BRIDGED HETERONINS, THIECINONE, AND RELATED SYSTEMS FROM MESOIONIC COMPOUNDS

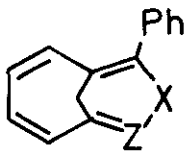
Hiroshi Kato, Masafumi Hashimoto, and Keiko Ikona

Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto 390, Japan

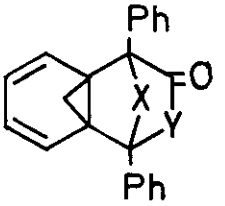
We have prepared methanoheteronins (1a) and (1b), ten π-electron hetero[9]annulenes, by cycloaddition--extrusion--ring expansion reactions of mesoionic compounds with benzocyclopropene. As an extension of these studies, we report now the preparation of a methanothiecinone (4), a potentially aromatic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

The cycloadduct (2a) between a mesoionic dithiolone (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]thiophen (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, infrared 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.

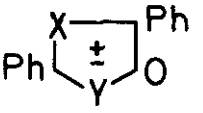
The reaction of a mesoionic oxazol-4-one (3b) with benzocyclopropene gave the cycloadduct (2c). Work is now under way to prepare the desired methano-oxonin (1c) by selective extrusion of phenyl isocyanate from the adduct (2c).



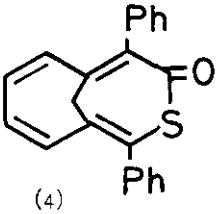
1a: X = S; Z = N
1b: X = S; Z = C(Ph)
1c: X = O; Z = C(Ph)



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



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



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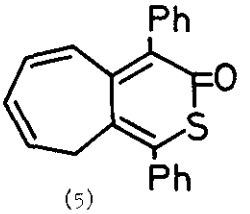
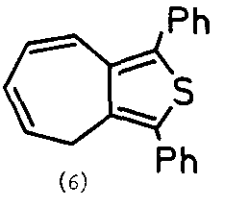


(5)



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