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# UNUSUAL TRANSFORMATION IN THE CYCLOADDITION OF AROYLIMINOCHLORO-METHANESULFENYL CHLORIDES TO 3,3-DIMETHYL-2-BUTENE

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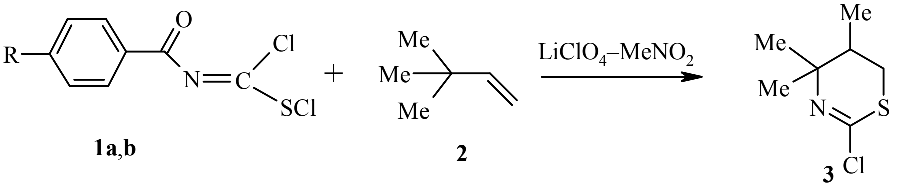
Fragment R is usually retained in the product structure upon heterocycle formation in the reactions of N-substituted iminochloromethanesulfenyl chlorides RN=CClSCl with alkenes [1-6].

We have found that a sequence of transformations occurs in the reaction of N-benzoyl- (**1a**) and N-4-chlorobenzoyliminochloromethanesulfenyl (**1b**) chlorides with 3,3-dimethyl-2-butene (**2**) in nitromethane in the presence of lithium perchlorate, involving addition of the sulfur-containing electrophile at the double bond, 1,2-shift of methyl group, ring closure with nucleophilic participation of the nitrogen atom of the sulfenyl fragment, and elimination of the aroyl group. Heterocyclization product **3** is formed in 57% yield (in the case of sulfenyl chloride **1a**) and 52% yield (in the case of **1b**).



**1a**,**b** **2** **3**

**1 a** R = H, **b** R = Cl

**2-Chloro-4,4,5-trimethyl-5,6-dihydro-4H-1,3-thiazine (3).** Sample of lithium perchlorate (30 mmol) in nitromethane (40 ml) and solution of alkene **2** (10 mmol) in nitromethane (10 ml) were added with stirring to solution of sulfenyl chloride **1a** or **1b** (10 mmol) in nitromethane (100 ml) at 20°C. After 30 min, the solvent was distilled off in vacuum. The residue was dissolved in methylene chloride (200 ml). The precipitates of LiCl and $LiClO_4$ were filtered off and washed repeatedly on the filter with methylene chloride. The filtrate was evaporated in vacuum. Recrystallization of the residue from 1:5 hexane–methylene chloride gave compound **3**; mp 122°C (dec.). IR spectrum (vaseline oil), ν, $cm^{-1}$: 1565 (C=N). $^1H$ NMR spectrum (DMSO-$d_6$, 300 MHz), δ, ppm, *J* (Hz): 3.17 and 2.92 (2H, dd and dd, $^3J = 3.8, 8.0$, $^2J = 12.6$, $CH_2S$); 1.75 (1H, m, CH); 1.17 and 1.06 (6H, s and s, $2CH_3$); 0.95 (3H, d, $^3J = 6.6$, 5-$CH_3$). Found, %: C 47.20; H 6.73; N 7.81; S 17.92. $C_7H_{12}ClNS$. Calculated, %: C 47.32; H 6.81; N 7.88; S 18.04. Mass spectrum, *m/z* ($I_{rel}$, %): 179 [M+2] (4), 177 [$M^+$] (12), 135 (20), 100 (100), 41 (35).

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