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CYCLOADDITION OF HETARENESULFENYL CHLORIDES TO 3,4-DIHYDROPYRAN

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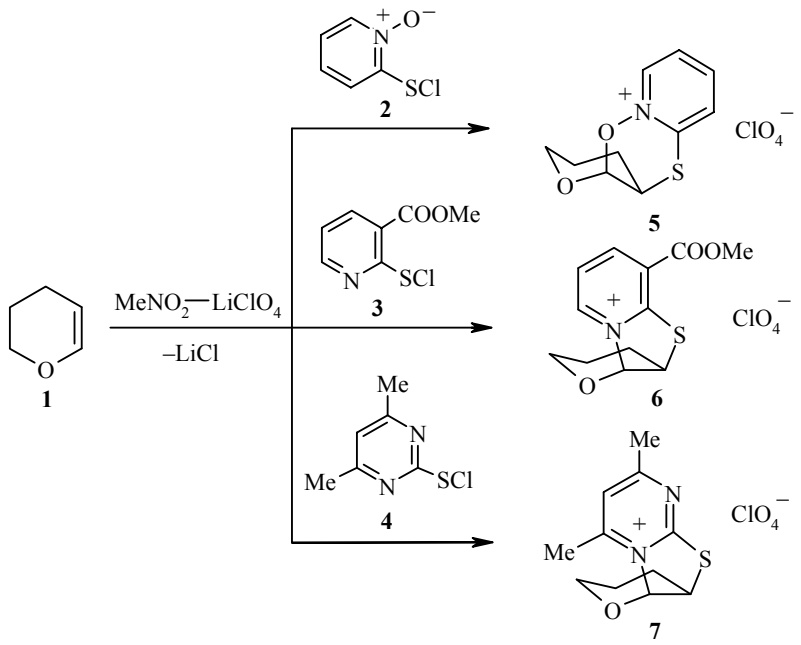
Reactions of 3,4-dihydropyran **1** with electrophilic reagents, including sulfenyl chlorides, usually lead to 1,2-addition products [1-4].

We have shown that the lithium perchlorate–nitromethane system stimulates polar cycloaddition of 2-chlorosulfenyl-1-pyridine-1-oxide (**2**), 3-methoxycarbonyl-2-pyridinesulfenyl chloride (**3**), and 4,6-dimethyl-2-pyrimidinesulfenyl chloride (**4**) at the multiple bond of the unsaturated ether **1**, where ring closure occurs as a result of nucleophilic participation of the oxygen or nitrogen atom of the thiohetaryl moiety of the reagent to form tricyclic compounds **5-7**. Judging from the ^{1}H NMR spectra, all the studied reactions occur regiospecifically and stereospecifically; in the spectra of compounds **5-7**, the spin–spin coupling constant for the proton of the CHO moiety is in the range 2.5-5.1 Hz while the width of the signal from the proton of the CHS moiety (calculating from the outside peaks) is 14.0-18.6 Hz. Taking into account the known criteria for determining the stereochemistry of addition to dihydropyran [1] and also the results we obtained earlier [5, 6], we may assume that formation of the condensed systems **5-7** occurs according to a *cis*-cycloaddition scheme.



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The ^1H and ^{13}C NMR spectra were taken on a Bruker DRX-500 (500 MHz and 125 MHz respectively) in DMSO-d_6; the mass spectra were taken on a Finnigan MAT INCOS 50 quadrupole mass spectrometer (ionization energy 70 eV); the IR spectra were taken on a Specord M-80.

Reactions of 3,4-Dihydropyran 1 with Sulfenyl Chlorides 2-4. A solution of $LiClO_4$ (1.06 g, 10 mmol) in nitromethane (30 ml) and a solution of sulfenyl chloride **2-4** (10 mmol) in nitromethane (10 ml) were added to a solution of compound **1** (0.84 g, 10 mmol) in nitromethane (20 ml) at 20°C. After 10 min, the LiCl precipitate was filtered out and the filtrate was evaporated down under vacuum. After recrystallization of the residue from methylene chloride, compounds **5-7** were obtained.

***cis*-3,4,4a-11a-Tetrahydro-2H-pyrano[3,2-*e*]pyrido[1,2-*b*][1,4,2]oxathiazin-10-ium Perchlorate (5).** Yield 65%; mp 151-153°C. IR spectrum (KBr), ν, cm^{-1}: 1604, 1564, 1464, 1280, 1154, 1084, 832, 712. ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.10 (1H, d, ^3J = 6.7, Het); 8.22 (2H, m, Het); 7.75 (1H, dt, ^3J = 7.2, *J* = 2.0, Het); 6.22 (1H, d, ^3J = 2.5, CHO); 4.21 (1H, m, *J* = 15.6, CHS); 3.95 (2H, m, CH_2O); 2.23 and 1.77 (4H, m, $2CH_2$). ^{13}C NMR spectrum, δ, ppm: 149.21, 140.93, 140.53, 127.12, 123.27 (CHet); 98.52 (CHO_2); 64.91 (CH_2O); 41.15 (CHS, in $CDCl_3$); 26.36 and 21.65 ($2CH_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 209 [M^+–$HClO_4$] (2); 192 (5); 162 (47); 127 (9); 111 (67); 78 (100); 67 (47); 51 (55). Found, %: C 38.32; H 3.76; N 4.41; S 10.47. $C_{10}H_{12}ClNO_6S$. Calculated, %: C 38.78; H 3.91; N 4.52; S 10.35.

***cis*-6-Methoxycarbonyl-3,4,4a-10a-tetrahydro-2H-pyrano[2',3':4,5][1,3]thiazolo[3,2-*a*]pyridin-10-ium Perchlorate (6).** Yield 87%; mp 84-86°C. IR spectrum (shoulder), ν, cm^{-1}: 1716, 1598, 1576, 1456, 1436, 1418, 1304, 1146, 1088, 924, 878, 828, 766. ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.10 (1H, d, ^3J = 6.3, Het); 8.92 (1H, d, ^3J = 7.5, Het); 7.97 (1H, t, ^3J = 6.3, ^3J = 7.5, Het); 6.54 (1H, d, ^3J = 5.2, CHN^+); 4.36 (1H, m, *J* = 18.6, CHS); 4.02 (3H, s, OCH_3); 3.92 and 3.75 (2H, m, CH_2O); 2.27 and 1.95 (4H, m, $2CH_2$). Mass spectrum, *m*/*z* (I_{rel}, %): 251 [M^+–$HClO_4$] (25); 220 (98); 194 (14); 111 (8); 78 (12); 60 (15); 50 (100). Found, %: C 41.45; H 4.11; N 3.85; S 9.27. $C_{12}H_{14}ClNO_7S$. Calculated, %: C 40.97; H 4.01; N 3.98; S 9.11.

***cis*-2,4-Dimethyl-7,8,9,9a-tetrahydro-5H-pyrano[2',3':4,5][1,3]thiazolo[3,2-*a*]pyrimidin-5-ium Perchlorate (7).** Yield 45%; mp 147-149°C (decomposes). IR spectrum, (KBr), ν, cm^{-1}: 1610, 1536, 1448, 1380, 1280, 1084, 1040, 918, 672. ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.81 (1H, s, Het); 6.63 (1H, d, ^3J = 4.4, CHN^+); 4.59 (1H, m, *J* = 14.0, CHS); 3.90 and 3.78 (2H, m, CH_2O); 2.74 and 2.63 (6H, s, $2CH_3$); 2.37 and 1.77 (4H, m, $2CH_2$). ^{13}C NMR spectrum, δ, ppm: 177.51, 170.38, 161.45, 119.35 (C_{Het}); 89.93 (CHN^+); 64.37 (CH_2O); 43.45 (CHS); 24.80 and 23.35 ($2CH_2$); 19.03 and 18.64 ($2CH_3$). Mass spectrum, *m*/*z* (I_{rel}, %): 222 [M^+–$HClO_4$] (33); 192 (100); 108 (42); 67 (63); 53 (25). Found, %: C 40.69; H 4.77; N 8.51; S 10.11. $C_{11}H_{15}ClN_2O_5S$. Calculated, %: C 40.39; H 4.68; N 8.68; S 10.93.

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