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Laser-Powered Decomposition of Spiro[2.*n*]alkanes (*n* = 2–5)

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The laser heating of spiro[2.*n*]alkanes (*n* = 2–5) and of their 1,1,2,2-tetradeuterated isotopomers reveals dissimilar modes of their thermal decomposition. Spiropentane decomposes into ethene and propadiene via two competing routes: the direct cleavage and the more important cleavage via intermediary methylenecyclobutane. Spirohexane decomposes through two important concurrent pathways which are the expulsions of ethene from the three-membered ring and a more feasible expulsion of ethene from the four-membered ring. Spiroheptane and spirooctane decompose by a radical-chain mechanism and afford complex mixtures of products; upon addition of propene both compounds rearrange into two cycloalkanes wherein the larger ring of the spiroalkane is preserved and substituted with ethylidene and a vinyl group.

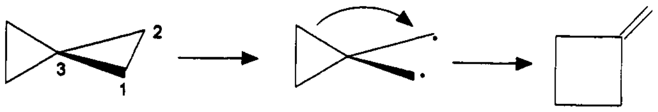
Introduction

The gas-phase thermolysis of organic molecules has been broadly investigated in the past,[1] but the vast majority of studies relates to conditions (glass, metal, or "aged" reactors) where heterogeneous contributions from the reactor surface can obstruct identification of truly homogeneous routes of the decomposition. Of several techniques recently designed to minimize surface effects, the infrared laser heating of a restricted gas phase volume far from cold reactor walls appears most reliable. The technique of CO_2 laser photosensitized gas-phase reactions[2] has been used by us[3] to determine the truly homogeneous course of thermal decomposition of thermally induced reactions of various organic molecules.

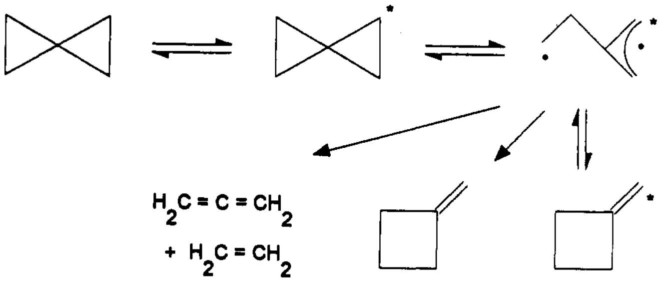
This paper reports on laser-powered homogeneous decomposition (LPD) of spiro[2.*n*]alkanes with *n* = 2–5. As for the thermal behavior of this family of compounds, spiropentane has attracted a lot of attention[4] and this thermolysis has been investigated in aged reactors. Spirohexane has been studied only briefly under conditions of LPD, while other homologues have not been studied at all so far.

In conventional thermolysis[4] spiropentane can undergo epimerization;[4b–e] it rearranges to methylenecyclobutane and also yields[4a,f] ethene and propadiene. It has been proven[4b,c] that the rearrangement takes place via a cleavage of the peripheral bond in the first ring and a vicinal shift of a methylene group in the second ring (Scheme I), but the origin of both decomposition products still remains to be solved. It has been proposed[4d,f] that ethene and propadiene can be formed directly from spiropentane and/or from methylenecyclobutane.[4d,f] The RRKM theory of unimolecular reactions applied[4f] to this problem revealed that both pathways (Scheme II and III) are plausible, but no experimental appraisal of the relative feasibility of both routes has been provided.

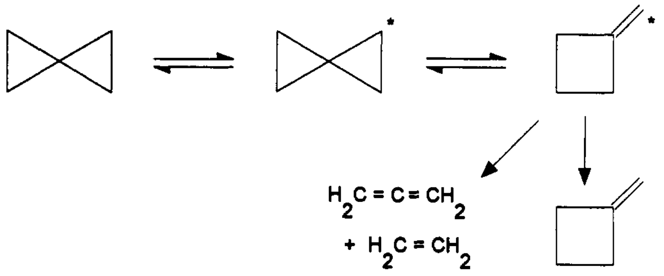
Scheme I



Scheme II



Scheme III



Thermolysis of spirohexane under conditions of LPD yields[5] ethene, methylenecyclopropane, and buta-1,3-diene, and at higher temperature also a rearranged product, methylenecyclopentane. It was suggested to occur via either concerted or nonconcerted (the C_1–C_3 bond cleavage) elimination of ethene to produce intermediary cyclobutylidene, or via a sequence of the C_1–C_3 cleavage, a migration to form vinylcyclobutane and allylic stabilized

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[●] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

(1) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980. *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H. Eds.; Elsevier: Amsterdam, 1972; Vol. 5.

(2) Shaub, W. M.; Bauer, S. H. *Int. J. Chem. Kinet.* **1975,** *7,* 509. Russell, D. K. *Chem. Soc. Rev.* **1990,** *19,* 407.

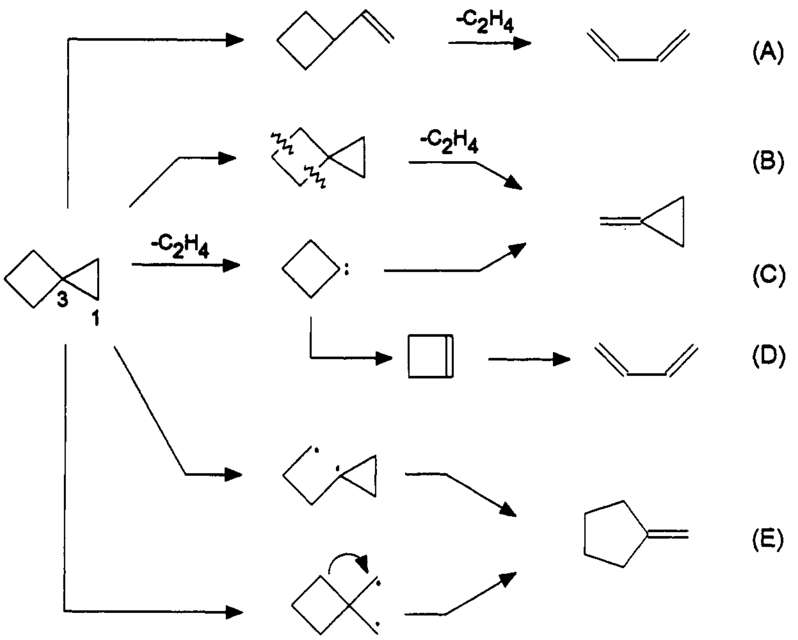
(3) Pola, J. *Spectrochim. Acta, Part A* **1990,** *46,* 607 and refs therein. Pola, J. *J. Chem. Soc., Perkin Trans.* **1983,** 231. Pola, J. *Tetrahedron* **1989,** *45,* 5065. Pola, J.; Lycka, A.; Guselnikov, L. E.; Volkova, V. V. *J. Chem. Soc., Chem. Commun.* **1992,** *20.* Kubát, P.; Pola, J. Collect. Czech. Chem. Commun. **1990,** *55,* 2460. Pola, J.; Ludvik, J. *J. Chem. Soc., Perkin Trans. 2* **1987,** 1727. Jakoubková, M.; Urbanová, M.; Pola, J. *J. Anal. Appl. Pyrol.* **1993,** *26,* 21.

(4) (a) Flowers, M. C.; Frey, H. M.; *J. Chem. Soc.* **1961,** 5550. (b) Gajewski, J. J.; Burka, L. T.; *J. Am. Chem. Soc.* **1972,** *94,* 8857. (c) Gajewski, J. J. *J. Am. Chem. Soc.* **1970,** *92,* 3688. (d) von E. Doering, W.; Gilbert, J. C. *Tetrahedron Suppl.* **1966,** *7,* 397. (e) Gilbert, J. C. *Tetrahedron* **1969,** *25,* 1459. (f) Flowers, M. C.; Gibbons, A. R. *J. Chem. Soc., Perkin Trans. 2* **1972,** 548.

(5) Volnina, E. A.; Kubát, P.; Pola, J. *J. Org. Chem.* **1988,** *53,* 2612.

0022-3263/93/1958-7709$04.00/0

Scheme IV



cyclobutane decomposition (expulsion of ethene from the four-membered ring). Other possibilities are initial cleavage of C_4–C_5 leading to ethene and methylenecyclopropane, and C_1–C_2 cleavage together with migration of C_4 resulting in the formation of methylenecyclopentane (Scheme IV).

In an effort to clarify the importance of the particular pathways with spiropentane and spirohexane and to determine the decomposition mode of other spiro[2.*n*]alkanes (n = 4, 5) we synthetized the spiroalkanes tetradeuterated in the three-membered rings and examined their thermal LPD by analyzing the distribution of deuterium in decomposition products using the technique of gas chromatography-mass spectrometry. This approach enables us to report the first evidence for the direct decomposition pathway of spiropentane. This route is shown to be less significant compared to the decomposition via the rearrangement into methylenecyclobutane. We also reveal that the decomposition of spirohexane takes place by a simultaneous cleavages of both three- and four-membered rings, and we show that the former cleavage is, contrary to our previous suggestion,[5] less feasible. Finally, we also show that higher spiro[2.*n*]alkanes (n = 4, 5) do not decompose through a molecular route, but that they undergo radical-chain decomposition; if radical chains are suppressed, both compounds rearrange into vinyl- and ethylidene-substituted cycloalkenes. This paper thus manifests that the thermal decomposition of the spiroalkanes cannot be described by a common process controlled by the cleavage of the three-membered ring and that the thermal mode of the spiroalkanes decomposition is affected by the size of the larger ring.

Results and Discussion

LPD of Spiropentane. LPD of spiropentane [spiropentane (4.4 kPa)–SF_6 (2.2–13.2 kPa)–Ar (9.4–20.4 kPa)] affords methylenecyclobutane (the product of the rearrangement) together with ethene and propadiene (products of decomposition(s)). Apart from these compounds, methane and propene were observed at temperature T_{eff} above 760 K, but their amounts were always below 2%. Typical mass balances for the irradiated spiropentane–SF_6–ethyl acetate–Ar mixtures are shown in Table I.

In order to determine whether equimolar amounts of ethene and propadiene are formed by the decomposition of intermediary methylenecyclobutane or directly from spiropentane we studied LPD of 1,1,2,2-tetradeuteriospiropentane. A mixture of spiropentane-d_4–SF_6 (both 5.3 kPa)–CH_4 (2.7 kPa)–Ar (13.3 kPa) was irradiated using the output of the CO_2 laser 9, 10 and 12 W. The reaction progress was monitored by gas chromatography, and mass spectra of produced ethene isotopomers were determined by using the GC-MS spectrometer. The direct decomposition of spiropentane-d_4 through synchronous cleavage of the two bonds leading to the $CH_2CH_2C(CH_2)_2$ biradical (allowed within the ground state according to the Woodward–Hoffmann rules; Scheme II) would result in the formation of only fully deuteriated and fully hydrogenated isotopomers of ethene. If we assume a reasonable secondary kinetic isotope effect of about 10% per deuterium,[6] C_2H_4 can be predicted as formed about 1.4 times faster than C_2D_4. Another alternative, the rearrangement of spiropentane into methylenecyclobutane and the decomposition of methylenecyclobutane[7] would take place via primary fission of the C_1–C_2 bond of spiropentane and would afford two different isotopomers of methylenecyclobutane **I** and **II** (Scheme V).

The Arrhenius parameters for the rearrangement of α,α-dideuteriomethylenecyclobutane (log A (s^{-1}) = 14.77, E_A = 207 kJ mol^{-1})[4d] (Scheme VI) and those for thermal decomposition of methylenecyclobutane[7] (log A (s^{-1}) = 15.68, E_A = 265 kJ mol^{-1}) are consistent with the fact that the CD_2 interchange is in the temperature range T_{eff} = 660–770 K, about 10^3–(5×10^3) times faster than the decomposition. This implies that both **I** and **II** would undergo multifold interchange of CD_2 groups prior to their decomposition. The ratios of ethene isotopomers C_2H_4/$CH_2{=}CD_2$/C_2D_4 can be predicted from symmetry numbers of both methylenecyclobutane isotopomers **I** and **II** (formed by each pathway, Scheme V) and of 2,2,4,4- and

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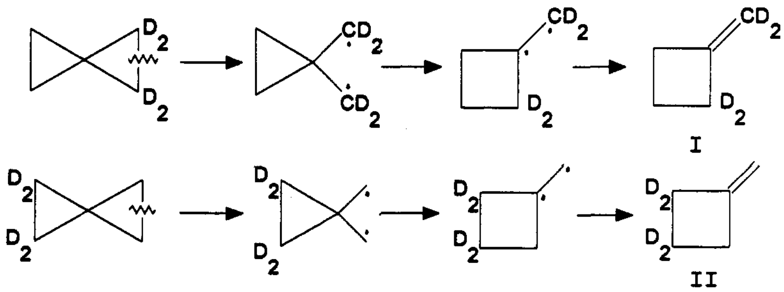
[6] Srinivasan, R.; Kellner, S. M. E. *J. Am. Chem. Soc.* **1959**, *81*, 5891. Carr, R. W.; Walters, W. D. *J. Am. Chem. Soc.* **1966**, *88*, 884. Dolbier, W. R.; Alonso, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 442. Chickos, J. S. *J. Chem. Soc. Perkin Trans. 2* **1987**, 1109 and refs therein.

[7] Chesick, J. P. *J. Phys. Chem.* **1961**, *65*, 2170. Brandauer, R. L.; Short, B.; Kellner, S. M. E. *J. Phys. Chem.* **1961**, *65*, 2269.

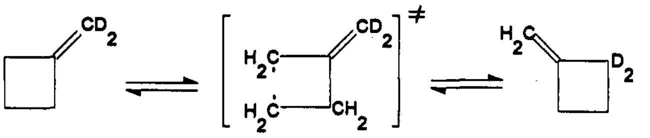
Table I. Product Distribution in LPD of Spiropentane

			mass %					
T_{eff}, K	incident energy, W cm^{-2}	irradn time, s	Ia	Ib	propadiene	ethene	ethyl acetate	methane
659	11	0	45.0	0.5			54.5	
		180	34.2	19.6	5.3	7.0	33.9	
		360	13.1	19.3	6.1	8.3	53.2	
		540	8.1	24.2	7.0	9.6	51.0	
		780	4.5	26.7	8.2	11.6	49.8	
703	22	0	46.9	0.6			52.5	
		10	38.7	7.4	1.8	2.0	50.2	
		20	34.3	12.1	3.1	3.5	47.0	
		30	28.3	16.1	4.6	5.1	45.8	
		40	26.2	19.7	5.7	6.2	42.1	
756	125	0	44.6	0.5			54.9	
		2	40.6	1.9	2.6	3.3	51.5	
		4	39.2	3.0	5.5	6.7	45.7	
		6	34.7	3.5	7.7	9.1	44.9	
		8	31.5	4.1	10.0	11.4	43.1	
767	600	0	44.9	0.5			54.6	
		2	40.2	2.2	3.7	4.5	49.7	
		4	36.8	3.1	6.7	8.4	44.6	0.4
		6	31.8	3.8	9.3	11.2	42.8	1.0
		8	27.5	4.5	11.9	13.7	40.6	1.7

Scheme V



Scheme VI



α,α,3,3-tetradeuteriomethylenecyclobutanes upon assumption of their rapid rearrangement (Scheme VI) leading to an equilibrium distribution of isotopomers. The secondary kinetic isotope effect of about 10% per deuterium[6] suggests that **II** will be formed about 1.4 times faster than I, and this would lead to a predicted $C_2H_4/CH_2{=}CD_2/C_2D_4$ ratio of about 1:4.8:1.4.

The experimentally observed C_2H_4, $CH_2{=}CD_2$, and C_2D_4 and the ratios of the isotopomers $CH_2{=}CD_2C_2H_4$ (or $CH_2{=}CD_2C_2D_4$) approaching 2 (Table II) provide the confirmative evidence for the operation of both direct and undirect pathways. On the basis of the experimentally observed yield of ethene (all the isotopomers), the observed $CH_2{=}CD_2/C_2H_4$ ratio (Table II) and the presumption that the indirect decomposition would result in the predicted $C_2H_4/CH_2{=}CD_2/C_2D_4$ ratio of about 1:4.8:1.4, we can infer that the observed $C_2H_4/CH_2{=}CD_2$ ratio (1.8–2.4, Table II) indicates about 10–30% excess of C_2H_4 (C_2D_4) and that this amount can be ascribed to the direct decomposition. The knowledge of the total mass balance (Table II) then allows us to estimate that the direct decomposition is, in the T_{eff} range studied, roughly 3–10 times less significant than the indirect one.

LPD of Spirohexane. LPD of spirohexane [spirohexane (2.6 kPa)–SF_6 (3–4.6 kPa)–CH_4 (1.2 kPa)–1-chloropropane (5.3 kPa)–Ar] yields ethene, buta-1,3-diene, and methylenecyclopropane and at higher temperatures also methylenecyclopentane. Methane, ethane, and propene were observed only at temperatures T_{eff} higher than 740 K, but their yield at the highest T_{eff} (810 K) does not exceed 5 mass %. Typical mass balances for the irradiated spirohexane–SF_6–chloropropane–Ar are given in Table III. An earlier observed[5] almost invariant ratio of methylenecyclopropane to buta-1,3-diene (0.20–0.30) at different reaction progress in the absence of Ar made us believe that spirohexane decomposes via expulsion of ethene from the three-membered ring, which leads to an intermediary cyclobutylidene which is a common precursor to methylenecyclopropane and buta-1,3-diene (routes C and D, Scheme IV). We assumed[5] that the invariance of the above ratio at different T_{eff}'s can be consistent with very similar E_A of both cyclobutylidene pathways. (The absence of cyclobutene among the detected products is in line with a feasible cyclobutene to buta-1,3-diene rearrangement;[8] it can be inferred that the rate of this rearrangement is, within the temperature range studied, 6 orders of magnitude higher than the rate of cyclobutene formation from spirohexane). Similar pathways of cyclobutylidene, i.e. its ring-contraction rearrangement and its 1,2-hydrogen shift, were also claimed to occur in the thermal liquid-phase decomposition of cyclobutanone and bicyclo[3.1.1]-heptan-6-one tosylhydrazones.[9] Apart from the primary cleavage of the three-membered ring (routes C and D), there is also possibility for its alternative C_1–C_3 cleavage

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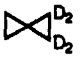
(8) Vogel, E. *Angew Chem.* **1956**, *68*, 189. Vogel, E. *Liebigs Ann. Chem.* **1958**, *615*, 14.

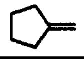
(9) Friedman, L.; Schechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. G. Maier, G. Strasser, M. *Tetrahedron Lett.* **1966**, 6453. Langer, U.; Musso, M. *Justus Liebigs Ann. Chem.* **1976**, 1180.

Table II. Product Distribution in LPD of 1,1,2,2-Tetradeuteriospiropentane

		mass %				
T_{eff}, K	irradn time, s			ethene*	propadiene	$H_2C{=}CD_2C_2H_4$[a]
732	25	57.5	10.1	14.2[b]	18.2	1.8
	50	31.9	4.5	29.5[c]	34.1	2.0
748	15	53.6	9.0	17.7[d]	19.7	1.8
	30	28.6	12.5	28.5[e]	30.5	1.7
777	4	72.5	6.3	9.2[f]	11.9	2.4
	8	52.0	8.8	17.3[g]	21.9	2.2
	16	11.7	9.1	33.5[h]	45.7	2.2

[a] Error ± 20%. * Mass spectrum of ethene (*m/z* rel inten %): [b] 32/29, 30/100, 29/41, 28/87, 27/56, 26/37. [c] 32/28, 30/100, 29/43, 28/88, 27/60, 26/38. [d] 32/29, 30/100, 29/43, 28/92, 27/66, 26/43. [e] 32/28, 30/100, 29/43, 28/93, 27/65, 26/43. [f] 32/16, 30/83, 29/47, 28/100, 27/86, 26/69. [g] 32/23, 30/95, 29/53, 28/100, 27/76, 26/55. [h] 32/22, 30/88, 29/49, 28/100, 27/70, 26/53.

Table III. Product Distribution in LPD of Spirohexane

			mass %					
T_{eff}, K	incident energy, W cm^{-2}	irradn time, s		$CH_2{=}CH_2$				methane + propene
704	14	80	99.7	0.3				
		160	96.6	0.9	1.3	0.3	0.9	
		300	87.1	1.4	2.9	0.7	8.0	
		450	84.4	2.3	3.9	0.8	8.6	
725	19	50	96.6	0.7	1.0	0.2	1.5	
		150	90.6	2.1	2.7	0.4	4.2	
		250	84.1	3.7	5.2	0.8	5.3	
		400	78.5	5.8	7.9	1.2	6.5	
739	21	60	94.0	2.0	1.9	0.3	1.5	
		100	88.9	3.0	4.4	0.7	3.0	
		150	85.2	4.7	6.4	0.9	2.8	
		220	71.9	7.6	9.9	1.6	9.1	
797	52	10	90.9	2.5	3.0	0.5	2.9	0.2
		20	81.1	4.8	6.1	0.9	6.3	0.8
		30	62.3	8.4	13.5	2.3	11.6	1.9
		40	41.4	14.8	18.2	6.2	16.4	3.1

Scheme VII

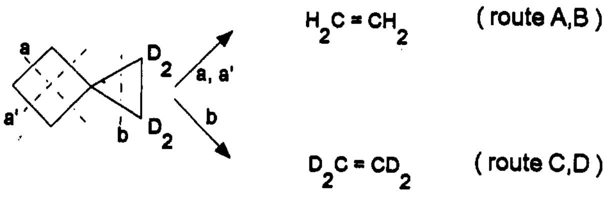


Table IV. Ethene Isotopomers Ratio in LPD of Spirohexane

T_{eff}, K	C_2H_4/C_2D_4 ratio (conversion, %)[a]			
674	5.1 (7)	5.9 (12)	6.6 (18)	
694	7.9 (41)	7.2 (43)		
721	16.0 (39)	9.6 (44)	6.1 (57)	5.3 (60)
750	7.3 (10)	7.5 (56)		
754	8.6 (16)	7.0 (42)	5.1 (52)	4.7 (55)

[a] Error ● 20%.

which is ensued by a migration (to form vinylcyclobutane) and allylic-stabilized cyclobutane (four-membered ring) decomposition (route A). Another decomposition pathway can occur via solely cleavage of the four-membered ring (route B).

Deuterium labeling has been applied to distinguish between expulsions of ethene from the three- and four-membered rings. These expulsions can be monitored by analysis of deuterium-labeled ethene isotopomers obtained from the decomposition of 1,1,2,2-tetradeuteriospirohexane (Scheme VII).

The values of the C_2H_4/C_2D_4 ratio as dependent on T_{eff} and decomposition progress are gathered in Table IV. The ratios reveal that LPD of spirohexane takes place through both (a + a′) and b pathways in Scheme VII and show that the rate of the fission(s) of the four-membered ring is several times higher than that of the three-membered one. The observed presence of deuterium in both buta-1,3-diene [mass spectrum (*m/z* rel inten): 58/91/, 57/42/, 56/43/, 55/12/, 54/28/, 53/23/, 52/23/, 51/18/] and methylenecyclopropane [mass spectrum (*m/z* rel inten): 58/100/, 57/29/, 56/29/, 55/6/, 54/9/, 53/15/, 52/17/, 51/11/, 50/8/] provide support for the occurrence of routes A and B (rearrangement of methylenecyclopropane into buta-1,3-diene is improbable due to a high thermal stability of methylenecyclopropane which can be assumed to undergo only degenerate rearrangement[10]). These findings, together with formation of more buta-1,3-diene compared to methylenecyclopropane (Table III), suggest that route A is predominant.

LPD of Spiro[2.4]heptane. The laser irradiation of spiro[2.4]heptane–SF_6 (both 3.0 kPa)–Ar (21 kPa) (incident energy 11–144 W cm^{-2}) yields a complex mixture of products containing mostly methane, ethene, ethane, and propene along with smaller amounts of C_4 (mostly buta-1,3-diene), C_5 hydrocarbons, vinylcyclopentane, and ethylidenecyclopentene (Figure 1). These compounds reveal the occurrence of radical reactions (C–C bond cleavage, H-abstraction, etc.) and show that the course of homogeneous decomposition of spiro[2.*n*]alkanes is dramatically changed by increasing the number of CH_2 groups in one ring. The products of LPD of spiro[2.4]heptane demonstrate the involvement of a radical chain mechanism so

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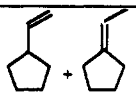
[10] Gajewski, J. J. Hydrocarbon Thermal Isomerization; Academic Press: New York, 1981.

Table V. Mass Balance in LPD of Spiro[2.4]heptane

		mass %				
T_{eff}, K	irradn time, s			1-chloropropane	propene	methane + ethene
663	0	52.7		31.2	16.1	
	240	49.6	0.2	31.6	18.5	
	840	48.3	0.6	30.2	20.7	
	1440	46.1	2.9	30.2	20.8	
	2340	42.3	3.6	29.2	24.9	
728	0	54.2		30.9	14.8	
	120	45.2	1.9	29.7	23.2	
	240	31.3	13.2	29.2	26.3	
	480	29.8	11.2	26.1	32.8	
	600	12.6	26.3	24.8	36.3	
747	0	53.0		32.0	14.9	
	16	48.3	0.4	35.2	16.1	
	24	45.3	2.9	35.0	16.7	
	32	44.3	3.5	34.7	17.5	
	40	42.1	5.5	33.7	18.7	
806	0	52.4		33.9	13.7	
	4	41.1	3.6	31.9	23.1	0.3
	12	28.4	16.6	26.9	27.0	1.0
	20	28.7	12.3	24.7	32.4	1.9
	28	12.1	24.8	21.2	39.7	2.1

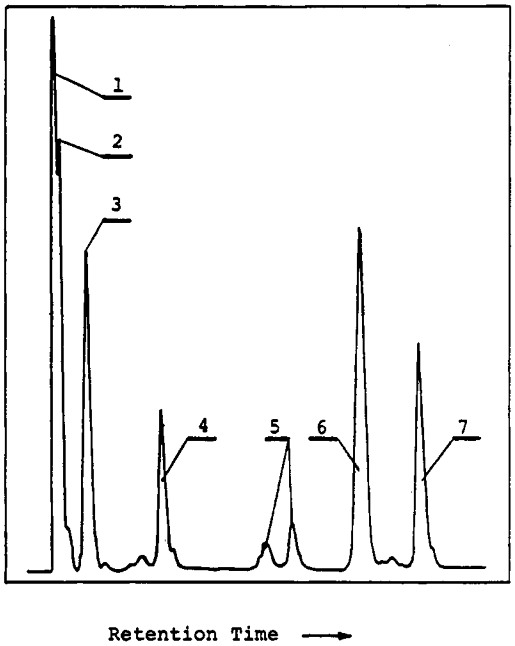
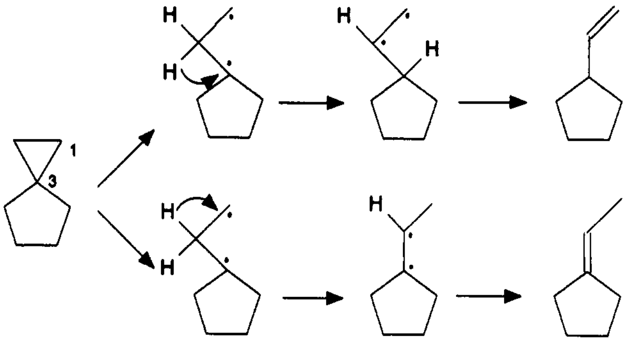


Figure 1. Typical GC trace of the mixture obtained by LPD of spiroheptane carried out in the absence of propene. Squalane, peaks: 1 = methane, 2 = ethene, 3 = propene, 4 = buta-1,3-diene, 5 = C_5 hydrocarbons, 6 = spiroheptane and vinylcyclopentane, 7 = ethylidenecyclopentane.

frequently encountered with pyrolysis of hydrocarbons.[11] We used a standard experimental approach to eliminate chain reaction by adding an excess of propene as a radical scavenger, which should lead to a fast reaction of reactive chain-propagating radicals with C_3H_6 to yield nonreactive (resonance-stabilized) radicals that eventually terminate. The irradiation of spiro[2.4]heptane (2.9 kPa)–1-chloropropane–propene (both 2.5 kPa)–SF_6 (5.4–6.7 kPa)–Ar (total pressure 27 kPa) afforded (Table V) only two new compounds which were identified through their ^1H and ^{13}C NMR spectra as vinylcyclopentane and ethylidenecyclopentane. LPD of spiro[2.4]heptane in the presence in propene is thus consistent with substantially simplified reaction scheme (Scheme VIII), where initial compound undergoes two different rearrangements. We assume that the rearrangements are initiated by a cleavage of the C_1–C_3 bond and that the formed biradical stabilizes via two different H-shifts. Typical mass balances of this reaction are gathered in Table V.

Scheme VIII



We remark that methylenecyclohexane, the product of a ring extension, is absent among the observed products in spite of the enlargement of rings in LPD of spiropentane and spirohexane as an active channel. This fact can be attributed to a high stability of the five-membered ring. We also note that the ratio of both products of the rearrangement is linearly dependent on temperature and changes, with increasing T_{eff}, in favor of ethylidenecyclopentane (Figure 2). Ethene might be assumed to be formed by the expulsion from the three-membered ring. Such a reaction would produce cyclopentylidene (Scheme IX) which is known[12] to rearrange into cyclopentene. However, the absence of cyclopentane among the decomposition products and the fact that ethene is formed only under conditions of radical chains (Figure 1) suggest that ethene originates from another route.

In an effort to reveal decomposition progress of spiro[2.4]heptane under conditions of conventional pyrolysis (CP) and compare it to the results of LPD, we decomposed spiro[2.4]heptane in a glass (unseasoned) ampoule. The distribution of products in CP (Table VI) is not much different from that achieved in LPD and the ratios of

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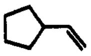
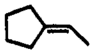
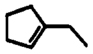
[11] Laidler, K. J.; Loucks, L. F. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds., Elsevier: Amsterdam, 1982; Vol. 5.

[12] Schechter, H.; Friedman, L. *J. Chem. Soc., Chem. Commun.* **1976**, 631.

Table VI. Typical Mass Balance in CP of Spiro[2.4]heptane

		mass %						
temp, K	time, min					CH_4	$C_2H_4 + C_2H_6$	unidentified
450	20	67.4	10.7	12.5	2.7	2.2	0.89	3.6
460	10	64.8	10.6	11.9	4.9	1.9	0.8	5.1
470	3	81.4	4.4	4.8	2.8	3.2	1.4	2.0
	6	66.2	6.5	5.7	2.8	4.9	3.7	10.2
	10	44.7	9.7	10.5	2.9	7.9	6.1	18.2

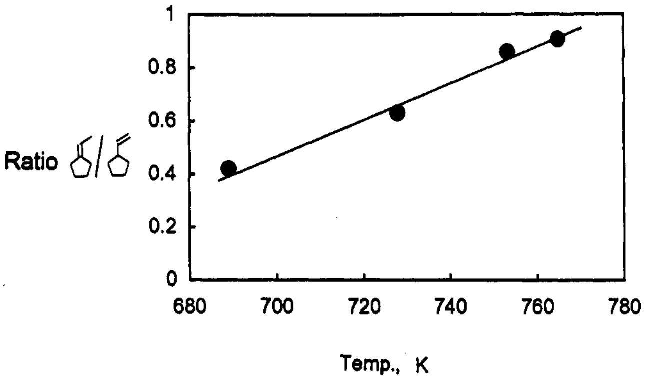
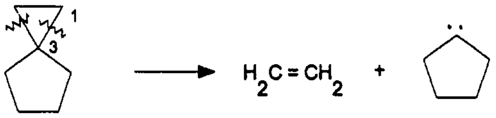
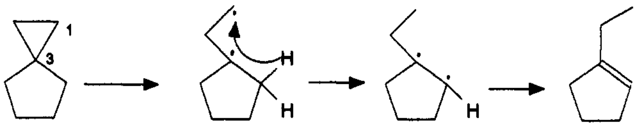


Figure 2. The ethylidenecyclopentane/vinylcyclopentene ratio as dependent on T_{eff}.

Scheme IX



Scheme X



both rearranged products formed under both different conditions are similar. The only difference is the formation of 1-ethylcyclopentene in CP but not in LPD. We assume that this compound is formed by a heterogeneously assisted reaction (Scheme X).

LPD of Spiro[2.5]octane. The laser irradiation of spiro[2.5]octane (2.0 kPa)–SF_6(4 kPa)–Ar (21 kPa) (incident energy 20 W cm^{-2}) affords vinylcyclohexane, ethylidenecyclohexane, methane, ethane, propene, and also small amounts of C_4 hydrocarbons (mostly buta-1,3-diene) (Figure 3). In the excess of propene (6 kPa), the irradiation yields only vinylcyclohexane and ethylidenecyclohexane together with small amounts of ethene (Table VII). These products suggest that LPD of spiro[2.5]octane takes place as the rearrangement initiated, similarly as with spiro[2.4]heptane, by the cleavage of the C_1–C_3 bond and by an ensuing stabilization of the formed biradical through H-shift (Scheme XI).

Ethene produced in the absence of propene is apparently formed by a radical mechanism and not by the expulsion from the three-membered ring. The formation of ethene being suppressed by the addition of propene, and the absence of cyclohexene, presumably formed[13] from cyclohexylidene through a shift of hydrogen, support this assumption.

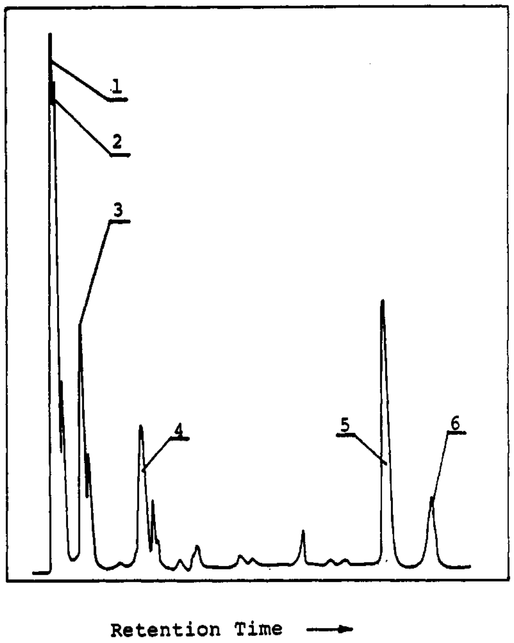
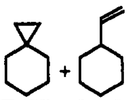
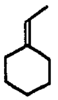


Figure 3. Typical GC trace of the mixture obtained by LPD of spirooctane carried out in the absence of propene. SE-30 elastomer, peaks: 1 = methane, 2 = ethene, 3 = propene, 4 = buta-1,3-diene, 5 = spirooctane and vinylcyclohexane, 6 = ethylidenecyclohexane.

Table VII. Product Distribution in LPD of Spiro[2.5]octane

			mass %		
incident energy, W cm^{-2}	irradn time, s	T_{eff}, K			$CH_2=CH_2$
19	700	716	93.4	5.9	0.7
20	1100	721	91.8	7.4	0.8
20	200	730	86.7	12.7	0.6
21	650	734	91.6	7.5	0.8
22	270	755	89.1	10.4	0.4
57	60	793	93.8	5.9	0.3

CP of spiro[2.5]octane carried out in the absence of propene in an unseasoned glass ampoule at 420–445 °C results in the formation of the same rearranged products as LPD. At temperatures higher than 445 °C these products are accompanied with other hydrocarbons (Table VIII).

CP of 1,1,2,2-tetradeuterio[2.5]octane conducted at the same conditions (450 °C, 45 min) yields, apart from other products, ethene containing ca. 60% of C_2H_4 and 40% of $C_2H_nD_{4-n}$ (n = 1–3). This indicates that C_2H_4 is formed through the cleavage of the six-membered ring and proves a complex decomposition mechanism.

These data show that the thermal decomposition of the spiro[2.n]alkanes (n = 2–5) is strongly affected by the size of the more-membered ring: spiropentane and spirohexane undergo molecular fragmentation into ethene and another

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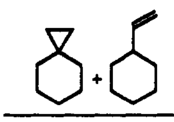
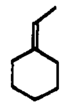
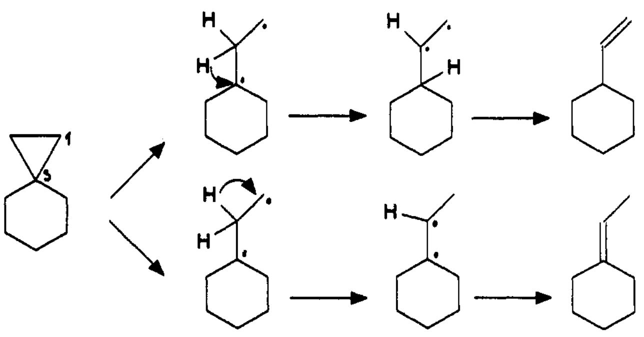
[13] Forester, A. R.; Sadd, J. S. J. Chem. Soc., Chem. Commun. 1976, 631. Wojnarovits, L. Proc. Tihany Symp. Radiat. Chem. 1977, 5, 529. Kyba, E. P. J. Am. Chem. Soc. 1977, 99, 8330.

Table VIII. Distribution of Products in CP of Spiro[2.5]octane (in mass %, 450 °C, 45 min)

		CH_4	C_2H_4	C_2H_6	propene			unidentified
81.2	7.5	1.0	1.3	0.5	0.6	1.2	1.3	5.4

Scheme XI



unsaturated fragments, whereas spiroheptane and spirooctane afford a variety of products by a radical-chain mechanism, or rearrange, in the presence of propene, into two products in which ethylidene and the vinyl group is attached to the preserved larger ring of the initial spiroalkane.

Note on the Arrhenius Parameters of LPD of Spiro[2.*n*]alkanes. The dependence of the first-order rate constant k_{total} (ref 2) on the mean effective temperature T_{eff} (659–767 K) for LPD of spiropentane is illustrated in Figure 4. The Arrhenius parameters of LPD of spiropentane obtained from this plot are log A (s^{-1}) = 8.2 and E_A = 135 kJ mol^{-1}. These are noticeably lower than those obtained for the conventional rearrangement of spiropentane into methylenecyclobutane occurring in the temperature range 633–683 K (log A (s^{-1}) = 15.86, E_A = 242 kJ mol^{-1}, ref[4a]) in which the amounts of produced ethene indicate 7–9% of a concurrently occurring decomposition pathway.

The dependence of the first-order rate constant k_{total} on the mean effective temperature T_{eff} (675–810 K) for the depletion of spirohexane by both the rearrangement and decomposition (k_r + k_d) (Scheme XII), which is also illustrated in Figure 4, leads to the Arrhenius parameters log A (s^{-1}) = 12.5 and E_A = 215.7 kJ mol^{-1}.

These values are in a good accord with those (log A (s^{-1}) = 15.1, E_A = 243 kJ mol^{-1}) obtained by us previously,[5] when we had used a different marker and irradiated spirohexane–SF_6–ethyl acetate in the absence of Ar. The dependence of the first-order rate constant for depletion of spirohexane by only decomposition (k_d) on T_{eff} (Figure 4) yields log A (s^{-1}) = 12.5 and E_A = 215.7 kJ mol^{-1}. Also these values are somewhat lower than those reported by Flowers and Frey for the thermal isomerization of 1,1-dimethylcyclopropane (log A (s^{-1}) = 15.4, E_A = 266 kJ mol^{-1}, ref 6).

The dependence of the first-order rate constant k_{total} of the rearrangement of spiro[2.4]heptane on the mean effective temperature T_{eff} (663–809 K) (Figure 4) leads to the Arrhenius parameters log A (s^{-1}) = 11.0 and E_A = 190 kJ mol^{-1}.

So low Arrhenius parameters are normally ascribed to heterogeneous mechanism. However surface assistance in the laser-induced gas-phase reactions is highly improbable, and it can arise only from impurities on reactor windows[14] which seems, with regard to a very thorough window cleaning in this work, very unlikely. Another explanation, that our measurements were carried out in the falloff region, can also be discarded.[4a,f] There is, to the best of our knowledge, only one example of a decrease in E_A due to minimizing surface effect, which relates to the thermal decomposition of tetramethylgermane in a wall-less reactor.[15] We can speculate that low Arrhenius parameters may be associated with a specific influence of collisions between spiropentane and SF_6 molecules, but a significant acceleration of thermal decomposition of hydrocarbons can be observed[16] at pressures of (laser energy nonabsorbing) SF_6 higher than those used in our study. We are thus unable to draw any conclusion, but describe these results to show that even an extreme care, which was taken in this investigation, can lead with LPD technique to Arrhenius parameters which are lower than those obtained by using conventional thermolytic homogeneous conditions.

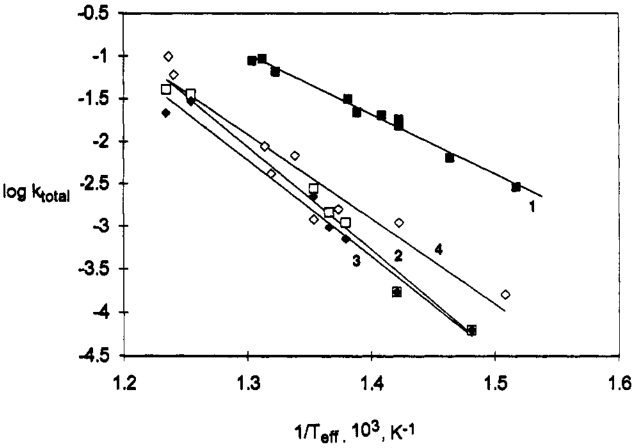
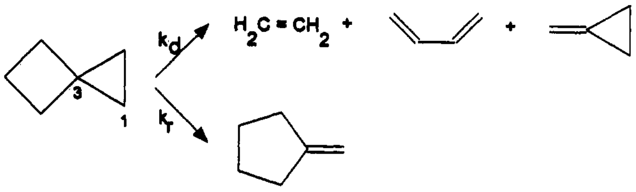


Figure 4. The log k_{total} vs T_{eff} plot for the LPD of spiropentane (1), spirohexane (d + r, 2), (d, 3) and spiroheptane (4). The correlation coefficients for the individual plots are, in the given order, 0.993, 0.991, 0.987, and 0.960.

Scheme XII



Experimental Section

Laser-Powered Decomposition. Continuous-wave (cw) CO_2 laser photosensitized (SF_6) decomposition of spiroalkanes was carried out in the setup which consisted of a glass tube reactor (10-cm long and 3-cm i.d., equipped with sodium chloride windows), a standard vacuum line for handling gaseous components, a 12-channel (250 μL in volume) sampling valve, and

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(14) Karny, Z.; Zare, R. N. *J. Phys. Chem.* **1977**, *23*, 321.

(15) Taylor, J. E.; Milazzo, M. *J. Phys. Chem.* **1978**, *82*, 847.

(16) Pola, J. *Chem. Listy* **1981**, *75*, 168. Jach, J.; Hinshelwood, C. *Proc. Roy. Soc., Ser. A* **1955**, *229*, 143. Jach, J.; Hinshelwood, C. *Proc. Roy. Soc., Ser. A* **1955**, *231*, 145. Parson, B.; Danby, C. J.; Hinshelwood, C. *Proc. Roy. Soc.*, Ser. A **1957**, *240*, 333.

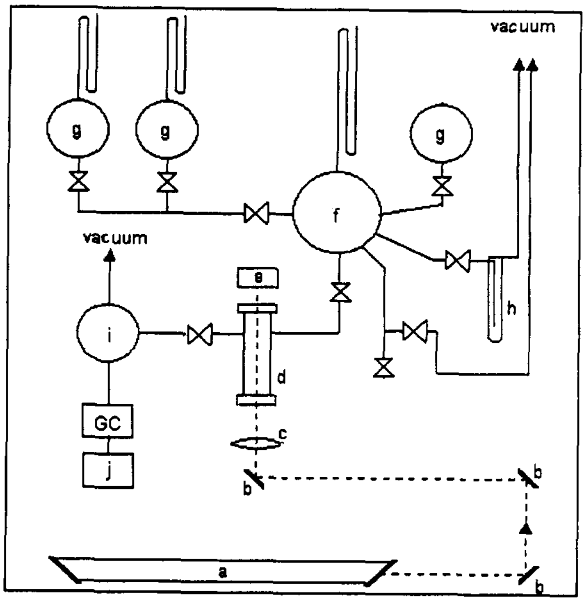

Figure 5. The setup for LPD of spiroalkanes. (a) CO_2 laser, (b) gold-plated mirror, (c) germanium lens, (d) reactor, (e) power meter, (f) flask for mixing gaseous components, (g) reservoir for gases, (h) collector cooled with liquid nitrogen, (i) sampling valve, (j) computing integrator.

a gas chromatograph (Figure 5). A cw CO_2 laser was operated at the P(20) line of the $00^\circ1 \rightarrow 10^\circ0$ transition and the laser beam was focused (Ge lens, focal length 10 cm) to provide the incident energy from 11 to 600 W cm^{-2}. The output of the laser was measured by a Coherent Model 201 power meter and the wavelength of the radiation was verified with a Model 16-A spectrum analyzer (Optical Eng.) Gaseous mixtures of spiroalkane–SF_6–internal standard[17]–marker[17]–buffer gas were irradiated with several different incident energies in the vertically positioned reactor, the beam entering from below. For particular cases, these initial mixtures were spiropentane (4.4 kPa)–SF_6-(2.2–13.2 kPa)–CH_4 (2.8 kPa)–ethyl acetate (3.4 kPa)–Ar, spirohexane (2.6 kPa)–SF_6 (3–4.6 kPa)–CH_4 (1.2 kPa)–1-chloropropane (5.3 kPa)–Ar, spiro[2.4]heptane (2.9 kPa)–1-chloropropane–propene (both 2.5 kPa)–SF_6 (5.4–6.7 kPa)–Ar, and spiro[2.5]-octane (2.0 kPa)–SF_6 (4.0 kPa)–Ar. Argon pressures were adjusted to obtain the total pressure 27 kPa.

The progress of the decomposition of the spiropentane, spirohexane, and spiro[2.4]heptane (and the marker) at measured intervals was determined by gas chromatography (a Shimadzu, Model GC 14 A chromatograph equipped with flame ionization detector (FID) and programmed temperature). Decomposition products obtained by LPD were analyzed on a 1-m long column packed with alumina deactivated by H_2O or on a 2.8-m long column packed with a silicon elastomer SE-30 on Chromaton N. The products were identified by gas chromatography-mass spectrometry (a GC-MS Shimadzu, Model QP 1000 quadrupole mass spectrometer) by comparison of their mass spectra and retention times with those of authentic samples.

Progress of LPD of spiro[2.5]octane could not be monitored by carrying periodical analyses using gas chromatography due to the failure to separate decomposition products in spite of using both packed and capillary columns. The products formed in the absence of propene were identified by comparison of retention times and mass spectra to those of authentic samples (the GC-MS Shimadzu QP 1000 spectrometer, 1-m long column packed with Porapak P, temperature 20–150 °C).

NMR analyses of the decomposition products prepared by LPD of spiro[2.4]heptane and spiro[2.5]octane in the presence of propene were conducted on a Varian Unity 200 spectrometer using two-dimensional correlation of ^1H–^1H and ^1H–^{13}C NMR spectra. The identification of vinylcyclohexane and ethylidenecyclohexane was achieved[18] using HETCOR and APT techniques (ref 19) and the assignment of signals in the region of alkene hydrogens in ^1H spectrum (δ = 4.8–5.9 ppm).

The products of isomerization of spiroheptane and spirooctane were identified after separation on a capillary column (DB-5, 30 m, 30 °C) through their mass spectra recorded on a Finigan Mat ITD 800 Varian spectrometer and compared with literature data.[20] Quantitative analyses were conducted using the computing integrator CI 100 (Laboratorní Přístroje) and the FID. Response factors *f* were measured in this work (compound, *f*:1-chloropropane, 0.46; spiropentane, 1.07; spirohexane and spiroheptane, 1.04; spirooctane, 1.02; buta-1,3-diene, 1.12) or were taken from ref 21.

Effective temperatures and Arrhenius parameters of the LPD's of the spiroalkanes were estimated by means of the technique for noninteracting systems using marker (chemical thermometer[2]). Mean effective temperatures T_{eff} were calculated as $E_A/2.303$ (log A–log k), where E_A and log A (s^{-1}) for conventional thermal decompositions of ethyl acetate (200.6 kJ mol^{-1}, 12.59) and 1-chloropropane (230.0 kJ mol^{-1}, 13.45) were taken from ref 22.

Conventional Thermal Decomposition. CP of spiro[2.*n*]-alkanes was carried out in an unseasoned Pyrex ampoule (25 mL in volume) heated in a bath of the Wood metal whose amount (5 kg) secured sufficient thermal capacity.

Mass spectra of the mixture of C_2H_4, $C_2H_2D_2$, and C_2D_4 isotopomers produced in LPD of spiropentane-d_4 and spirohexane-d_4 were obtained after separation from other decomposition products using GC-MS spectrometry and column packed with alumina (deactivated with 3% H_2O, 1-m long, 30 °C). The amounts of the individual isotopomers in $C_2H_nD_{2-n}$ (n = 0, 2, 4) were estimated on the basis of measured mass spectra of the particular isotopomers.

Spiropentane[23] and methylenecyclobutane[24] were prepared as described earlier and purified on a Fisher distillation apparatus (column MS-500). Mass spectra (70 eV, *m/z* rel inten) of spiropentane (99.7% purity, bp 37.5 °C): 68/8/, 67/98/, 66/3/, 65/5/, 53/36/, 51/6/, 50/7/, 42/13/, 41/22/, 40/94/, 39/100, 38/17/, 37/8/, 28/17/, 27/34/, 26/10/.

Spiro[2.*n*]alkanes (n = 4, 5) were synthesized after the procedures summarized in Scheme XIII in which diethyl esters of 1,1-cycloalkanedicarboxylic acid were reduced[25] by synhydride ($NaAlH_2(OCH_2OCH_3)_2$) in tetrahydrofuran to the appropriate diols (for n = 4 yield 79%, mp 91 °C, and for n = 5 yield 89%, mp 93 °C). The produced 1,1-bis(hydroxymethyl)cycloalkanes afforded[26] the ditosyl esters (for n = 4 yield 59%, and for n = 5 yield 68%) upon the treatment with *p*-toluenesulfonyl chloride in anhydrous pyridine. 1,1-Bis(bromomethyl)cycloalkanes (for n = 4 yield 83%, bp 95–99 °C/1.3 kPa, and for n = 5 yield 72%, bp 96–99 °C/0.3 kPa) were prepared[26] from the ditosyl esters by a reaction with lithium bromide in 2-ethoxyethanol. The debromination of these compounds by zinc in ethanol in the presence of tetrasodium salt of ethylenediaminetetraacetic acid yielded[23] spiro[2.*n*]alkanes which were distilled on a Fisher apparatus (MS-500 column) (for n = 4 yield 88%, bp 98 °C, purity 99.2%, and for n = 5 yield 75%, bp 124 °C, purity 99.4%). Structure of both final products was confirmed by mass and ^1H and ^{13}C NMR spectra.

1,1,2,2-Tetradeuteriospiro[2.*n*]alkanes (n = 2–5) were synthesized according the reaction Scheme XIV, in which the diesters

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[17] Internal standard (methane) is stable under the used irradiation conditions and it is used only for the quantitative estimation of depleted and formed compounds. Marker is a compound whose thermal decomposition of known Arrhenius parameters occurs in a unimolecular fashion and does not interfere with simultaneously occurring decomposition of spiroalkane. Reference 2, see also: Danen, W. C.; Jang, J. C. In *Laser Induced Chemical Processes*; Steinfeld, J. I., Ed., In Plenum Press: New York, 1981.

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(23) Applequist, D. E.; Fanta, G. F.; Henrikson, B. W. *J. Org. Chem.* **1958**, *23*, 1715.

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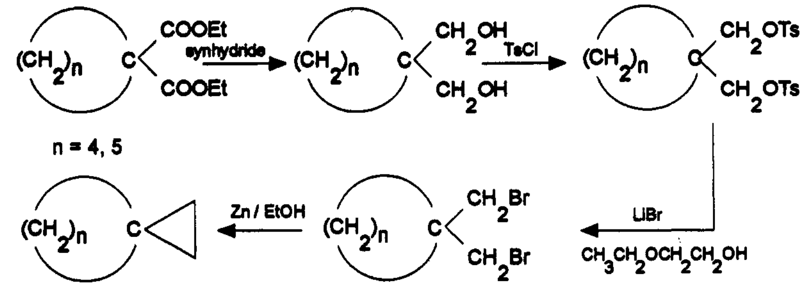
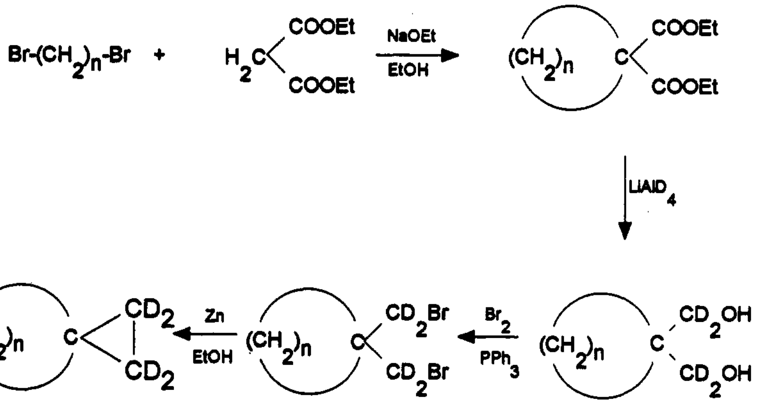
(25) Hajos, A. *Complex Hydrides and Related Reducing Agents in Organic Syntheses*; Akademiai Kiado: Budapest, 1979. Itoh, O.; Kohmura, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 151.

(26) Buchta, E.; Billenstein, S. *Liebigs Ann. Chem.* **1967**, *702*, 51.

Scheme XIII



Scheme XIV



Scheme XV

$$CD_3COOCH_3 \xrightarrow[THF]{synhydrid} CD_3CH_2OH \xrightarrow{SOCl_2} CD_3CH_2Cl \xrightarrow[-DCl]{} CD_2=CH_2$$

(for $n = 2$ yield 52%, bp 126–128 °C/5.9 kPa; for $n = 3$ yield 57%, bp 101–104 °C/0.7 kPa; for $n = 4$ yield 44%, bp 98–99 °C/0.5 kPa; and for $n = 5$ yield 53%, bp 118–120 °C/1.2 kPa) were prepared using the procedure of Cason and Allen[27] and the diols (for $n = 2$ yield 42%, bp 116–120 °C/1.2 kPa; for $n = 3$ yield 43%, bp 115 °C/0.7 kPa; for $n = 4$ yield 44%, bp 98–99 °C/0.5 kPa; and for $n = 5$ yield 53%, bp 118–120 °C/1.2 kPa) were obtained by reported procedures.[25,28] The latter were treated with bromine and triphenylphosphine in dimethylformamide and afforded[29] 1,1-bis(bromomethyl-d_2)cycloalkanes (for $n = 2$ yield 49%, bp 85–90 °C/1.9 kPa; for $n = 3$ yield 50%, bp 115 °C/0.7 kPa; for $n = 4$ yield 54%, bp 94–98 °C/1.1 kPa; and for $n = 5$ yield 61%, bp 97–99 °C/0.3 kPa).

1,1,2,2-tetradeuteriospiro[2.*n*]alkanes ($n = 2$–5) were prepared by the following procedure: 1,1-Bis(bromomethyl-d_2)cycloalkane (0.05 mol) was added during 1 h to the stirred mixture of the tetrasodium salt of ethylenediaminetetraacetic acid (20.34 g), NaOH (16.14 g), NaI (1.0 g), water (30 mL), ethanol (60 mL), and zinc (7.2 g) kept at 50 °C. The resulting mixture was subsequently heated for 3 h, and the spiroalkane was distilled off under a mild stream of nitrogen. The obtained liquid portions were redistilled on the Fisher apparatus (MS-500 column) and spiroalkanes were obtained as fractions boiling at 37 °C ($n = 2$, yield 74%, 99.2% purity), at 69.5 °C ($n = 3$, yield 65%, 98.4% purity), at 99 °C ($n = 4$, yield 58%, 99% purity), and at 124 °C ($n = 5$, yield 62%, 99.2% purity).

Mass spectra (70 eV, m/z/rel inten) for 1,1,2,2-tetradeuteriospiropentane, 1,1,2,2-tetradeuteriospirohexane, 1,1,2,2-tetradeuteriospiroheptane, and 1,1,2,2-tetradeuteriospirooctane (in the given order): 72/48/, 71/71/, 70/30/, 69/27/, 68/14/, 56/19/, 55/8/, 54/12/, 52/20/, 50/14/, 46/9/, 44/40/, 42/100/, 41/96/, 40/80/, 38/33/, 37/16/, 30/64/, 29/20/, 28/35/, 27/51/, 26/17/, 25/7/. 85/2/, 71/6/, 70/8/, 69/8/, 68/5/, 59/5/, 58/100/, 57/18/, 56/15/, 55/6/, 54/9/, 53/6/, 44/7/, 43/9/, 42/17/, 41/27/, 40/19/, 39/18/, 30/10, 29/10, 28/16/, 27/15/.

100/4.7/, 99/3/, 85/4/, 84/4/, 83/5/, 82/8/, 72/6/, 71/11/, 70/9/, 69/9/, 68/36/, 67/100/, 66/11/, 65/3/, 59/8/, 58/15/, 57/7/, 56/8/, 55/10/, 54/7/, 53/8/, 43/7/, 41/14/, 40/21/, 39/15/, 38/19/, 31/4/, 30/4/, 29/6/, 28/8/, 27/9/, 26/10/.

115/2/, 114/21/, 99/8, 96/8/, 86/7/, 85/8/, 83/13/, 82/38/, 81/100/, 79/9/, 72/11/, 71/13/, 70/14/, 69/18/, 68/26/, 67/75/, 58/10/, 55/11/, 54/31/, 53/8/, 44/8/, 43/13/, 42/14/, 41/33/, 40/10/, 39/17/, 29/9/, 28/9/, 27/14/.

1,1-Dideuterioethene was prepared after the procedure illustrated in Scheme XV.

Methyl ester of 2,2,2-trideuterioacetic acid was reduced by synhydride[26] in tetrahydrofuran (mixture heated to 65 °C for 5 h). After hydrolysis, 1,1,1-trideuterioethanol was distilled from the mixture as a ternary azeotrope (CD_3CH_2OH, water, and toluene) which was dried by $MgSO_4$. The mixture of alcohol and toluene was treated with thionyl chloride, and the resulting ester was decomposed at 150 °C. At this temperature the resulting CD_3CH_2Cl was undergoing dehydrochlorination and 1,1-dideuterioethene was collected in a flask cooled with liquid nitrogen. Mass spectrum (70 eV, m/z/rel inten): 30/100/, 29/64/, 28/60/, 27/55/, 26/23/.

Tetradeuterioethene and ethene were from the laboratory stock. Mass spectrum (70 eV, m/z/rel inten): C_2D_4 32/100/, 30/65/, 29/3/, 28/80/, 27/3/, 26/14/; C_2H_4 28/100/, 27/63/, 26/64/, 25/12/.

Sulfur hexafluoride (Aldrich) and argon (Technoplyn) were commercial samples.

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