DIELS-ALDER REACTION OF DEWAR THIOPHENE AND PYRROLE

Yoshiro Kobayashi, Akira Ando, Kosuke Kawada, and Itsumaro Kumadaki
Tokyo College of Pharmacy, Horinouchi, Hachioji, 192-03 Japan

In the course of the study of valence-bond isomers of trifluoromethylated aromatic compounds, the Diels-Alder reaction of Dewar thiophene and Dewar pyrrole, the latter of which was derived from the former, was investigated. The Dewar thiophene reacted with most cyclic and acyclic dienes, if a large substituent is absent on the bridge or the terminal part of dienes, whereas the Dewar pyrrole reacted with the cyclic dienes, but not with acyclic dienes.

The Diels-Alder adduct (1) of the Dewar thiophene with butadiene was brominated to cis-dibromide (2), which was desulfurized with triphenylphosphine and dehydrobrominated to a bicyclo[4.2.0]octa-3,7-diene compound (3). On the other hand, the treatment of the adduct (1) with triphenylphosphine, followed by bromination of the bicyclic diene (5), gave trans-dibromide (6), which was dehydrobrominated to a cyclooctatetraene compound (8) through a bicyclo[4.2.0]octatriene compound (7).

Some reactions of tetrakis (trifluoromethyl)cyclooctatetraene (8) will be presented.