2. The rearrangement of the radicals with a 1,3-migration of hydrogen during telomerization is much more sensitive to variation in the reaction temperature than in the case of the 1,5-transition of hydrogen.

## LITERATURE CITED

1. A. B. Terent'ev, N. S. Ikonnikov, V. I. Dostovalova, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR, 213, 1345 (1973).
2. N. S. Ikonnikov and A. B. Terent'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 371 (1975).
3. R. Kh. Freidlina, A. B. Terent'ev, and N. S. Ikonnikov, Dokl. Akad. Nauk SSSR, 193, 605 (1970).

---

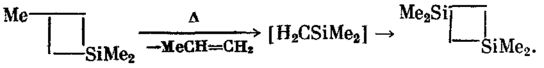
# NEW INFRARED SPECTROSCOPIC OBSERVATION OF 1,1-DIMETHYL-1-SILAETHYLENE IN AN ARGON MATRIX

A. K. Mal'tsev, V. N. Khabashesku, and O. M. Nefedov

UDC 543.422.4:547.1'128

Previously [1, 2], on the example of 1,1-dimethyl-1-silaethylene (I), which was obtained by the vacuum pyrolysis of 1,1-dimethyl-1-silacyclobutane (II), we were the first to accomplish the low-temperature matrix stabilization and IR-spectroscopic identification of a compound with an unsaturated carbon−silicon bond. Later were obtained the matrix IR spectra of trimethylsilaethylene, which was generated by photolysis directly in a trimethylsilyldiazomethane matrix [3, 4], and the mass spectrometric data for (I) in the gas phase [5].

The present study was undertaken for the purpose of obtaining additional proof for the IR spectrum of (I) via the independent preparation of this particle by the vacuum pyrolysis of 1,1,3-trimethyl-1-silacyclobutane (III). The preparation of the cyclic dimer of particle (I), namely 1,1,3,3-tetramethyl-1,3-disilacyclobutane (IV), and the isolation of the adducts of (I) with $C_2H_4$ [6], served as indirect proof for the intermediate formation of (I) during the thermal decomposition of (III).



(III) (I) (IV)

The starting compound (III) was synthesized as described in [7], and its IR spectrum was obtained at 77°K, and also in an argon matrix at 10°K. In the matrix spectrum of (III) were present bands that are characteristic for silacyclobutanes: 1124 $cm^{-1}$ (fan vibration of the $CH_2$ groups of the ring), 933.5, 887.3, and 861.8 $cm^{-1}$ (vibrations of the ring), and also for the $C-CH_3$ fragment at 1325, 1370, and 956 $cm^{-1}$.

The thermal dissociation products of (III) (780-860°C, $10^{-2}$-$10^{-4}$ torr) were frozen at 77°K, and also in an argon matrix at 10°K, by the method used in [1, 2]. Among the products, frozen at 77°K, were observed propylene and the cyclic dimer (IV); allyltrimethylsilane, whose formation was mentioned in [6], was not detected. Besides the bands of the undecomposed (III) compound and propylene, in the IR spectrum of the thermal decomposition products isolated in a matrix at 10°K (Fig. 1), were present intense bands at 643.0, 825.2, and 1003.5 $cm^{-1}$, which coincided exactly with the strongest bands of the unstable particle that was detected when the thermal decomposition of (II) was studied [1, 2]. This coinciding reliably proves the assignment of the indicated frequencies to particle (I), which is formed during thermal decomposition by the cleavage of an ethylene molecule from compound (II) [1, 2], or a propylene molecule from compound (III).

The synchronous disappearance of the bands at 643.0, 825.2, and 1003.5 $cm^{-1}$ occurred when the matrix was warmed from 10 to 40°K (which testifies that they belong to an unstable particle), whereas the bands of the starting (III) compound and $C_3H_6$ were retained in the spectrum. At the same time, an increase was observed in the intensity of the bands, belonging to the cyclic dimer (IV), at 934.6, 870.3, 821.0, and 693.0 $cm^{-1}$, which indicates that (I) dimerizes when the matrix is warmed. A similar increase in the amount of the (IV) dimer in the pyrolysis products was also observed in the case of raising the pressure and increasing the number of

---

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2152-2153, September, 1979. Original article submitted March 26, 1979.

0568-5230/79/2809-1980$07.50

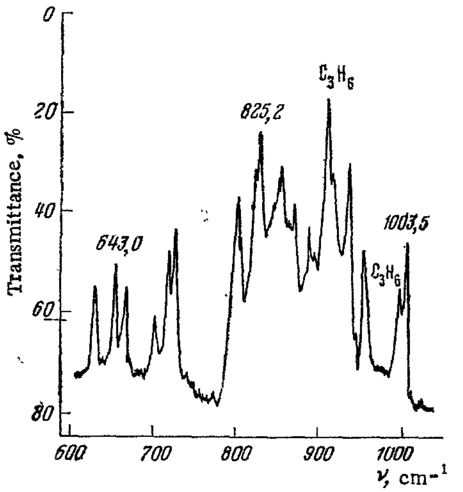


Fig. 1. Infrared spectrum (Ar, 10°K) of pyrolysis products of (III) (840°C, $5 \cdot 10^{-2}$ torr).

intermolecular collisions of (I) in the gas phase [1, 2]. The polymer $[(CH_3)_2SiCH_2]_x$ is formed when the dilution of the pyrolysis products of (III) (900-1000°) with argon is decreased [1, 2].

As a result, the obtained data confirm the fact that the 643.0, 825.2, and 1003.5 $cm^{-1}$ frequencies characterize the IR spectrum of 1,1-dimethyl-1-silaethylene (I) and make it possible to realize the spectroscopic identification of this particle in various reaction systems.

## EXPERIMENTAL

1,1,3-Trimethyl-1-silacyclobutane (III) was obtained by reacting MeMgI in ether with 1,1-dichloro-3-methyl-1-silacyclobutane [7], which was synthesized by the cyclization of $Cl_3SiCH_2CHMeCH_2Cl$ [8] in the presence of Mg. Compound (III) was purified by a triple freezing in a high vacuum; the purity of the sample was confirmed by mass spectrometry.

The vacuum pyrolysis of (III) was run in a quartz flow reactor, which was connected to a helium cryostat [1, 2]. The IR spectra were recorded on a Hitachi–Perkin–Elmer-225 spectrometer in the range 4000-450 $cm^{-1}$.

## CONCLUSIONS

The pyrolysis of 1,1,3-trimethyl-1-silacyclobutane in vacuo gave 1,1-dimethyl-1-silaethylene, which was stabilized in an argon matrix at 10°K, and its most intense IR absorption bands were recorded: 643.0, 825.2, 1003.5 $cm^{-1}$, which coincide exactly with the IR spectrum of the same particle when obtained by the pyrolysis of 1,1-dimethyl-1-silacyclobutane.

## LITERATURE CITED

1. A. K. Mal'tsev, V. N. Khabashesku, and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., 1193 (1976).
2. A. K. Mal'tsev, V. N. Khabashesku, and O. M. Nefedov, Dokl. Akad. Nauk SSSR, 233, 421 (1977).
3. O. L. Chapman, C. C. Chang, J. Kolc, M. E. Jemg, J. A. Lowe, T. J. Barton, and M. L. Tumey, J. Am. Chem. Soc., 98, 7844 (1976).
4. M. R. Chedekel, M. Skoglund, R. L. Kreeger, and H. Shechter, J. Am. Chem. Soc., 98, 7846 (1976).
5. L. E. Gusel'nikov, K. S. Konobeevskii, V. M. Vdovin, and N. S. Nametkin, Dokl. Akad. Nauk SSSR, 235, 1086 (1977).
6. N. S. Nametkin, R. L. Ushakova, L. E. Gusel'nikov, E. D. Babich, and V. M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., 1676 (1970).
7. J. Dubac, P. Mazerolles, and M. Joly, Unpublished data.
8. J. W. Ryan, G. K. Menzie, and J. L. Speier, J. Am. Chem. Soc., 82, 3601 (1960).