REACTION OF DIAZOINDENOTHIOPHENES WITH ACETYLENIC ESTERS

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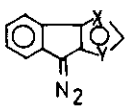
The reaction of diazoindenothiophenes 1a-c with dimethylacetylenedicarboxylate, 2a, and methyl propiolate, 2b, was investigated. The reaction of 1a with 2a gave unstable 3H-pyrazoles 3a and 3b. In refluxing toluene, 3a afforded the cyclopropene 4a and the rearranged product 5a. The compound 3b also gave unstable cyclopropene 4b which gave the lactone derivative 6 on silica gel columnchromatography

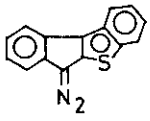
On the other hand, both 3a and 3b rearranged into 5a and 5b when being kept in chloroform or benzene at room temperature for 3 days. The 5 might be formed via the Van Alphen-Hüttel rearrangement followed by the migration of an ester group.

Methyl propiolate 2b reacted with 1a to give 1H-pyrazoles, 7a, while the reaction of 1b with 2b gave 1H-pyrazole, 7b, and the thermally labile diazoalkene, 8, which corresponds to the ring-opened product of the initial adduct of 1b and 2b.

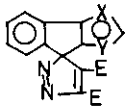
The reaction of 1c with 2a gave the compound 8 of the molecular formula corresponding to the 2:1-adduct of 1c and 2a with a loss of nitrogen. The compound 9 liberated one mole of nitrogen when being heated in toluene at reflux to give a crystalline compound 10 of mp 141-145 °C, however, the structures of 9 and 10 are not known yet.



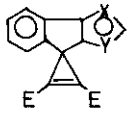
1a,b



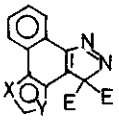
1a



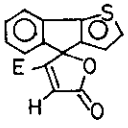
3



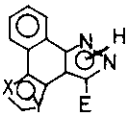
4a,b



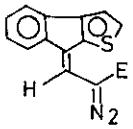
5a,b



6



7a,b



8

a; X=S, Y=CH

b; X=CH, Y=S

$E=CO_2CH_3$