EXPERIMENTAL

The proton-coupled ^{13}C NMR spectra in $CDCl_3$ were taken on a Tesla BS-567A spectrometer at 25.1 MHz. The assignment of the direct $^{13}C-^{1}H$ coupling constants of the β-carbon of the vinyl group was carried out using satellite signals in the PMR spectra. The error in the coupling constants was not greater than ±0.1 Hz.

CONCLUSIONS

The $^{13}C-^{1}H$ direct coupling constants in the vinyl group of 1-vinylpyrazoles are stereospecific and vary with change in the conformer ratio.

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ADDITION OF POLYHALOALKANES TO 1-VINYLSILATRANE

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UDC 542.955:547.412:547.345

In our previous work [1], we showed that the homolytic reaction of 1-allylsilatrane with polyhaloalkanes gives 1-halosilatranes:

$$R^{Hal}X + CH_2{=}CHCH_2Si(OCH_2CH_2)_3N \rightarrow XSi(OCH_2CH_2)_3N + CH_2 = \\ = CHCH_2{-}R^{Hal}$$

$$R^{Hal}X = CCl_4,\ CCl_3Br,\ C_3F_7I.$$

In the present work, we discovered the addition of polyhaloalkanes to 1-vinylsilatranes both upon photochemical initiation and in the presence of peroxides:

$$R^{Hal}X + CH_2{=}CHSi(OCH_2CH_2)_3N \rightarrow R^{Hal}CH_2CH(X)Si(OCH_2CH_2)_3N$$

$$R^{Hal}X = CHCl_3,\ CCl_3Br,\ CF_3I,\ C_3F_7I.$$

The ease of this reaction, its regiospecificity and high product yields permit us to recommend it as a preparative method for the synthesis of 1-polyhaloalkylsilatranes.

EXPERIMENTAL

1-(3,3,3-Trichloropropyl)silatrane (I). A solution of 2 g (10 mmoles) 1-vinylsilatrane and 0.1 g benzoyl peroxide in 100 ml $CHCl_3$ was heated in a sealed ampul for 1 h at 100°C. The solution was evaporated to half volume. The precipitate formed was recrystal-

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*Deceased.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 204-205, January, 1987. Original article submitted March 10, 1986.

0568-5230/87/3601-0182$12.50

lized from CCl_4 to give 2.85 g (89%) (I) as colorless crystals, mp 206-207°C, M^+ m/z 319. ^1H NMR spectrum in $CDCl_3$ at 100 MHz (δ, ppm): 3.78 t (OCH_2), 2.83 t (NCH_2), 2.60 m (Cl_3CCH_2), 1-0.6 m (CH_2Si). Found: C 33.60; H 5.11; Cl 33.01; Si 8.54%. Calculated for $C_9H_{16}Cl_3NO_3Si$: C 33.71; H 5.03; Cl 33.17; Si 8.76%.

1-(3,3,3-Trichloro-1-bromopropyl)silatrane (II). A mixture of 2 g (10 mmoles) 1-vinylsilatrane, 1.98 g (10 mmoles) Cl_3CBr, and 0.1 g benzoyl peroxide in 20 ml $CHCl_3$ was heated in a sealed ampul for 6 h at 80°C. The reaction mixture was poured into 50 ml dry hexane. The precipitate was filtered off, dried and sublimed in vacuum to give 3.42 g (85.2%) (II) as colorless crystals, mp 175°C. ^1H NMR spectrum in $CDCl_3$ (δ, ppm): 3.86 t (OCH_2), 3.43 m (Cl_3CCH_2CHBr), 2.90 t (NCH_2). Found: C 27.00; H 3.81; Br 19.70; Cl 26.56; Si 6.98%. Calculated for $C_9H_{15}BrCl_3NO_3Si$: C 27.06; H 3.75; Br 19.8; Cl 26.70; Si 7.01%.

1-(3,3,3-Trifluoro-1-iodopropyl)silatrane (III). A solution of 3 g (14.9 mmoles) 1-vinylsilatrane and 3.9 g (20 mmoles) trifluoroiodomethane in a mixture of 50 ml CCl_4 and 10 ml $CHCl_3$ was maintained for 30 h in a sealed ampul in diffuse sunlight. The precipitate formed was recrystallized from 1:1.5 chloroform-heptane, washed with hexane, and dried to give 94.5% (III) as colorless crystals, mp 119.5-120.5°C. ^1H NMR spectrum in $CDCl_3$ (δ, ppm): 3.84 t (OCH_2), 2.89 t (NCH_2). Found: C 27.49; H 4.03; F 14.04, I 31.85; Si 6.80%. Calculated for $C_9H_{15}F_3INO_3Si$: C 27.31; H 3.81; F 14.35; I 31.95; Si 7.06%.

1-(2-Perfluoropropyl-1-iodoethyl)silatrane (IV). A solution of 1.7 g (8.4 mmoles) 1-vinylsilatrane and 4.1 g (14 mmoles) perfluoropropyl iodide in 30 ml $CHCl_3$ in a sealed Pyrex ampul and irradiated for 3 h using a PRK-2 UV lamp to give 98.1% (IV) as colorless crystals, mp 137-138°C (from $CHCl_3$–hexane). ^1H NMR spectrum in $CDCl_3$ (δ, ppm): 3.85 t (OCH_2), 2.90 t (NCH_2). Found: C 26.53; H 3.03; I 26.70; Si 5.73%. Calculated for $C_{11}H_{15}F_7INO_3Si$: C 26.57; H 3.04; I 26.58; Si 5.65%.

CONCLUSIONS

Polyhaloalkanes react readily with 1-vinylsilatrane upon photoinitiation or in the presence of peroxides with almost quantitative formation of the products of the regiospecific addition of the perhaloalkyl radical to the terminal carbon atom of the vinyl group.

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