singlets at 9.62 (IVa) and 9.85 ppm (IVb) in the spectra is not dependent on the temperature of exposure of the samples. These signals do not belong to the aldehyde group protons since, in the ^{13}C spectrum NMR spectrum, the signal of the formyl group carbon atom is absent. The weak-field singlet observed in the ^{1}H NMR spectra can be ascribed to the 1-H proton (the signal is broadened due to long range spin–spin coupling with the 3-H proton, $^{4}J = 1.4$ Hz).

Compound IVa, yield 30%, mp >300°C. IR spectrum (mineral oil), ν: 3110 (C—H), 1620, 1605, 1585, 1520 (C═N, C═O, CH═CH, NO_2), 1305 cm^{-1} (NO_2). UV spectrum ($CHCl_3$), λ_{max} (log ε): 250 (4.27), 340 nm (3.85). Mass spectrum, m/z: 456 (M^+), 426 $[M - NO]^+$, 398 $[M - CO]^+$. ^{1}H NMR spectrum, (DMSO-D_6): 1.48 (t, 3H, CH_3), 4.51 (quart., 2H, CH_2), 7.72-8.14 (m, 6H), 8.26 (d, 1H), 8.37 (d, 1H), 8.49 (d, 1H), 8.63 (d, 1H), 9.62 ppm (s, 1H).

Compound IVb, yield 40%, mp >350°C (from DMFA). IR spectrum (mineral oil), ν: 3260 N—H), 3090 (C—H), 1640, 1595, 1510 (C═N, C═O, CH═CH, NO_2), 1335 cm^{-1}ν(NO_2). ^{1}H NMR spectrum (DMSO-D_6): 7.58 (t, 1H), 7.73-7.91 (m, 5H), 7.95 (t, 1H), 8.29 (d, 1H), 8.50 (d, 1H), 8.75 (d, 1H), 9.85 ppm (s, 1H). ^{13}C NMR spectrum (DMSO-D_6), δ: 167.4, 163.8, 142.5, 139.9, 138.8, 136.1, 134.7, 133.0, 131.5, 129.9, 128.4, 127.8, 126.4, 126.1, 125.2, 125.1, 119.4, 117.7, 117.6 ppm.

These data of the elemental analysis of compounds IVa, b correspond to the calculated ones.

LITERATURE CITED

1. V. G. Granik. Usp. Khim., 49, 651 (1984).
2. A. G. Cook (ed.), Enamines: Synthesis, Structure and Reactions, Marcel Dekker, New York—London (1969), p. 101.

REARRANGEMENT OF 2-DIMETHYLSILYLTETRAHYDROPYRAN INTO 2,2-DIMETHYL-1-OXA-2-SILACYCLOHEPTANE

É. Lukevits, L. I. Borisova,
and V. N. Gevorgyan

UDC 547.245'517.07

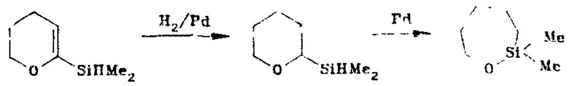
It has previously been shown [1] that under the conditions of liquid-phase catalytic hydrogenation (1 atm H_2, 25°C, 0.1 mole/liter solution in hexane, 5% Pd/Al_2O_3 or Pd/C, [I]:[Pd] = 100:1), 2-dimethylsilyl-4,5-dihydrofuran (I) undergoes several successive transformations: It is hydrogenated into 2-dimethylsilyltetrahydrofuran (II), and after the complete conversion of the initial dihydrofuran I, the tetrahydro-derivative II readily and quantitatively (15 min) rearranges into the six-membered 2,2-dimethyl-1-oxa-2-silacyclohexane (III) with the silicon atom entering the ring. The II → III transformation also proceeds in the absence of hydrogen, when silane II is contacted with a supported palladium catalyst [1].

To clarify the influence of the ring size on the possible occurrence of such a rearrangement, we studied the catalytic transformations of 2-dimethylsilyl-5,6-dihydro-4H-pyran (IV), obtained by treating 2-lithium-5,6-dihydro-4H-pyran with dimethylchlorosilane at −50°C in a 1:1 tetrahydrofuran—hexane solvent mixture.

Under conditions similar to those for compound I, silane IV readily (60 min, yield 95%, according to GLC) hydrogenates into 2-dimethylsilyltetrahydropyran (V), which then rearranges into a seven membered 2,2-dimethyl-1-oxa-2-silylcycloheptane (VI):

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 136-137, January, 1987. Original article submitted July 9, 1986.

0009-3122/87/2301-0114$12.50



IV V VI

The V → VI transformation proceeds much more slowly (25°C, 6 h, yield 70%) than in the case of the II → III transformation, which is probably due to the higher stability of the six-membered systems, compared with the five-membered systems. The structure of the compounds obtained conforms completely with the IR, PMR, and mass spectral data.

LITERATURE CITED

1. É. Lukevits (Lukevics), V. Gevorgyan, Y. Goldberg, J. Popelis, M. Gavars, A. Gaukhman, and M. Shimanskaya (Shimanska), Heterocycles, 22, 987 (1984).