SELECTIVE LASER-INDUCED PHOTOCHEMICAL CHLORINATION OF METHYLTRICHLOROGERMANE AND METHYLTRICHLOROSILANE

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UDC 541.14:542.944:547.246'131:547.245'131

$\mathrm{ClCH_2GeCl_3}$ (I) holds interest as a starting reagent for the synthesis of many organogermanium compounds, but its preparation has been difficult.

The reported method for the preparation of (I) by the photochemical chlorination of $\mathrm{CH_2GeCl_3}$ (II) upon UV irradiation from a mercury lamp is nonselective even under conditions for the removal of (I) from the reaction zone [1] and leads to the formation of considerable amounts of polychlorinated products with the yield of (I) $\leq$ 18-20% [2, 3]. $\mathrm{ClCH_2SiCl_3}$ (III) was obtained under these conditions in 53% yield [1].

We have found that the use of an LGI-21 flash nitrogen laser (4-mW mean output, 1.5-kW flash output, and 100 Hz frequency) permits the selective chlorination of (II) to (I) in 48% yield. This procedure permitted a significant improvement in the chlorination of $\mathrm{CH_3SiCl_3}$ (IV) to (III) in 70% yield.

The products of the chlorination of (II) were shown by gas–liquid chromatography and PMR spectroscopy to contain 72% (I), 17% $\mathrm{Cl_2CHGeCl_3}$, and 11% $\mathrm{Cl_3CGeCl_3}$, while the products of the chlorination of (VI) were found to contain 94% (III), 5% $\mathrm{Cl_2CHSiCl_3}$, and 1% $\mathrm{Cl_3CSiCl_3}$.

This enhancement in the chlorination selectivity is apparently related to the replacement of hard radiation characteristic of the mercury lamp (2400-5800 Å) by the more selective emission of the nitrogen laser (3370 Å) which virtually coincides with the maximum for the absorption of chlorine in the vicinity of 3300 Å, providing for milder and more selective chlorination.

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REGIOSPECIFIC γ-OXYGENATION OF ALKANESULFONAMIDES

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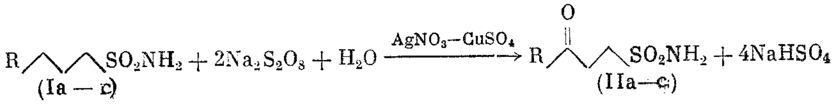
UDC 542.97:547.269.352

N-Methylsulfonylalkylamines upon the action of $\mathrm{Na_2S_2O_8-CuCl_2}$ regiospecifically cyclize to give N-methylsulfonylpyrrolidines [1], while alkanesulfonamides undergo chlorination with the formation of 3- and 4-chloroalkanesulfonamides with considerable predominance of the 3-chloro products [2].

We have found that the $\mathrm{Na_2S_2O_8-CuSO_4-AgNO_3}$ system with 1:0.2:0.15 component ratio causes the regiospecific oxidative Γ-oxygenation of N-unsubstituted alkanesulfonamides (I) at the nonactivated C^3 atom to form 3-oxoalkanesulfonamides (II):

Institute of General Physics, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1448-1449, June, 1986. Original article submitted January 16, 1986.

Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1449-1450, June, 1986. Original article submitted January 21, 1986.



R=CH_3(a), C_2H_5 (b), C_3H_7 (c).

Compound (Ia) undergoes 46% conversion to give (IIa) formed in 90% yield relative to converted (Ia). Compound (Ib) undergoes 30% conversion to give (IIb) formed in 90% yield relative to converted (Ib). Compound (Ic) undergoes 20% conversion to (IIc) formed in 100% yield relative to converted (Ic). The reaction mechanism apparently entails the generation of sulfonylamidyl radicals $R(CH_2)_3SO_2\dot{N}H$ which undergo regiospecific rearrangement with 1,5-hydrogen migration to transfer the reaction site to the nonactivated C^3 atom. Compound (II) is formed upon the oxidation of the rearranged radicals $R\dot{C}H(CH_2)_2SO_2NH_2$, probably through intermediate 3-hydroxysulfonamides $RCH(OH)(CH_2)_2SO_2NH_2$. We previously studied the long-range oxygenation of ketones in the $Na_2S_2O_8-FeSO_4$ system to form 1,4- and 1,5-diketones [3].

A sample of 0.5 g (0.002 mole) $CuSO_4 \cdot 5H_2O$ and 0.26 g (0.0015 mole) $AgNO_3$ were added to a suspension of 1.37 g (0.01 mole) (Ia) in 20 ml water and heated to 85-90°C. Then, a solution of 2.38 g (0.01 mole) $Na_2S_2O_8$ in 20 ml water was added dropwise. The reaction mixture was stirred for 5 h at 90°C, cooled, and extracted with three 30-ml portions of ether. The extract was dried over Na_2SO_4 and evaporated. The mixture of (IIa) and (Ia) obtained was treated with 2,4-dinitrophenylhydrazine, and the 2,4-dinitrophenylhydrazone of (IIa) was isolated with mp 177.5-179°C (from ethanol). Found: C 36.69; H 4.08; N 21.13; S 9.75%. Calculated for $C_{10}H_{13}N_5O_6S$: C 36.25; H 3.96; N 21.14; S 9.67%. Mass spectrum: m/z 331 (M^+). Reductive hydrolysis [4] regenerated (IIa) from its 2,4-dinitrophenylhydrazone as an oil. PMR spectrum in $CDCl_3$ at 250 MHz (δ, ppm, TMS): 2.29 s (3H), 3.22 s (4H). ^{13}C NMR spectrum in $CDCl_3$ (δ, ppm, TMS): 21.717 q (CH_3), 37.920 t and 44.382 t (CH_2CH_2), 183.24 s (C=O). Mass spectrum: m/z 151 (M^+).

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$[(CH_3)_3NH][Rh_2I_7]$ AS A CATALYST FOR THE CONVERSION OF CARBON MONOXIDE AND CARBONYLATION OF METHANOL

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UDC 542.91:541.128:541.49:546.97

Rhodium compounds are catalysts for several reactions involving carbon monoxide [1, 2]. In the present work, we report the synthesis of a catalytically active rhodium complex prepared by the reaction of a solution of $[(CH_3)_3NH]_3[RhCl_6] \cdot 3H_2O$ (I) in DMF acidified with hydrochloric acid, with analytical-grade (45.1%) hydriodic acid upon heating. We used 2 g (I), 100 ml DMF, 5 ml hydrochloric acid, and 25 ml hydriodic acid. These components were heated at 80-100°C for 30 min. The complex product was isolated as a black powder, washed on a filter with ethanol and ether, and dried at 20°C (0.1 mm) for 3 h. The yield was 90%. The IR spectral and elemental analysis data indicate that this complex is $[(CH_3)_3NH][Rh_2I_7]$ (II). Found: Rh 17.7; C 3.4; H 1.3; N 1.5; I 76.0%. Calculated for $Rh_2C_3H_{10}NI_7$: Rh 17.84; C 3.12; H 0.86; N 1.21; I 76.97% IR spectrum (ν, cm^{-1}): 800 (CN), 1010 (Rh), 1450 (CH_3), 1595 (NH), 3085 (NH). Complex (II) decomposes without melting above 300°C, is nonhygroscopic, and is soluble in DMF.

Division of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, p. 1450, June, 1986. Original article submitted January 31, 1986.