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THE CHEMISTRY OF PHOTOLYTICALLY AND THERMALLY GENERATED α-KETOCARBENES FROM IODONIUM YLIDES OF β-DIKETONES

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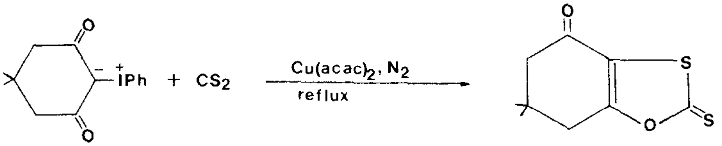
Summary:The reactions of Phenyliodonium dimedonate,1,with various double bonds were investigated.The products are always heterocyclic copmounds(5-member ring) in good yield.

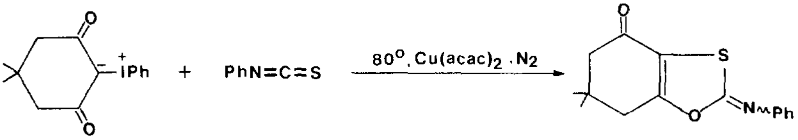
Until today,chemical studies on I-ylide 1 have been limited to its reactivity toward highly electrophilic agents[3] and thermal decomposition.

When a suspension of I-ylide 1 in carbon disulfide was heated under reflux in the presence of catalytic amounts of Cu(acac)$_2$,in an atmosphere of N$_2$,the 4-oxo-4,5,6,7-tetrahydro-6,6-dimethyl-1,3-benzoxathiole-2-thione[4] ,2,was isolated in 85% yield.



1 2

In the same way,ysing phenyl isothiocyanate,the isolated product was 2-phenylimino-4-oxo-4,5,6,7-tetrahydro-6,6-dimethyl-1,3-benzoxathiole,3,in 74% yield.



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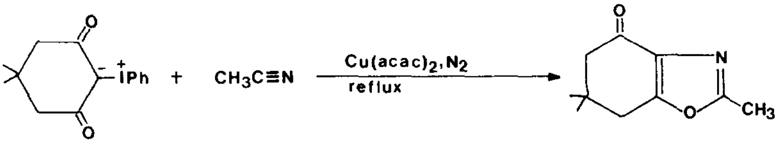
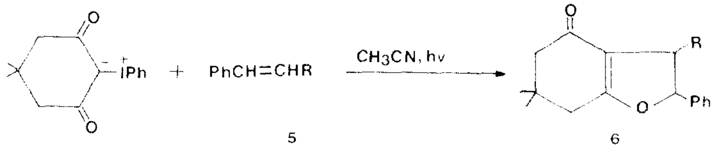
In the reaction of I-ylide 1 with acetonitril under reflux in the presence of Cu(acac)$_2$,in an atmosphere of N$_2$,the 1-methyl-4-oxo-4,5,6,7-tetrahydro-6,6-dimethyl-1,3-benzoxazol,4,was isolated in 84% yield.



1 4

When a suspension of I-ylide 1 in acetonitril was irradiated(400W lamp, low pressure Hg) in the presence of an alkene,5,the corresponding 2-phenyl-4-oxo-2,3,4,5,6,7-hexahydro-benzofuran[5],6,was isolated.



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5
5a,R=H
5b,R=PhCH=CH

6
6a,R=H 95%
6b,R=PhCH=CH,50%

In all the above reactions,we believe that the I-ylide decomposes(on irradiation or thermally in the presence of catalytic amounts[6] of Cu(acac)$_2$) to a diketocarbene and PhI.The spin multiplicity of the carbene which is responsible for the reaction has estimated to be triplet[7] in view of the results obtained from the sensitized photolysis of diazodimedone.

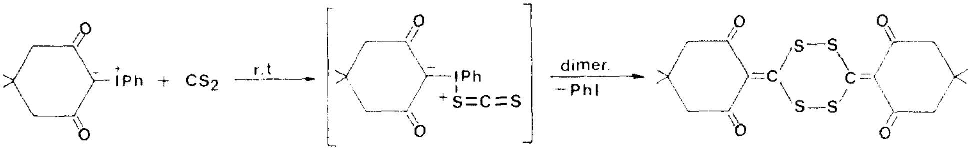
REFERENCES AND NOTES:

1.Fellow of "NAPOLEON ZERVAS"Foundation for years 1985 and 1986.

2.Present address:Organische Chemie,Universitat des Saarlandes,Fachbereich14.1, D-6600 Saarbrucken,W.Germany.

3.Koser F.G.,"The Chemistry of Functional groups",Wiley-Interscience,New York 1983,Supplement D,Chapter 18,pp 774-806.

4.Papadopoylou M.;Spiroudis S.:Varvoglis A.,J.Org.Chem.,1985,50,1510. The authors believe that they have prepared the thione 2.The correct is that they prepared the dimer,7,which comes from the dimerization of the species after the elimination of PhI.



1

7

Using their procedure,the isolated product in ^{1}H NMR(DMSO-d_6)has a singlet for the methylenes of dimedone ring in the region of 2,40δ.This is in agreement with the proposed structure 7.The thione 2 has two singlets for the two methylenes of dimedone ring with 23 Hz difference,which is difficult to be masked by the solvent.

5.Yoshida J.;Yano S.;Ozawa T.;Kawabata N.,J.Org.Chem.,1985,50,3467.

6.The amount of Cu(acac)$_2$ is 20mg per mmole of I-ylide 1.

7.Hayasi Y.;Okada T.;Kawanisi M.,Bull.Chem.Soc.Jpn.,1970,43,2506.

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