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TANDEM REARRANGEMENT-HETERO-CYCLIZATION IN THE REACTIONS OF TETRAFLUOROBENZOBARRELENE WITH HETARENESULFENYL CHLORIDES

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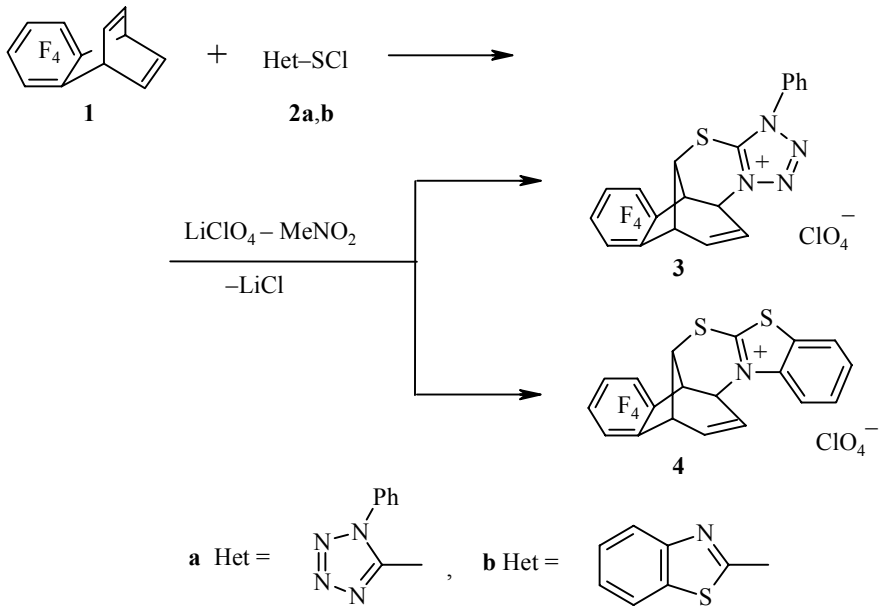
Zefirov et al. [1] have carried out a detailed study of the reactions of tetrafluorobarrelene (**1**) with arenesulfenyl and methanesulfenyl halides.

In the present work, the reaction of diene **1** with hetarenesulfenyl chlorides, containing a potentially nucleophilic nitrogen atom in the hetaryl fragment, was studied in an effort to develop a new approach for the synthesis of sulfur heterocycles. We found that a system containing lithium perchlorate and nitromethane induced the cycloaddition of 1-phenyl-5-tetrazolesulfenyl chloride (**2a**) and 1,3-benzo-2-thiazolesulfenyl chloride (**2b**) to diene **1**. Ring closure is preceded by a Wagner–Meerwein rearrangement. These reactions lead to polycyclic systems **3** (72% yield) and **4** (79% yield).



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General Method for the Sulfenylation of Diene 1. A solution of $LiClO_4$ (1.06 g, 10 mmol) in nitromethane (30 ml) and a solution of sulfenyl chloride **2a** or **2b** (10 mmol) in nitromethane (15 ml) were added to a solution of diene **1** (2.26 g, 10 mmol) in nitromethane (20 ml) at 20°C. After 30 min, the LiCl precipitate was filtered off and the filtrate was evaporated in vacuum. Recrystallization of the residue from methylene chloride gave **3** and **4**.

3,4,5,6-Tetrafluoro-15-phenyl-17-thia-12-azonia-13,14,15-triazapentacyclo[9.7.0.0^{2,7}.0^{8,18}.0^{12,16}]-octadeca-(2(7),3,5,9,12(16),13-hexaene Perchlorate (3); mp 285-287°C (dec). IR spectrum (KBr), ν, cm^{-1}: 1492, 1452, 1400, 1408, 1296, 976, 764, 738, 692, 624 (Het, Ph), 1092 (ClO_4). ^{1}H NMR spectrum (500 MHz, CD_3CN), δ, ppm: 7.81 (5H, m, Ph); 6.86 (1H, dd, $J_{8,9}$ = 6.4, $J_{9,10}$ = 9.2, H–$C_{(9)}$); 6.08 (1H, dd, $J_{1,11}$ = 2.5, $J_{10,11}$ = 4.3, H–$C_{(11)}$); 5.59 (1H, ddd, $J_{1,10}$ = 2.0, H–$C_{(10)}$); 4.63 (1H, t, $J_{1,18}$ = $J_{8,18}$ = 4.7, H–$C_{(18)}$); 4.34 (1H, m, H-$C_{(1)}$); 4.17 (1H, m, H-$C_{(8)}$). ^{13}C NMR spectrum (125 MHz, CD_3CN), δ, ppm (*J*, Hz): 151.17 ($C_{(16)}$), 135.90 ($C_{(10)}$), 132.16, 130.87, 130.24, 129.36, 124.27, 123.28 (C_{Ar}), 118.25 (DMSO-d_6, $C_{(9)}$), 53.49 ($C_{(11)}$), 48.74 ($C_{(8)}$), 41.39 ($C_{(18)}$), 39.75 ($C_{(1)}$). ^{19}F NMR spectrum (188 MHz, CD_3CN), δ($CFCl_3$), ppm: -138.46, -144.12, -154.36, -156.68. Found, %: C 44.98; H 2.11; N 10.87; S 6.21. $C_{19}H_{11}ClF_4N_4O_4S$. Calculated, %: C 45.39; H 2.20; N 11.14; S 6.38.

15,16,17,18-Tetrafluoro-9,11-dithia-2-azoniahexacyclo[11.9.0.0^{2,10}.0^{3,8}.0^{12,20}.0^{14,19}]docosa-2(10),-3(8),4,6,14(19),15,17,21-octaene Perchlorate (4); mp 270-272°C (dec). IR spectrum (KBr), ν, cm^{-1}: 1652, 1488, 1450, 1412, 1310, 1272, 1144, 990, 752, 730, 700 (Het, Ar). ^{1}H NMR spectrum (500 MHz, DMSO-d_6), δ, ppm (*J*, Hz): 8.39 (1H, d, *J* = 3.4, Ar); 8.37 (1H, d, *J* = 3.4, Ar); 7.81 (1H, t, *J* = 3.4, Ar); 7.70 (1H, t, *J* = 3.4, Ar); 6.77 (1H, dd, $J_{20,21}$ = 7.0, $J_{21,22}$ = 9.5, H–$C_{(21)}$); 6.38 (1H, s, $C_{(1)}$); 5.30 (1H, dd, $J_{13,22}$ = 2.5, H–$C_{(22)}$); 4.61 (1H, t, $J_{12,13}$ = $J_{12,20}$ = 4.5, H–$C_{(12)}$); 4.34 (1H, m, H–$C_{(13)}$); 4.25 (1H, m, H–$C_{(20)}$). ^{19}F NMR spectrum (188 MHz, DMSO-d_6), δ($CFCl_3$), ppm: -137.04, -143.13, -153.98, -156.20. Found, %: C 46.04; H 1.97; N 2.75; S 12.87. $C_{19}H_{10}ClF_4NO_4S_2$. Calculated, %: C 46.40; H 2.05; N 2.85; S 12.34.

REFERENCES

1. G. A. Nisnevich, V. I. Mamatyuk, V. A. Barkhash, T. N. Velikokhat'ko, N. K. Sadovaya, N. S. Zefirov, O. I. Lyubinskaya, G. S. Mikaelyan, V. A. Smit, E. Yu. Grudzinskaya, E. V. Skorobogatova, V. R. Kartashov, T. I. Novikova, and I. V. Bodrikov, *Zh. Org. Khim.*, **26**, 84 (1990).
2. A. V. Borisov, V. K. Bel'skii, G. N. Borisova, V. K. Osmanov, Zh. V. Matsulevich, and T. V. Goncharova, *Khim. Geterotsikl. Soedin.*, 763 (2001).