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REACTIONS OF 1,3-DIPOLAR CYCLOADDUCTS OF "DEWAR" THIOPHENE WITH AZIDES

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Reaction of 1,2,3,4-tetrakis(trifluoromethyl)-5-thiabicyclo[2.1.0]pent-2-ene, the "Dewar" thiophene, with azides (RN_3:R=Ph, C_6H_{11}, t-Bu, H) gave the adducts, 3-thia-6,7,8-triazatricyclo[3.3.0.$0^{2,4}$]oct-6-ene compounds (3_{a-d}). The compounds (3) were desulfurized with triphenylphosphine to the corresponding 2,3,4-triazabicyclo[3.2.0]-hepta-2,5-diene compounds (7).

Compounds (7) underwent thermal retro-1,3-dipolar reaction at room temperature to give 1-alkylimino-4-diazo-1,2,3,4-tetrakis(trifluoromethyl)but-2-enes (8). The compounds (8) were thermally converted to 1,2,3-tris(trifluoromethyl)cycloprop-2-enyl trifluoromethyl ketone N-substituted imines (10) and 2,3,4,5-tetrakis(trifluoromethyl)-pyrroles (11), where conversion of 10 to 11 was not observed. Therefore, the pyrroles (11) were not formed through 10 nor "Dewar" Pyrroles (5), but directly from the carbene intermediates (12), which were transiently formed from 8 by the loss of molecular nitrogen. While photolysis of 7 gave "Dewar" pyrroles (5) by (2+2) reaction, thermolysis of 7 occurred by (4+2) reaction.

Thermolysis of the adducts (3) gave 2,3,4-tris(trifluoromethyl)thiet-2-yl trifluoromethyl ketone N-alkylimines (16) through opening of the triazoline part, followed by rearrangement with loss of molecular nitrogen.

The compounds (16) with a substituent on nitrogen were converted to N-substituted 2,3,4,5-tetrakis(trifluoromethyl)pyrrole by triphenylphosphine, while non-N-substituted compound (16_d) was rearranged to 3,4,5,6-tetrakis(trifluoromethyl)-4H-1,2-thiazine (18).

In conclusion, thermolysis of 3 and 7 caused opening of the triazoline ring in (4+2) fashion, while their photolysis of them resulted in the loss of nitrogen by (2+2) reaction

The mechanism of conversion of 7 to 11 were discussed.