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ANNELATION OF THE NORBORNENE SKELETON IN REACTIONS OF HETARENE SULFENYL CHLORIDES WITH NORBORNADIENE

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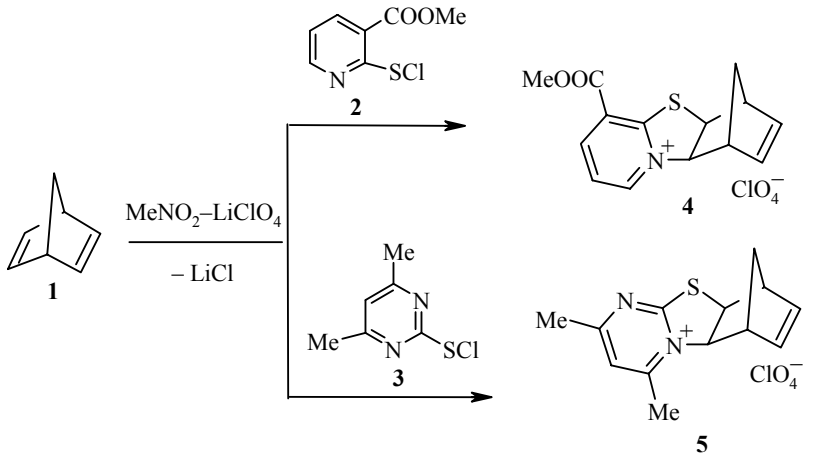
Reaction of norbornadiene (**1**) with arenesulfenyl chlorides occurs nonselectively and leads to a mixture of isomeric β-chlorosulfides and rearrangement products [1, 2].

We have established that the only direction for the reactions of diene **1** with 3-methoxycarbonyl-2-pyridinesulfenyl chloride (**2**) and 4,6-dimethyl-2-pyrimidinesulfenyl chloride (**3**) in nitromethane in the presence of lithium perchlorate at 20°C is stereospecific cycloaddition of the sulfenylating reagent at the multiple bond, with closure of the ring by the nitrogen atom of the thiohetaryl moiety and formation of condensed systems **4, 5** in 87% and 75% yields respectively.



In the ^{1}H NMR spectra of compounds **4,5**, the signals from the protons of the CHS and CHN^+ moieties appear as doublets with spin–spin coupling constant 7.9-8.0 Hz, which suggests an *exo–cis* configuration for these products [3, 4].

The ^{1}H and ^{13}C NMR spectra were taken on a Bruker DRX-500 (500 MHz and 125 MHz respectively) in DMSO-d_6.

Sulfenylation of Diene 1 (General Procedure). A solution of $LiClO_4$ (1.06 g, 10 mmol) in nitromethane (30 ml) and a solution of sulfenyl chloride **2** or **3** (10 mmol) in nitromethane (10 ml) were added to a solution of compound **1** (0.92 g, 10 mmol) in nitromethane (20 ml) at 20°C. After 10 min, the LiCl

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precipitate was filtered out and the filtrate was evaporated under vacuum. After recrystallization of the residue from methylene chloride, we obtained compounds **4, 5**.

exo-**7-Methoxycarbonyl-9-thia-3-azoniatetracyclo[9.2.1.0^{2,10}0^{3,8}]tetradeca-3(8),4,6,12-tetraene Perchlorate (4).** Mp 137-139°C. IR spectrum (KBr), ν, cm^{-1}: 1726, 1610, 1560, 1452, 1304, 1144, 766; 1094 (ClO_4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.20 (1H, d, ^3J = 6.1, Het); 8.81 (1H, d, ^3J = 7.9, Het); 7.88 (1H, t, ^3J = 6.1, ^3J = 7.9, Het); 6.39 (1H, dd, *J* = 5.3, *J* = 2.7, HC=); 6.31 (1H, dd, *J* = 5.3, *J* = 2.7, HC=); 5.53 (1H, d, ^3J = 8.0, CHN^+); 4.23 (1H, d, ^3J = 8.0, CHS); 3.99 (3H, s, OCH_3); 3.65 (1H, br. s, C^{1}H); 3.28 (1H, br. s, C^{11}H); 1.73 and 1.64 (2H, d and d, ^2J = 10.4, CH_2). ^{13}C NMR spectrum, δ, ppm: 164.31 (C=O); 162.40, 145.51, 145.28, 124.22, 122.54 (C_{Het}); 139.70, 135.60 (HC=); 77.74 (CHN^+); 53.51 (CHS); 52.25 (CH_3O); 49.22 (C^1); 48.99 (C^{11}); 41.50 (CH_2). Found, %: C 46.95; H 3.81; N 3.75; S 8.72. $C_{14}H_{14}ClNO_6S$. Calculated, %: C 46.74; H 3.92; N 3.89; S 8.91.

exo-**4,6-Dimethyl-9-thia-3-azonia-7-azatetracyclo[9.2.1.0^{2,10}0^{3,8}]tetradeca-3(8),4,6,12-tetraene Perchlorate (5).** Mp 84-86°C. IR spectrum (KBr), ν, cm^{-1}: 1610, 1528, 1428, 1376, 1276, 748; 1092 (ClO4). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.62 (1H, s, Het); 6.33 (2H, td, *J* = 6.0, *J* = 2.8, HC=); 5.27 (1H, d, ^3J = 7.9, CHN^+); 4.19 (1H, d, ^3J = 7.9, CHS); 3.60 (1H, br. s, C^{1}H); 3.26 (1H, br. s, C^{11}H); 2.83 and 2.59 (6H, s and s, $2CH_3$); 1.93 and 1.74 (2H, d and d, ^2J = 11.3, CH_2). Found, %: C 47.03; H 4.65; N 8.31; S 9.48. $C_{13}H_{15}ClN_2O_4S$. Calculated, %: C 47.20; H 4.57; N 8.47; S 9.69.

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