

REACTIONS OF TETRAKIS(TRIFLUOROMETHYL)DEWAR PYRROLES

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The reactions of N-cyclohexyl and N-unsubstituted tetrakis(trifluoromethyl)-Dewar pyrroles (1 and 2) with cyclic and acyclic dienes, and several 1,3-dipoles were examined. Compound 1 reacted with furan and cyclopentadiene to give the adducts, but did not react with 2,5-dimethylfuran and pyrrole which reacted with tetrakis(trifluoromethyl)Dewar thiophene(3). The reaction of 1 with 2,3-dimethyl-1,3-butadiene, a highly reactive acyclic diene, needed several weeks at room temperature. Further, 1,3-butadiene which reacted with 3 for seven days at room temperature, did not react with 1 under even more drastic conditions.

The reaction of 2 with furan, cyclopentadiene and pyrrole gave the cycloadducts in good yields, respectively. Further, 2,5-dimethylfuran and N-methylpyrrole which did not react with 1, reacted with 2 to give the corresponding cycloadducts in good yields with small amounts of isomers. Similarly, the reactions of 2 with 1,3-butadiene and several methyl substituted derivatives gave the cycloadducts, respectively.

These results and the previous ones for the Dewar thiophene(3) show large differences in the reactivities of these Dewar compounds. These results may be explained reasonably by considering that the transition state in the Diels-Alder reaction of 1-3 is an exo-anti form, and that the trifluoromethyl groups at the bridge-heads hinder the diene to approach by the repulsion between the trifluoromethyl groups and diene component. This hindrance seems to be larger in 3 than 1 due to the difference in the bond lengths of the C-S and C-N bonds. The difference in the reactivities of 1 and 2 may be due to the buttressing effect of the N-substituent.