30.8 (27.5 [49], 33 [50], 29.6 [51])	–	1.545/1.544 (1.552 [49])	–	–	87.9/87.8 (88.5 [49], 88.7 [54])
NH[b]	31.7 (33.1 [53], 35.1 [54], 29.7 [55])	1.484/1.482 (1.482 [53])	1.540/1.538 (1.553 [53])	89.3/89.3 (92.2 [53], 92.3 [54], 91.2 [55])	88.2/88.1	85.3/85.2 (84.6 [55])
O	17.4 (0 [56])	1.452/1.451 (1.483 [56])	1.534/1.533 (1.546 [56])	90.1/90.1 (91.9 [56])	91.5/91.4	84.2/84.1 (84.6 [56])
SiH$_2$	32.4 (37 [57])	1.901/1.900	1.557/1.556	78.0/77.9	86.4/86.4	100.3/100.2
PH	36.3	1.884/1.884	1.544/1.544	75.1/75.1	88.5/88.5	96.1/96.1
S	27.8 (26 [58])	1.840/1.839 (1.847 [58])	1.537/1.535 (1.549 [58])	76.1/76.0 (76.8 [58])	90.9/90.9	95.1/95.0 (95.3 [58])

[a]Values given in parenthesis refer to literature data.
[b]For structure of azetidine, also see reference [49].

TABLE 4 Optimized Structural Parameters for Heterocyclobutanes **2** (in angstroms and degrees)[a]

X	Dihedral angle, γ	r XC	∠CXC	∠XCX
NH (cis)	29.8 (21.0 [59][b])	1.479/1.478 (1.501 [59],[b] 1.478 [60][c])	87.0/87.0 (90.3 [59],[b] 87.0 [60][c])	89.0/89.0 (89.0 [60][c])
NH (trans)	23.2 (16.0 [60][c])	1.482/1.480 (1.484 [60][c])	86.3/86.5 (86.3 [60][c])	91.4/91.4 (91.4 [60][c])
O	0 (0 [59][b])	1.433/1.432 (1.470 [59],[b] 1.404 [61][c])	86.5/86.5 (88.8 [59],[b] 87.5 [61][c])	93/93.5 (92.5 [61][d])
SiH$_2$	22.1 (25.2 [62], 24 [63], 23 [64])	1.907/1.906 (1.888 [62])	90.7/90.6 (90.6 [62])	87.3/87.3 (86.8 [62])
PH (cis)	35.5	1.880/1.879	83.5/83.4	90.5/90.7
PH (trans)	33.2	1.869/1.868	83.1/83.0	91.9/92.0
S	0 (0 [59][b])	1.829/1.828 (1.845 [59],[b] 1.813 [65][e])	84.3/84.2 (84.7 [59],[b] 83.9 [65][e])	95.7/95.8

[a]Values given in parenthesis refer to literature data.
[b]4-21 level of theory.
[c]G2 level of theory.
[d]HF/6-31G* level of theory.
[e]STO-3G level of theory.

characteristic of 1,3-dioxetane (X = O). Noteworthy, E_s of **1** with X being the first row elements does not practically depend on X, whereas for **2** it grows when X is altered from group 14 to group 16 elements. The second row elements release the strain, which generically lowers for X in going from elements of group 14 to group 16. The effect is more pronounced for **2** (X = PH). The great value of E_s in dioxetane may be due to the structure of HOMO shown in Fig. 5.

Two oxygen lone pair orbitals having the same phases mainly contribute to HOMO. Their strong exchange repulsion should result in the highest strain energy of 1,3-dioxetane.
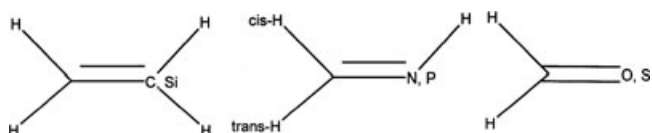
FIGURE 2 Schematic of heteroethenes.

Ring-Opening Enthalpies

Ring-opening enthalpies of heterocyclobutanes **1** and **2** (Table 12) were found by Eqs. (1)–(3) using the calculated C—C and C—X CBDEs in heterobutanes (Tables 7–9) and strain energies (Table 10). They vary between 48.0 and 69.7 kcal/mol, being lower by 0.3–5.9 kcal/mol at the level 2.

The dependence of the enthalpies of heterocyclobutanes **1** ring opening via C—C and C—X bonds homolysis on X calculated at the theoretical level 1 is shown in Fig. 6.

It is seen that for X being the first row element and for silicon the ring opening via C—C rather than C—X bond homolysis is predicted with the energy gap for azetidine, oxetane, and siletane being 1.6, 4.0, and 4.0 kcal/mol, respectively. On the contrary, for X being the second row element (excluding silicon), the ring opening via C—X rather than C—C bond homolysis is predicted. The energy gaps for phosphetane and thietane are 12.7 and 6.6 kcal/mol, respectively.

TABLE 5   Optimized Structural Parameters for Heteroethenes, $H_2C=X$ (in angstroms and degrees)[a]

X	$rC=X$	$rC-H$	$rX-H$	$\angle HCH$	$\angle HCX$	$\angle HXH$	$\angle HXC$
CH_2	1.336/1.335 (1.337 [66])	1.085/1.081 (1.086 [66])	1.085/1.081	116.6/116.9 (117.37 [66])	121.7/121.6	116.6/116.9	121.7/121.6
NH	1.282/1.281 (1.273 [66])	1.089/1.085[b] 1.095/1.090[c]	1.027/1.022	116.1/116.1	118.4/118.4[d] 125.5/125.4[e]	–	109.7/109.3
O	1.221/1.220 (1.206 [66])	1.104/1.100 (1.108 [66])	–	115.6/115.5 (116.8 [66])	122.2/122.2	–	–
SiH_2	1.718/1.716 (1.7039 [67])	1.085/1.081	1.482/1.470 (1.4671 [67])	116.1/116.2	121.9/121.9	115.1/114.9	122.5/122.5
PH	1.677/1.676 (1.673 [68])	1.087/1.082[b] (1.090 [68]) 1.086/1.081[c] (1.090 [68])	1.421/1.421 (1.420 [68])	115.9/116.0	119.2/119.2[d] (118.4 [68]) 124.8/124.7[e] (124.4 [68])	–	97.2/96.9 (97.4 [68])
S	1.617/1.616 (1.6138 [69])	1.090/1.086 (1.0962 [69])	–	116.0/115.9 (116.16 [69])	122.0/122.1	–	–

[a]Values given in parenthesis refer to literature data.
[b]trans-C—H bond to X—H bond.
[c]cis-C—H bond to X—H bond.
[d]trans-$\angle HXC$ to $\angle HCX$.
[e]cis-$\angle HXC$ to $\angle HCX$.

TABLE 6   2 + 2 Cycloreversion Enthalpies, ΔH_1 and ΔH_2 (in kcal/mol) (see Schemes 1 and 2)[a]

X	ΔH_1			ΔH_2		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
CH_2	19.3	19.3	12.5	19.3	19.3	12.5
NH	8.9	8.6	4.1	−1.3[a]	−1.6[a]	−3.6[a]
O	2.3	2.5	−0.4	−9.2	−9.1	−10.2
SiH_2	43.8	44.2	37.9	78.3	78.9	73.1
PH	25.3	25.6	20.9	32.8[b]	33.3[a]	28.5[b]
S	24.4	24.7	19.0	22.8	23.2	18.9

[a]For definition of theoretical levels, see footnotes to Table 1.
[b]trans.

In a qualitative sense, the dependence of the ring-opening enthalpies of heterocyclobutanes **1** on X calculated at the theoretical level 2 (Fig. 7) is similar to that calculated at the level 1.

Indeed, calculations predict ring opening via a C—C rather than C—X bond homolysis for azetidine and siletane, with the energy gaps being 1.4 and 2.0 kcal/mol, respectively. However, a preference of C—X to C—C bond homolysis is proper for phosphetane and thietane, with the energy gaps being equal to 15.7 and 9.7 kcal/mol, respectively. There is no energy gap between C—C and C—O ring openings of oxetane, indicating the equiprobability of both the homolyses.

It was worthy to check whether the predicted ring-opening enthalpies closely parallel the available experimental data on the activation energies of 2 + 2 cycloreversion, E_a, the reaction for which the ring opening is generally a limiting stage. This

should be expected because the activation energy for the reaction reverse to ring opening, that is, 1,4-diradicals ring closure by recombination of 1,4-diyl centers (so-called Benson's barrier), is known to be very small [74]. Indeed, the difference between $E_a = 62.5$ kcal/mol [75] and $\Delta H_{r.o.}$ (**1**, C—C) = 61.5/61.2 kcal/mol to be 1.0/1.3 kcal/mol may be well attributed to the Benson's barrier for cyclobutane case. The activation energies of oxetane's cycloreversion (62.6 and 63.1 kcal/mol via C—C and C—O bond cleavage, respectively [76]), are also close to the predicted ring-opening enthalpies, 60.7/60.2 and 64.7/60.2 kcal/mol. Taking into consideration the correction on the stabilization effects of silicon atom (see footnote to Table 12), our calculations predicted for siletane the initial cleavage of C—C bond, a conclusion widely accepted in the literature [2,3,77–83]. The enthalpy of the most economical ring opening via an initial cleavage of C—C bond

TABLE 7 Calculated Enthalpies of Reaction 3 and Central Bond Energies in $CH_3CH_2{-}XCH_3$ (in kcal/mol)[a]

X	ΔH_3				$D(CH_3CH_2{-}XCH_3)$				
	Level 1[a]	Level 2	Level 3	$\Delta_f H$	Level 1	Level 2	Level 3	$\Delta_f H$	[70a][b]
CH_2	9.7	10.1	13.0	10.1	87.7	87.3	84.4	87.4	86.8 ± 0.6
NH	12.7	13.8	15.3	–	83.5	82.4	80.9	–	79.8 ± 1
O	11.1	15.4	15.2	16.3	90.3	86.0	86.2	85.1	84.2 ± 1.3
SiH_2	2.8	5.1	6.8	1.6	86.2	83.9	82.3	87.4	–
PH	5.2	8.4	10.8	–	71.9	68.7	66.3	–	–
S	7.4	12.1	13.9	11.1	75.3	70.6	68.8	71.6	72.4 ± 1
Mean deviation	2.4[c]	1.1[d]	2.8[e]	–	2.6	1.4	3.0	–	–

[a]For definition of theoretical levels, see footnotes to Table 1.
[b]Recommended data.
[c]Arithmetic mean of differences between ΔH_3 calculated using a standard heats of formation and MP4/6-311G(d)//MP2/6-31(d) level of theory.
[d]Arithmetic mean of differences between ΔH_3 calculated using a standard heats of formation and MP4/6-311G(d,p)//MP2/6-31(d,p) level of theory.
[e]Arithmetic mean of differences between ΔH_3 calculated using a standard heats of formation and B3LYP level of theory.

TABLE 8 Calculated Enthalpies of Reaction 4 and Central Bond Energies in $CH_3CH_2{-}CH_2XH$ (in kcal/mol)[a]

X	ΔH_4				$D(CH_3CH_2{-}CH_2XH)$				
	Level 1	Level 2	Level 3	$\Delta_f H$	Level 1	Level 2	Level 3	$\Delta_f H$	[70a][b]
NH	7.8	8.7	10.9	8.7	81.9	81.0	78.8	81.0	81.5 ± 2.3
O	6.3	6.6	9.1	6.8	86.3	86.0	83.5	85.8	85.3 ± 1.3
SiH_2	12.1	12.4	15.4	11.0	85.7	85.4	82.4	86.8	–
PH	10.1	10.4	13.9	–	84.6	84.3	80.8	–	–
S	8.7	11.5	12.4	9.3	81.8	80.2	79.3	82.4	80.9 ± 2.4
Mean deviation	0.5[c]	0.3[d]	2.7[e]	–	0.8	1.0	3.0	–	–

[a]For definition of theoretical levels, see footnotes to Table 1.
[b]Recommended data.
[c]Arithmetic mean of differences between ΔH_4 calculated using a standard heats of formation and MP4/6-311G(d)//MP2/6-31(d) level of theory.
[d]Arithmetic mean of differences between ΔH_4 calculated using a standard heats of formation and MP4/6-311G(d,p)//MP2/6-31(d,p) level of theory.
[e]Arithmetic mean of differences between ΔH_4 calculated using a standard heats of formation and B3LYP level of theory.

TABLE 9 Calculated Enthalpies of Reaction 5 and Central Bond Energies in $CH_3X{-}CH_2XH$ (in kcal/mol)[a]

X	ΔH_5			$D(CH_3X{-}CH_2XH)$		
	Level 1	Level 2	Level 3	Level 1	Level 2	Level 3
NH	8.6	10.0	10.9	79.9	78.5	77.6
O	4.1	8.5	8.1	92.5	88.1	88.5
SiH_2	−0.1	2.2	4.5	89.5	87.2	84.9
PH	5.5	8.6	11.4	68.9	65.8	63.0
S	8.5	13.0	15.1	68.5	64.0	61.9

[a]For definition of theoretical levels, see footnotes to Table 1.

being 59.9/59.2 kcal/mol is only by 1.3–2.0 kcal/mol lower than the activation energy of $2 + 2$ cycloreversion of siletane (61.2 kcal/mol [4]). For thietane, the value $E_a = 57.4$ kcal/mol [84] corresponds to the predicted ring-opening enthalpy via an initial C—S bond cleavage, 56.2/50.3 kcal/mol, rather than to that via an initial C—C bond cleavage, 62.8/60.0 kcal/mol. The calculated enthalpy of azetidine's ring opening via an initial cleavage of C—C bond, 56.7/55.4

kcal/mol, is only a little preferred to the C—N homolysis, 58.3/56.8 kcal/mol. It is rather curious that these values turned out to be somewhat higher than the experimental activation energy of thermal decomposition of azetidine, being 54.8 kcal/mol [55]. The reasonable explanation could be that azetidine is consumed not only through $2 + 2$ cycloreversion but also through the reaction with methyleneimine [85].

TABLE 10 Strain Energies of Heterocyclobutanes, $E_s(\mathbf{1})$, and 1,3-diheterocyclobutanes,$E_s(\mathbf{2})$ (in kcal/mol)[a]

| X | $E_s(\mathbf{1}) = -\Delta H_6$ | | | | | $E_s(\mathbf{2}) = \Delta H_7$ | | |
	Level 1	Level 2	Level 3	$\Delta_f H$	From Literature	Level 1	Level 2	Level 3
CH_2	26.2	26.1	23.2	26.7	26.2 [70b]	26.2	26.1	23.2
NH	25.3	25.6	23.8	–	–	30.7/31.3[b]	30.6/31.0[b]	30.3/31.4[b]
O	25.6	25.8	24.1	26.1	25.6 [71b]	36.0	34.5	36.1
SiH_2	22.3	22.7	20.5	24.9	24.6 [14]	19.3	20.0	17.4
PH[a]	20.1	20.1	16.5	–	–	12.5/14.6[b]	12.8/15.0[b]	12.7/12.8[b]
S	19.0	20.3	17.0	19.6	–	16.6	14.3	15.8
Mean deviation	1.1[c]	1.0[d]	3.1[e]	–	–	–	–	–

[a]For definition of theoretical levels, see footnotes to Table 1.
[b]cis/trans.
[c]Arithmetic mean of differences between E_s calculated using a standard heats of formation and MP4/6-311G(d)//MP2/6-31(d) level of theory.
[d]Arithmetic mean of differences between E_s calculated using a standard heats of formation and MP4/6-311G(d,p)//MP2/6-31(d,p) level of theory.
[e]Arithmetic mean of differences between E_s calculated using a standard heats of formation and B3LYP level of theory.

Homolysis of a weaker bond is naturally favorable upon the ring opening, leading to 1,4-biradicals. Therefore, the enthalpies of the most economical bond cleavages for **1** were figured out at the top of Fig. 8, the bonds initially disrupted are shown in shadowed squares (level 1 calculations at the top, level 2 calculations at the bottom).
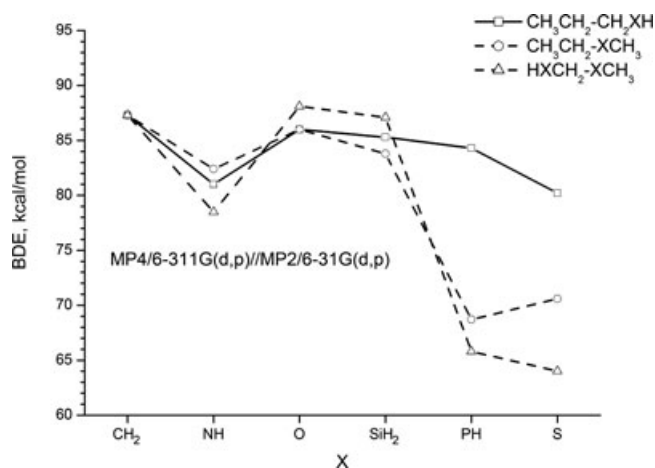
Notably, the enthalpies of the most economical ring openings for the whole series of heterocyclobutanes **1** do not exceed 60.7/60.2 kcal/mol, being close to those for cyclobutane (61.5/61.2 kcal/mol). The lowest ring-opening enthalpy of 51.8/48.5 kcal/mol is discovered for phosphetane.

Ring-opening enthalpies for heterocyclobutanes **2** are given in Table 12 and their dependence on X is plotted at the top in Fig. 9. There is naturally the only ring-opening route via a C—X bond cleavage (indicated in the shadowed squares) in the series of heterocyclobutanes **2**.

FIGURE 3 Dependence of central C—C and C—X bond energies in heterobutanes CH_3CH_2—CH_2XH, CH_3CH_2—XCH_3, and $HXCH_2$—XCH_3 on X as calculated at level 2.

TABLE 11 C—H and X—H Bond Dissociation Energies in CH_3XH (in kcal/mol)

Bond to be broken	This work	[a]
CH_3CH_2—H	100.8	100.5 ± 0.3
NH_2CH_2—H	93.1	93.9 ± 2
CH_3NH—H	99.2	101.6 ± 2
$HOCH_2$—H	96.0	96.06 ± 0.63
CH_3O—H	104.8	104.2 ± 0.9
CH_3SiH_2—H	92.4	92.7 ± 1.2
SiH_3CH_2—H	101.2	101.1 [11]
PH_2CH_2—H	98.1	–
CH_3PH—H	80.5	–
$HSCH_2$—H	95.1	93.9 ± 2
CH_3S—H	86.1	87.4 ± 0.5
H—H	104.4	104.4 [11]

[a]Data from Luo's Handbook [70a], unless other reference is given.
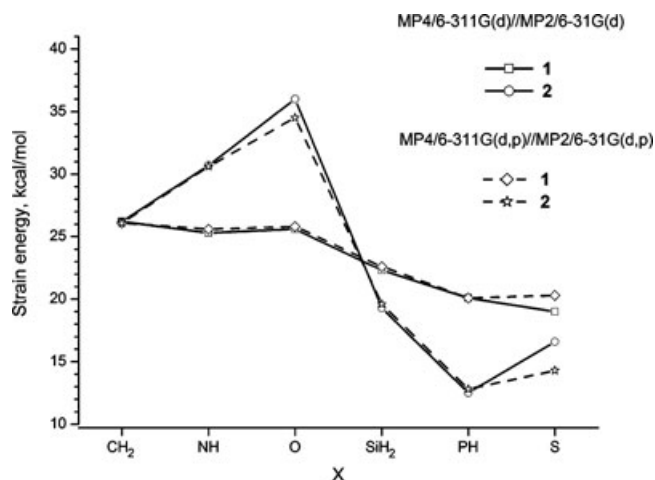
FIGURE 4 Dependence of heterocyclobutanes strain energies on X.
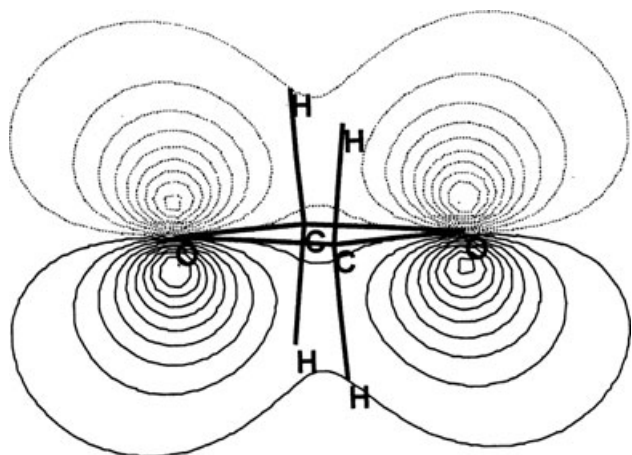
FIGURE 5 HOMO of 1,3-dioxetane calculated at MP2/6-31G(d,p) level of theory.

FIGURE 6 Dependence of ring-opening enthalpies of **1** on X as calculated at theoretical level 1.
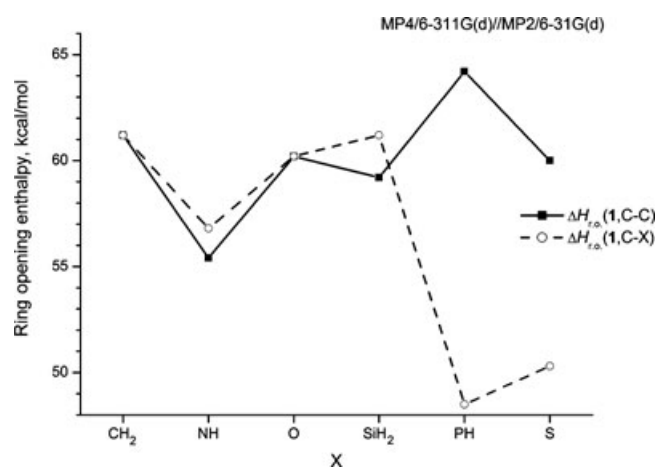
FIGURE 7 Dependence of ring-opening enthalpies of **1** on X as calculated at theoretical level 2.

The enthalpies calculated at both theoretical levels change similarly and differ between 1.2 and 3.4 kcal/mol. With the exception of 1,3-disiletane, they do not exceed 56.6/53.6 kcal/mol. On going from cyclobutane to 1,3-diazetidine, the ring-opening enthalpy falls down and then rises on going to 1,3-dioxetane and 1,3-disiletane. For X being the second row element, the enthalpy of C—X bond homolysis falls steeply for 1,3-diphosphetane and 1,3-dithietane. In the whole series of 1,3-diheterocyclobutanes, the highest ring-opening enthalpy is estimated for 1,3-disiletane (69.7/66.7 kcal/mol). These values are seemingly above the rather underestimated value of the ring-opening activation energy for **2** (X = SiH$_2$) calculated at CASPT2/6-31G*+ZPE level of theory (61.1 kcal/mol) [86].

2 + 2 Cycloreversion Enthalpies

2 + 2 Cycloreversion of heterocyclobutanes **1** containing heteroatom of the first or second row ele-
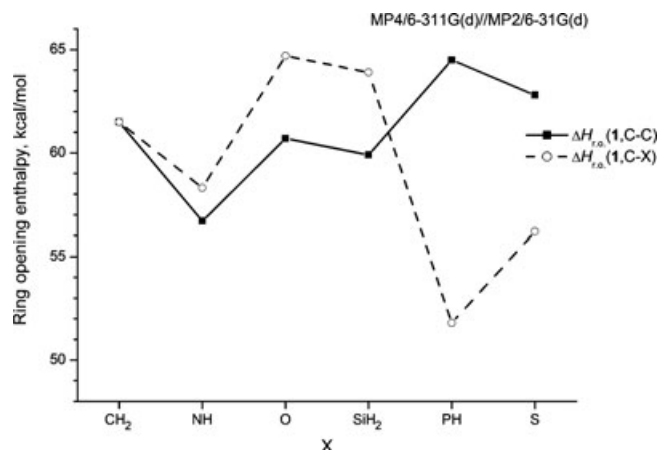
ments is endothermic and the endothermicity decreases on going from group 14 to group 16 elements (Fig. 8). In particular, the enthalpy of 2 + 2 cycloreversion, ΔH_1, is lower for X being the first row

TABLE 12 Ring-opening Enthalpies, $\Delta H_{\text{r.o.}}$ (in kcal/mol) (see Schemes 1 and 2)[a]

X	$\Delta H_{\text{r.o.}}$ (1, C—X)		$\Delta H_{\text{r.o.}}$ (1, C—C)		$\Delta H_{\text{r.o.}}$ (2, C—X)	
	Level 1	Level 2	Level 1	Level 2	Level 1	Level 2
CH$_2$	61.5	61.2	61.5	61.2	61.5	61.2
NH	58.3	56.8	56.7	55.4	49.2	48.0
O	64.7	60.2	60.7	60.2	56.6	53.6
SiH$_2$	63.9	61.2	59.9[b]	59.2[b]	69.7[b]	66.7[b]
PH	51.8	48.5	64.5	64.2	56.4	53.0
S	56.2	50.3	62.8	60.0	51.9	49.7

[a]For definition of theoretical levels, see footnotes to Table 1.
[b]With correction on stabilization effects of the silicon atom on the developing α- and β-radical sites [2] of 0.5 kcal/mol [72] and 3.0 kcal/mol [73], respectively.
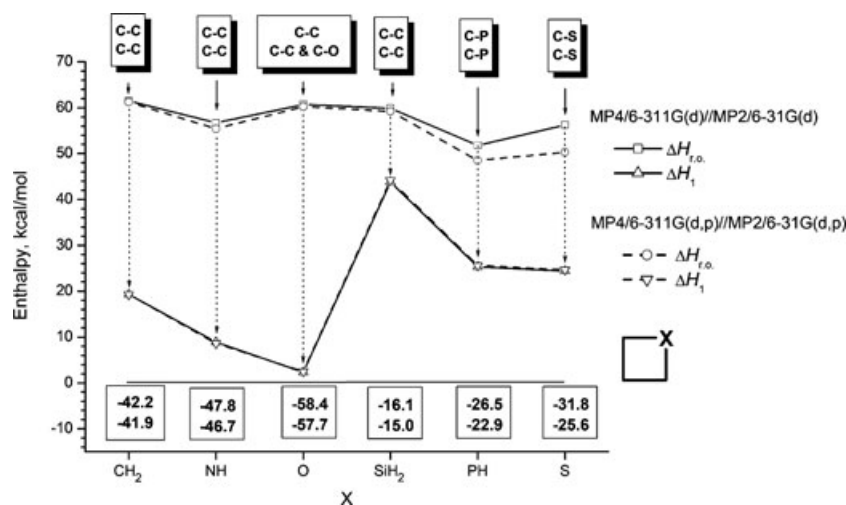
FIGURE 8 Plots of heterocyclobutanes **1** most economical ring-opening enthalpies (top lines) and 2 + 2 cycloreversion enthalpies (bottom line) versus X (the decomposition enthalpies of 1,4-diradicals calculated at two levels of theory are shown by the numerals in the squares and depicted by dot arrows).

element, cf. 19.3/19.3, 8.9/8.6, and 2.3/2.5 kcal/mol for X = CH$_2$, NH, and O, with 43.8/44.2, 25.3/25.6, and 24.4/24.7 kcal/mol for X = SiH$_2$, PH, and S.

Unlike **1**, for heterocyclobutane **2** series, 2 + 2 cycloreversion is not always the endothermic reaction. It is exothermic when X = NH and O (Fig. 9). The enthalpy of 2 + 2 cycloreversion of heterocyclobutanes **2** decreases on going from group 14 to group 16 elements. It is higher for X being the second row element, cf. 19.3/19.3, −1.3/−1.6, and −9.2/−9.1 kcal/mol for X = CH$_2$, NH, and O, with 78.3/78.9, 32.8/33.3, and 22.8/23.2 kcal/mol for X = SiH$_2$, PH, and S. The enthalpy of the most endothermic 1,3-disiletane 2 + 2 cycloreversion attains 78.3/78.9 kcal/mol.

1,4-Diradical Decomposition Enthalpies

1,4-Diradical decomposition enthalpies determined as a difference between 2 + 2 cycloreversion and ring-opening enthalpies are listed in Table 13 and shown in Figs. 8 and 9 by the numerals in the dark squares and dot arrows, respectively. With the exception of 1,3-disiletane, all the enthalpies are negative, indicating the exothermicity of 1,4-diradical decomposition being greater as X moves from group 14 to group 16 elements and being more pronounced for the first row elements.

The least exothermicity of decomposition is predicted for the diradical −CH$_2$SiH$_2$CH$_2$CH$_2$− ($\Delta H_{r.d.}$ (**1**, Si−C) = −16.1/−15.0 kcal/mol) that derived from
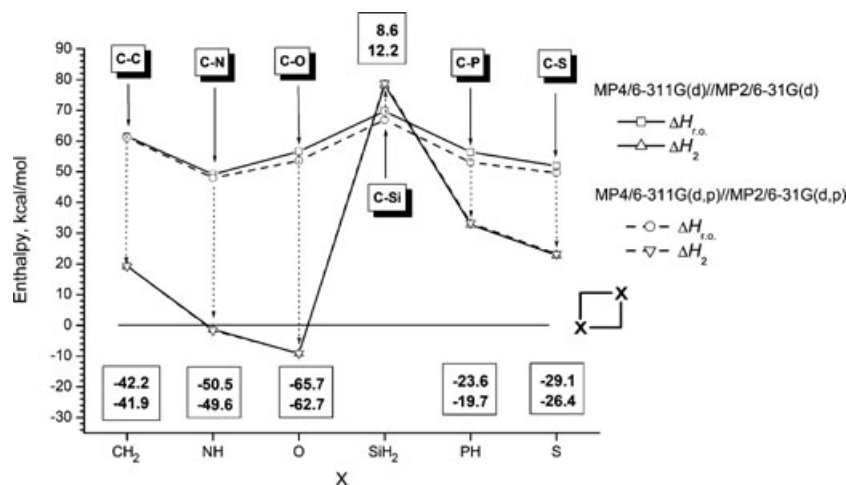

FIGURE 9 Plots of heterocyclobutanes **2** ring-opening enthalpies (top lines) and 2 + 2 cycloreversion enthalpies (bottom line) versus X (the decomposition enthalpies of 1,4-diradicals calculated at two levels of theory are shown by the numerals in the squares and depicted by dot arrows).

TABLE 13 1,4-Diradical Decomposition Enthalpies, $\Delta H_{r.d.}$ (in kcal/mol) (see Schemes 1 and 2)[a]

X	$\Delta H_{r.d.}$ (1, C—C)		$\Delta H_{r.d.}$ (1, C—X)		$\Delta H_{r.d.}$ (2, C—X)	
	Level 1	Level 2	Level 1	Level 2	Level 1	Level 2
CH_2	−42.2	−41.9	−42.2	−41.9	−42.2	−41.9
NH	−49.3	−48.1	−47.8	−46.7	−50.5	−49.6
O	−62.4	−57.7	−58.4	−57.7	−65.7	−62.7
SiH_2	−20.1	−17.0	−16.1	−15.0	8.6	12.2
PH	−26.5	−22.9	−39.2	−38.6	−23.6	−19.7
S	−31.8	−25.6	−38.3	−35.3	−29.1	−26.4

[a]For definition of theoretical levels, see footnotes to Table 1.

an initial cleavage of C—C bond in siletane (see Fig. 8). The only endothermic decomposition is predicted for diradical that contains two silicon atoms $-CH_2SiH_2CH_2SiH_2-$, $\Delta H_{r.d.}$ (**2**, Si—C) = 8.6/12.2 kcal/mol (see Fig. 9). As a result, the enthalpy of the overall process of 1,3-disiletane 2 + 2 cycloreversion rises to 78.3/78.9 kcal/mol, and hence one cannot expect its activation energy to be lower than this value. Thus, our calculations predict 1,3-disiletanes to be much more resistant to 2 + 2 cycloreversion than siletanes. Indeed, a comparison of the rate constants at 500°C calculated from the Arrhenius parameters of 1,1-dimethylsiletane [83] and 1,1,3,3-tetramethyl-1,3-disiletane [87] exhibits that the former decomposes by 4943 times faster than the latter.

CONCLUSION

A theoretical study of diradical mechanism of 2 + 2 cycloreversion of parent 1-heterocyclobutanes and 1,3-diheterocyclobutanes was undertaken, using the thermochemical approach within the limits of ab initio and DFT methods. Structural data of the starting heterocyclobutanes, resulting heteroethenes, and reaction enthalpies were derived by calculating the closed-shell singlet molecules at three levels of theory: MP4/6-311G(d)//MP2/6-31G(d)+ZPE, MP4/6-311G(d,p)//MP2/6-31G(d,p)+ZPE, and B3LYP/6-311+G(d,p)+ZPE. The calculated reaction enthalpies were compared with those evaluated, using the standard heats of formation when available. All conclusions were based on the ab initio calculations as they resulted in the minimal deviation.

Strain energies were calculated as the reversed sign enthalpies of homodesmic reactions. Ring-opening enthalpies to produce 1,4-diradicals via the initial cleavage of C—X or C—C bonds were found by subtracting the strain energies from the CBDEs of heterobutanes, $CH_3CH_2-CH_2XH$, $CH_3CH_2-XCH_3$, and $HXCH_2-XCH_3$. The latter ones were found via the enthalpies of the appropriate dehydrocondensa-tion reactions, using C—H and X—H bond energies in CH_3XH calculated at G2 level of theory.

The ring opening via a C—C bond homolysis was predicted for azetidine and siletane, whereas the initial homolysis of the C—X bond appeared to be the most likely route for phosphetane and thietane. For oxetane, both C—C and C—O bond homolyses seem to be equiprobable. The enthalpies of the most economical ring openings do not exceed 60.7/60.2 kcal/mol for the whole series of heterocyclobutanes **1** and 56.6/53.6 kcal/mol for all 1,3-diheterocyclobutanes, except 1,3-disiletane whose ring-opening enthalpy attains 69.7/66.7 kcal/mol.

The endothermicity of 2 + 2 cycloreversion of 1-heterocyclobutanes containing first or second row elements decreases on going from group 14 to group 16 elements. However, it is substantially higher for the second row elements. The 2 + 2 cycloreversion enthalpies for 1,3-diheterocyclobutanes are also being lowered on going from group 14 to group 16 elements and become even exothermic when X = NH and O.

The 1,4-diradical decomposition enthalpies were found as differences between 2 + 2 cycloreversion and ring-opening enthalpies. They are negative for both series of heterocyclobutanes, indicating the exothermicity of 1,4-diradical decomposition. The least exothermicity was calculated for siletane. The only exception is 1,3-disiletane whose 1,4-diradical decomposition is endothermic by 8.6/12.2 kcal/mol. Since the decomposition of the diradical containing two silicon atoms, $-CH_2SiH_2CH_2SiH_2-$, requires extra energy, 1,3-disiletane is predicted to be much more resistant to 2 + 2 cycloreversion than does siletane. This conclusion is in a perfect agreement with the available experimental data.

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