SYNTHESES AND REACTIONS OF BRIDGED HETEROCYCLIC COMPOUNDS

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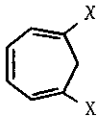
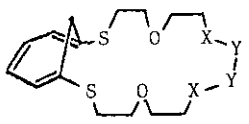
Several bridged heterocyclic compounds containing sulfur and nitrogen were synthesized from 1,6-dithiocyanato-(1) and 1,6-diiodocycloheptatriene (2).

Dithiolate (3) obtained from the reduction of 1 reacted with diiodomethane, 1,2-dibromoethane, and cis-dichloroethylene to give the corresponding sulfur heterocycles. Polythiaethers of type 7-11 were also synthesized from 6, which was prepared via 4 and 5, and ethanedithiol, dimercaptoethylene, 1,2-benzenedithiol, 1,2-benzenediol, and 1,6-dimercaptocycloheptatriene. These medium and large membered thioethers are the first example of thiacrowns having cycloheptatriene moiety in their skelton.



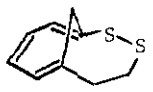
1 X=SCN
2 X=I
3 X=SNa

4 X=$SCH_2CH_2OCH_2CH_2OH$
5 X=$SCH_2CH_2OCH_2CH_2OTs$
6 X=$SCH_2CH_2OCH_2CH_2I$

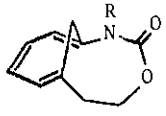


7 X=S, Y=CH_2CH_2
8 X=S, Y=CH=CH
9 X=S, Y=1,2-C_6H_4
10 X=O, Y=1,2-C_6H_4
11 X=S, Y=1,6-C_7H_6

Other bridged heterocyles such as 12, 13 and 14 were synthesized from the diiodide (2).



12



13 R=H
14 R=CH_3

Diels-Alder reactions of some of these bridged heterocycles with maleic anhydride or N-phenyl-1,2,4-triazoline-3,5-dione gave the corresponding 1:1 adduct, and the reactivity in the cycloaddition is briefly discussed.