

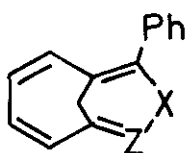
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We have prepared methanoheteronins (1a) and (1b), ten π -electron hetero[9]annulenes, by cycloaddition--extrusion--ring expansion reactions of mesoionic compounds with benzocyclopropene. As an extension of these studies, we report now the preparation of a methanothiecinone (4), a potentially aromatic eleven π -electron bridged hetero[10]annulenone, and attempts toward preparation of a methano-oxonin (1c).

The cycloadduct (2a) between a mesoionic dithione (3a) and benzocyclopropene was converted to the corresponding sulfoxide (2b). Photolysis of the sulfoxide gave the expected methanothiecinone (4), together with a rearrangement product (5) and its 5H-isomer. Irradiation of the cycloadduct (2a) resulted in extrusion of carbon oxysulfide accompanied by a similar rearrangement to give a cyclohepta[c]thiophene (6). The methanothiecinone (4) is a potentially aromatic system because a delocalization of ten π -electron will be possible if the ring carbonyl group is polarized. However, infra-red spectrum shows that the carbonyl group is not strongly polarized, and n.m.r. data do not show a high degree of delocalization of π -electrons within the ring.

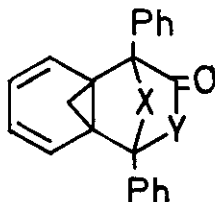
The reaction of a mesoionic oxazol-4-one (3b) with benzocyclopropene gave the cycloadduct (2c). Work is now under way to prepare the desired methano-oxonin (1c) by selective extrusion of phenyl isocyanate from the adduct (2c).



1a: X = S; Z = N

1b: X = S; Z = C(Ph)

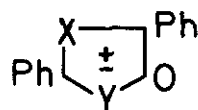
1c: X = O; Z = C(Ph)



2a: X = Y = S

2b: X = SO; Y = S

2c: X = O; Y = N(Ph)



3a: X = Y = S

3b: X = O; Y = N(Ph)

