IR SPECTRAL STUDY OF THE VACUUM PYROLYSIS OF 2,3-DIMETHYL-
AND 2,3,7,8-TETRAMETHYL-5-GERMASPIRO[4.4]NONA-2,7-DIENES
AS POSSIBLE SOURCES OF 3,4-DIMETHYLCYCLOPENTENE-3-GERMYLENE

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Organic germylenes have been postulated as intermediates in many thermal and photochemical reactions and have been the subject of intensive chemical investigation [1, 2]. Work is presently underway on the direct detection of these unstable species by physical methods. The UV spectra of a series of organic germylenes, generated photochemically in a hydrocarbon matrix at 77 K, have recently been detected [3, 4] as well as the UV spectrum of dimethylgermylene using liquid-phase flash photolysis [5]. On the other hand, no IR spectral data have been obtained for organic germylenes.

In the present work, we attempted to stabilize 3,4-dimethylcyclopentene-3-germylene (I), generated by the vacuum pyrolysis of 5-germaspiro[4.4]nona-2,7-dienes (II) [6, 7] in an inert matrix at 12 K and carry out the direct spectral detection of this species.
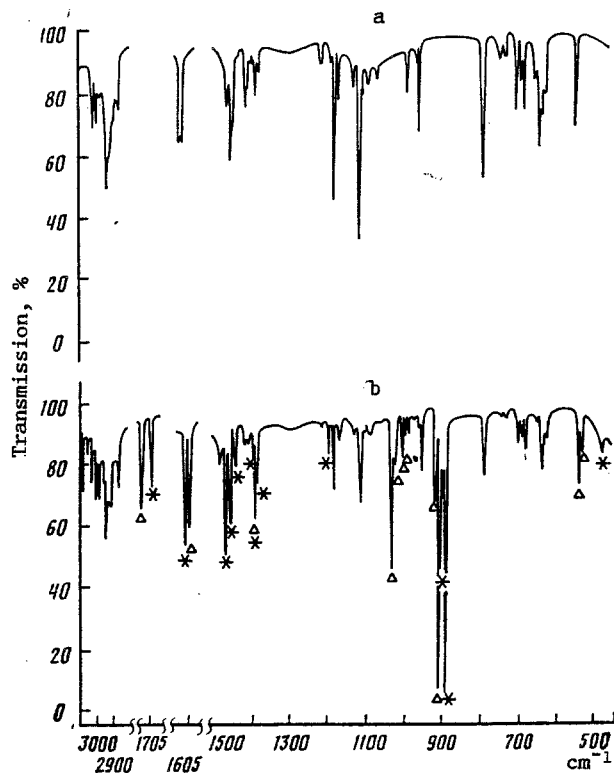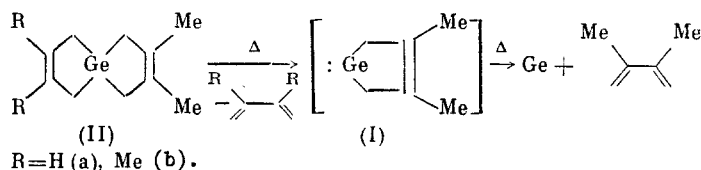

R=H (a), Me (b).

Fig. 1a, b

The possibility of the intermediate formation of germylene (I) was considered in our previous work [8, 9] on the basis of the temperature dependence of the composition of the final reaction products of the pyrolysis of (IIa) and its analogs in a helium stream in a flow system and the fragmentation of (IIa) upon electronic impact.

Upon carrying out this pyrolysis at 10^{-3}-10^{-4} torr and 430-700°C, we observed a complete change in the IR spectra of the products of the pyrolysis of (II) in comparison with the matrix IR spectra of the starting compounds (see Fig. 1). The conversion of (II) was increased from ~0 to 100%.

The matrix IR spectrum of the products of the vacuum pyrolysis of (IIa) at 550°C (Fig. 1b) has only bands for the s-cis and s-trans conformers of butadiene (BD) and 2,3-dimethylbutadiene (DBD) [10-12] in addition to the bands of the unreacted starting compound. A germanium film was formed concurrently on the quartz reactor walls. Upon warming the matrix from 12 to 40 K or repeated spraying of the reaction products and refreezing in a liquid nitrogen trap after warming of the base to ~20°C gave the complete disappearance of the bands for the s-cis conformer of DBD and a decrease in the intensities of the bands of the s-cis conformer of BD. The intensities of the bands for (IIa) and the s-trans conformers of BD and DBD are retained in the spectrum.

We should note that, at all the pyrolysis temperatures studied for (IIa), a constant ~1:1 ratio of the intensities of the bands for BD (907 cm^{-1}) and DBD (894 cm^{-1}) was observed in the spectra of the matrix-isolated products. This finding indicates the decomposition of both rings in (IIa), in contrast to the gas-liquid chromatographic data [8, 9], in which the amount of BD formed at low conversions of (IIa) in a helium stream is greater than the amount of DBD. This latter finding indicated that the predominant loss of the least substituted ring in (IIa) leads to the intermediate formation of germylene (I) [8, 9]. However, we failed to reward bands which are may attribute to the notified intermediate. Apparently, the temperature for the vacuum decomposition of (IIa) in our previous work [8, 9] increased the thermal lability of (I) and its fragmentation to metallic germanium and DBD.
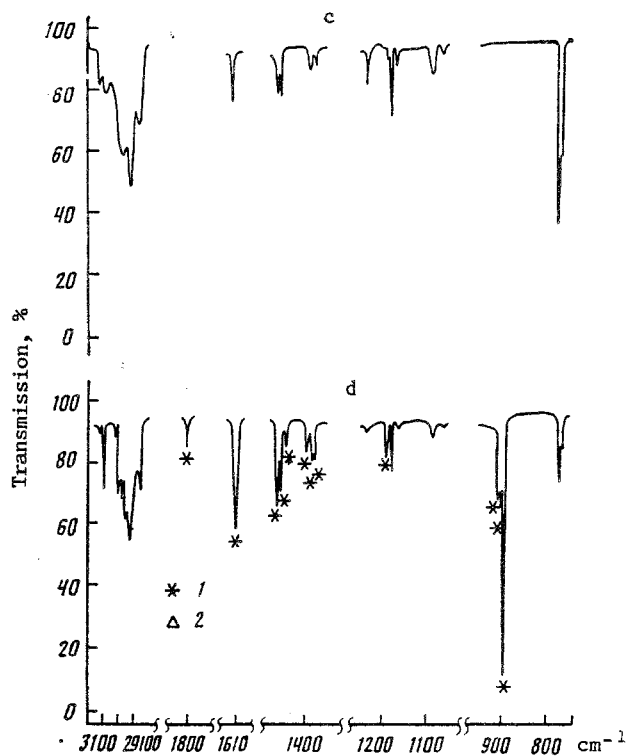

Fig. 1c, d

Fig. 1. Matrix IR spectra in argon at 12 K for (IIa) (a) and (IIb) (c) and the IR spectra of the products of the pyrolysis of (IIa) at 550°C and ~5·10^{-4} torr (b), and of (IIb) at 550°C and ~10^{-3} torr (d) frozen in an argon matrix at 12 K: 1) s-cis- and s-trans-DBD, 2) s-cis- and s-trans-BD.

TABLE 1. Vibrational Frequencies (cm^{-1}) for (II) and Their Pyrolysis Products Frozen in Argon Matrices at 12 K

(IIa)	Products of the pyrolysis of (IIa) (550°C, 10^{-3}-10^{-4} torr)	Assignment	(IIb)	Products of the pyrolysis of (IIb) (550°C, 10^{-3}-10^{-4} torr)	Assignment
	468 w	DBD	766 sh	766 sh	(IIb)
	527 w	BD	768 s	768 m	(IIb)
	533 m	BD		894 v.s	DBD
536 m				898 m	DBD*
623 m	623 w	(IIa)		903 sh	DBD
628 m	628 w	(IIa)	1057 w	1057 v.w	?
633 m	633 m	(IIa)	1080 w	1080 w	?
647 w	647 v.w	(IIa)	1160 w		
677 m	677 m	(IIa)	1174 m	1175 m	(IIb)
686 w	686 w	(IIa)	1182 w		
696 m	696 m	(IIa)		1185 m	DBD
726 w	726 w	(IIa)	1226 w		
738 w	738 w	(IIa)	1375 w	1376 m	DBD +(IIb)
786 s	786 m	(IIa)		1380 m	DBD +(IIb)
	894 v.s	DBD	1383 w		
	898 m	DBD*		1389 w	DBD
	902 sh	DBD		1437 w	DBD
	907 v.s	BD	1449 m	1449 m	DBD +(IIb)
	914 m	BD*	1457 m	1457 m	DBD +(IIb)
952 m	952 m	(IIa)		1607 m	DBD
958 w	958 v.w	(IIa)	1611 m		
	967 v.w	?		1797 m	DBD
982 m	982 w	(IIa)	2863 m	2862 m	(IIb)+?
	989 w	BD	2928 s	2931 s	DBD + (IIb)
	997 m	BD*	2957 m	2955 m	DBD + (IIb)
	1017 m	BD		2962 m	DBD
	1024 s	BD		2982 m	DBD
				2988 m	DBD
1057 w	1057 w	?		2996 m	DBD +(IIb)
1080 w	1080 w	?	2996 m		
1097 w	1097 v.w	(IIa)	3006 w		
1103 s	1103 m	(IIa)		3030 w	?
1121 w	1121 w	(IIa)		3098 m	DBD
1159 m	1159 w	(IIa)		3114 v.w	DBD
1173 s	1173 m	(IIa)			
1183 v.w					
	1185 m	DBD			
1210 w	1210 w	(IIa)			
1377 w	1377 m	(IIa)+DBD			
1382 m	1382 m	BD + DBD+(IIa)			
	1389 m	DBD			
1397 v.w					
1402 w	1402 w	(IIa)			
1408 m	1408 w	(IIa)			
	1438 w	DBD			
1445 sh					
1449 m	1449 m	(IIa)+DBD			
	1455 sh	DBD			
1459 m	1458 m	(IIa)			
	1475 w	?			
	1596 m	BD			
	1606 m	DBD			
1611 m					
1617 m					
	1797 m	DBD			
	1822 m	BD			
2863 m	2860 m	(IIa)+?			
2877 sh	2875 sh	(IIa)+?			
2890 sh					
2925 s					
	2936 s	DBD + (IIa)			
	2955 m	DBD + BD			
	2961 sh	DBD			
	2981 m	DBD			
2983 m					
	2986 m	BD* + DBD			
	2995 m	BD + DBD			

TABLE 1 (continued)

(IIa)	Products of the pyrolysis of (IIa) (550°C, 10^{-3}-10^{-4} torr)	Assignment	(IIb)	Products of the pyrolysis of (IIb) (550°C, 10^{-3}-10^{-4} torr)	Assignment
2998 m 3026 m 3031 w	3026 m	(IIa)			
	3063 w	BD			
	3098 m	DBD			
	3112 v.w	DBD			

*s-cis conformer.

The vacuum pyrolysis of (IIb) proceeds analogously. The matrix IR spectrum of the products of the pyrolysis of this compound at 550°C (Fig. 1d) shows only bands for the s-cis and s-trans conformers of DBD in addition to the bands of starting (IIb) (Table 1). A decrease in the intensities of the s-cis-DBD bands was observed upon warming the matrix from 12 to 40 K, while the bands for s-trans-DBD and starting (IIb) retained their intensities. Bands of an unstable molecule such as (I) were not detected. On the other hand, the deposition of a germanium film was also observed on the reactor walls. The formation of this film is most likely a result of the thermal decomposition of labile (I) under the conditions studied.

The possibility of the formation of germylene (I) upon the thermal decomposition of (II) was demonstrated in our work chemically by the capture of this germylene. Thus, the corresponding 1,4-cycloadduct of germylene (I), namely spirodiene (IIa) was detected in the copyrolysis of (IIb) in a large excess of butadiene at 400°C. The yield of (IIa) was only 1-2% relative to converted (IIb). This low yield is apparently also related to the predominance of more extensive thermal decomposition of germylene (I) under these conditions.

EXPERIMENTAL

Starting (IIa) and (IIb) were synthesized according to our previous procedures [6, 7]. The vacuum pyrolysis of (II) was carried out in a 55-100-mm-long quartz flow system with 5-8 mm inner diameter connected directly to an optical helium cryostat. The rate of introduction of the samples into the pyrolyzer was controlled using a valve made of glass and Teflon. The sample of (IIa) was evaporated in vacuum at ~20°C, while the sample of (IIb) was evaporated at 70-80°C.

The products of the pyrolysis of (IIa) and (IIb) were frozen in the cryostat at 12 K together with the approximately 1000-fold excess of argon on a copper mirror base located ~50 mm from the pyrolyzer exit. The base was cooled using a helium cryogenic system with Displex CSW-208R closed cycle. The layer of the argon matrix sufficient for recording strong IR spectra was sprayed over 1.5-2 h.

The IR spectra were taken at 400-3200 cm^{-1} by reflection of the beam off the mirror base. The beam twice passed through the matrix layer and was directed into the monochromator of an IKS-24-LOMO spectrophotometer by an optical attachment.

The copyrolysis of (IIb) with butadiene was carried out in a 110 × 7 mm quartz reactor in a nitrogen stream. The reaction products were condensed at 77 K and then analyzed by gas-liquid chromatography and chromato-mass spectrometry.

CONCLUSIONS

1. The matrix IR spectra of 2,3-dimethyl- and 2,3,7,8-tetramethyl-5-germaspiro[4.4]-nona-2,7-dienes in argon at 12 K are reported for the first time.

2. The possibility of the formation of the corresponding germylene, namely, 3,4-dimethylcyclopentene-3-germylene in the thermal decomposition of 2,3,7,8-tetramethyl-5-germaspiro[4.4]non-2,7-diene was demonstrated by chemical capture and matrix IR spectroscopy. This germylene undergoes complete decomposition under the vacuum pyrolysis conditions to metallic germanium and 2,3-dimethyl-1,3-butadiene.

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THERMAL TRANSFORMATIONS OF TETRAFLUOROETHYLENE IN THE PRESENCE

OF 1,3-CYCLOPENTADIENE AND HYDROGEN CHLORIDE

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According to Atkinson [1] and Butler [2], reversible carbene decomposition and cyclo-dimerization are the first steps of the thermolysis of tetrafluoroethylene (TPE), leading to hexafluoropropylene (HFP) and octafluorocyclobutane (OFCB). However, while the formation of OFCB by the cyclodimerization of TFE is not subject to doubt, various viewpoints exist relative to the formation of HFP. In particular, Atkinson [1] and Butler [2] proposed the formation of HFP upon the thermal decomposition of OFCB, while Politanskii [3] proposed that the formation of this compound by the thermal isomerization of hexafluoro-cyclopropane (HCP) is more likely.

$$ \text{cyclo-}C_4F_8 \xrightarrow[-:CF_2]{\Delta} CF_2{=}CFCF_3 \xleftarrow{\Delta} \text{cyclo-}C_3F_6 \rightleftarrows C_2F_4 + :CF_2 $$
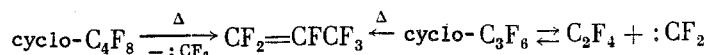
However, a study of the high-temperture transformations of HFCP in dilute argon mixtures did not show HFP in the reaction products [4]. Later conclusions concerning the intermediate formation of HFCP and its transformation to HFP on the basis of a study of the pyrolysis of $CHF_2CF_2CClF_2$ [5] and $CHClF_2$ [6] were unconvincing.

Hence, we have examined the possibility of the formation of HFP in thermal reactions due to the olefin—carbene isomerization of TFE and its subsequent recombination with di-fluorocarbene.

$$ C_2F_4 \xrightarrow{\Delta} :CFCF_3 \xrightarrow{:CF_2} CF_2 = CFCF_3 $$
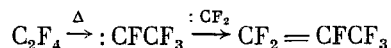
In order to check this hypothesis experimentally, experiments were carried out on the thermal transformation of TFE, including runs in the presence of CPD and HCl as efficient halocarbene traps [7, 8]. These experiments were carried out under comparable conditions.