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CYCLOADDITION OF 3-CYANO-4,6-DIMETHYL-2-PYRIDINESULFENYL CHLORIDE TO NORBORNENE

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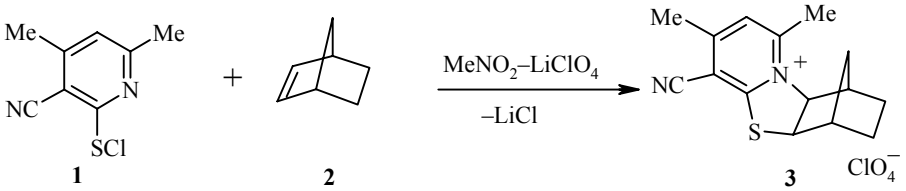
Depending on the nature of the reagent, cycloaddition to norbornene leads to compounds with retention of the structure of the starting substrate or rearrangement products [1-5].

We have found that the reaction of 3-cyano-4,6-dimethyl-2-pyridinesulfenyl chloride (**1**) with norbornene (**2**) in nitromethane in the presence of lithium perchlorate proceeds without change in the carbon skeleton of the alkene and leads to the formation of a tetracyclic system **3** in 74% yield, namely, the product of the *exo-cis*-cycloaddition of the sulfenylating reagent at the double bond with ring closure by the pyridine nitrogen atom. We should note that the ordinary β-chlorosulfide obtained in the reaction of sulfenyl chloride **1** with alkene **2** in chloroform is not transformed in the lithium perchlorate–nitromethane system. Thus, the formation of heterocycle **3** occurs directly during the Ad_E-process.



1 **2** **3**

The ^{1}H NMR spectrum of **3** shows protons for the CHS fragment at δ 4.42 ppm and CHN^+ fragment at δ 5.47 ppm. These signals appear as doublets with ^3J = 8.3 Hz, which indicates the *endo* arrangement of these protons [1, 2, 6, 7].

***exo*-7-Cyano-4,6-dimethyl-9-thia-3-azoniatetracyclo[9.2.1.0^{2,10}0^{3,8}]tetradeca-3(8),4,6-triene Perchlorate (3).** A solution of $LiClO_4$ (1.06 g, 10 mmol) in nitromethane (30 ml) and a solution of alkene **2** (0.94 g, 10 mmol) were added to a solution of sulfenyl chloride **1** (1.98 g, 10 mmol) in nitromethane (20 ml) at 20°C and stirred. The mixture was left stand until LiCl precipitated out. After 30 min, the precipitate was filtered off and the filtrate was evaporated in vacuum. Recrystallization of the residue from methylene chloride gave 2.64 g (74%) of **3**; mp 200-202°C. IR spectrum (vaseline oil), ν, cm^{-1}: 2260 (C≡N), 1645, 1572 (Het), 1098 (ClO_4). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm, *J* (Hz): 7.68 (1H, Het); 5.47 (1H, d, ^3J = 8.3, CHN^+); 4.42 (1H, d, CHS); 2.92 (1H, d, ^3J = 3.2, H–$C_{(1)}$); 2.82 and 2.60 (6H, s and s, 2CH_3); 2.48 (1H, m, H-$C_{(11)}$); 1.86 (1H,

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d, ^{2}J = 10.6, H-*anti*-$C_{(14)}$); 1.63 (1H, m, ^{3}J = 4.5, H–$C_{(13)}$); 1.51 (1H, m, H–$C_{(12)}$); 1.41 (1H, d, H-*syn*-$C_{(14)}$). ^{13}C NMR spectrum (CD_3CN, 50.3 MHz): 162.67, 160.52, 157.68, 126.97, 105.04 (Het), 113.02 (CN), 80.67 (CHN^+), 53.34 (CHS), 45.50 ($C_{(11)}$), 44.44 ($C_{(1)}$), 33.66 ($C_{(14)}$), 27.04 ($C_{(13)}$), 26.02 ($C_{(12)}$), 21.49 (CH_3), 21.26 (CH_3). Found, %: C 50.27; H 4.69; N 7.74; S 8.81. $C_{15}H_{17}ClN_2O_4S$. Calculated, %: C 50.49; H 4.80; N 7.85; S 8.98. Mass spectrum, *m/z* (I_{rel}, %): 256 [M^+ - ClO_4] (87), 241 (25), 223 (47), 215 (57), 189 (45); 165 (88), 91 (100), 77 (93).

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