Cycloaddition Reactions of Cyclic and Acyclic 1,3-Dipoles with Diphenylcyclopropenone and Related Compounds. A New Rearrangement

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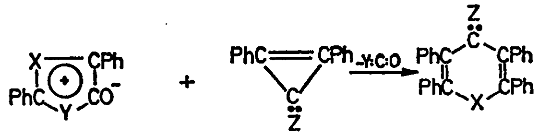
Summary Cycloaddition of mesoionic compounds with diphenylcyclopropen-one and -thione, and tosylimino- and dicyanomethylene-cyclopropene occurs across the endocyclic C=C double bond, whereas cycloaddition of benzonitrile oxide with diphenylcyclopropenone occurs across the C=O double bond to give triphenyl-1,3-oxazin-6-one by a new type of rearrangement.

WE have found, independently of Potts and Baum,[1] that the reaction of mesoionic 3-methyl-2,4-diphenyloxazol-5-one (**1a**) and diphenylcyclopropen-one (**2a**) and -thione (**2b**) gave the pyridone (**3a**) and the pyridinethione (**3b**) respectively.†§ Compounds (**3a**) and (**3b**) were also prepared by the cycloaddition–extrusion reaction of mesoionic 3-methyl-2,4-



(1)
a; X = NMe, Y = O
b; X = NMe, Y = S
c; X = Y = S

(2)
a; Z = O
b; Z = S
c; Z = NTs
d; Z = $C(CN)_2$

(3)
a; X = NMe, Z = O
b; X = NMe, Z = S
c; X = S, Z = O
d; X = NMe, Z = NTs
e; X = NMe, Z = $C(CN)_2$

SCHEME 1

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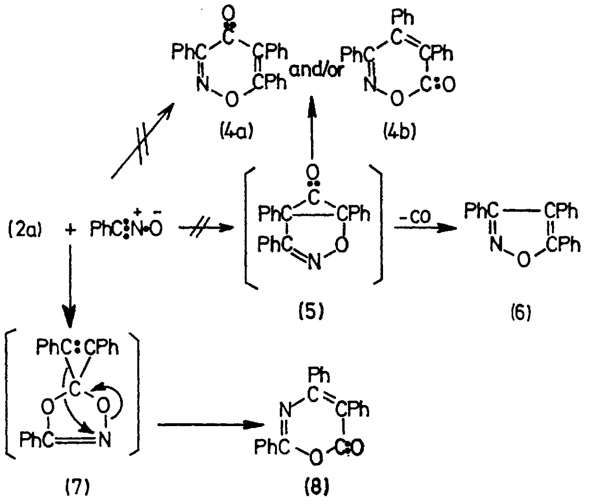
† All new compounds gave satisfactory elemental analyses and spectra.

§ Properties of (**3a**) and (**3b**) generally agree with those reported by Potts.[1] However, (**3b**) decomposed at 341—342° (capillary tube) and its n.m.r. signals of aromatic protons consist of two singlets at δ 6·98 and 7·20 [$(CD_3)_2SO$–$CDCl_3$]. One of the three peaks reported by Potts should be due to chloroform, in which (**3b**) is only sparingly soluble.

diphenylthiazol-5-one (**1b**) with (**2a**) and (**2b**) in yields of 55 and 48%. Further, the reaction of mesoionic 2,5-diphenyl-1,3-dithiol-4-one (**1c**) and cyclopropenone (**2a**) gave tetraphenylthiapyran-4-one (**3c**)[2] (38%), and the reaction of oxazolone (**1a**) with tosylimino- and dicyanomethylene-diphenylcyclopropene (**2c**) and (**2d**) gave 63 and 33% yields of the pyridines (**3d**) [m.p. 310·5—312·5°, i.r. 1608 cm^{-1}, δ 2·19 (s, 3H), 3·14 (s, 3H), 6·68—7·65 (m, 14H)] and (**3e**) [m.p. 360—361° (decomp.), i.r. 2180 cm^{-1}, δ 2·98 (s, 3H), 7·06 (s, 10H), 7·17 (s, 10H)]. Compounds (**3d**) and (**3e**) were identical with the specimens prepared by the treatment of 1-methyl-4-ethoxy-2,3,5,6-tetraphenylpyridinium fluoroborate with *p*-toluenesulphonamide and dicyanomethide ion respectively. Thus, the cycloaddition of mesoionic compounds always occurs across the endocyclic C=C double bond of (**2**) irrespective of the nature of the exocyclic atom. However, the dipolarophilic reactivity of (**2**) is not very pronounced, and the cycloadducts could not be obtained by the reaction of (**2a**) with 3-phenylsydnone, mesoionic 4-phenyl-1,3,2-oxathiazole, and mesoionic triphenylthiazol-4-one, or by the reaction of (**2b**) with (**1c**) and some other mesoionic ring systems.

The cycloaddition of benzonitrile oxide, an acyclic 1,3-dipole, with the C=C bond of the cyclopropenone (**2a**) should give an unstable bicyclic adduct (**5**), which may be stabilised by extrusion of carbon monoxide to give the isoxazole (**6**). Alternatively, the formation of either 1,2-oxazin-4- or -6-one (**4a** or **4b**) by skeletal rearrangement of (**5**) or by addition of benzonitrile oxide at the 1,2-position of (**2a**) may also be expected. The reaction at room temperature actually took quite an unexpected course, and gave triphenyl-1,3-oxazin-6-one (**8**)[3] in 40% yield. The formation of (**8**) may be rationalised by assuming an initial 1,3-dipolar cycloaddition of benzonitrile oxide across the C=O double bond of cyclopropenone (**2a**) to give an intermediate spiro compound (**7**), followed by its rearrangement as shown in Scheme 2.



Scheme 2

(*Received*, 28*th January* 1974; *Com.* 126.)

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[1] K. T. Potts and J. Baum, *J.C.S. Chem. Comm.*, 1973, **833**.
[2] K. W. Hubel and E. H. Braye, U.S.P., 3,280,017; *Chem. Abs.*, 1967, **66**, 2462.
[3] T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, 1971, **36**, 2451.