

Selectivity in the Thermal and Photochemical Fragmentation of the Cycloadduct from Benzyne and a Mesoionic Thiazol-4-one

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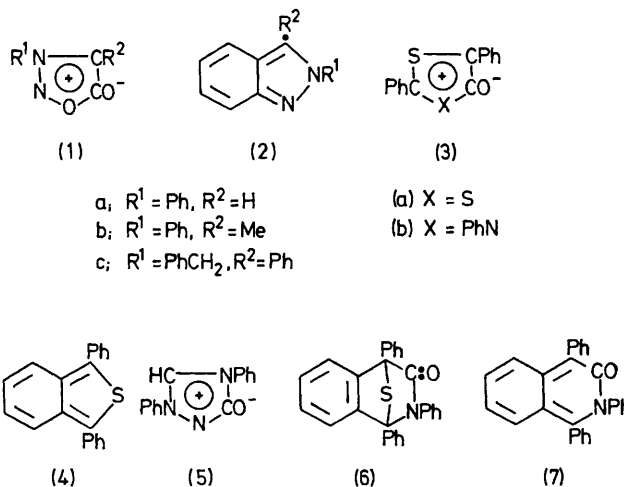
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Summary During the preparation of benzo-condensed five-membered heterocycles by cycloaddition-extrusion reaction of benzyne with mesoionic compounds, a cycloadduct with a thiazol-4-one was isolated, which behaved differently on pyrolysis and photolysis.

ALTHOUGH the reactivity of mesoionic compounds towards 1,3-dipolarophiles is well known,¹ the reaction of five-membered mesoionic compounds with benzyne has been reported only for 3-phenylsydnone.² We now find that the reaction of benzyne generated from 1-aminobenzotriazole³ with 3-phenyl-, 3-phenyl-4-methyl-, and 3-benzyl-4-phenylsydnone (**1a-c**) gave the corresponding indazoles (**2a-c**) in 73, 64, and 68% yields† and the reaction with the mesoionic diphenyl-1,3-dithiol-4-one (**3a**) gave diphenylbenzo[*c*]thiophen (**4**) in 36% yield. The mesoionic 1,4-diphenyl-1,2,4-triazol-3-one (**5**) did not react with benzyne from aminobenzotriazole, but it did react with benzyne generated by pyrolysis of diphenyliodonium-2-carboxylate to give 2-phenylindazole (**2a**) albeit only in 34% yield. Thus, reactions of this type provide a convenient general synthetic procedure for benzo-condensed five-membered heterocycles in which the benzene ring has a formal 'quinonoid' structure.

In the reaction of the mesoionic triphenylthiazol-4-one (**3b**) and benzyne generated from aminobenzotriazole, the intermediate cycloadduct (**6**) could be isolated (78%) [m.p. 140° (decomp.), ν (C=O) 1720 cm⁻¹]. Pyrolysis of the adduct in refluxing xylene caused fragmentation to phenyl isocyanate and diphenylbenzo[*c*]thiophen (**4**) (58%). In strong contrast to this, irradiation of the adduct (**6**) in

benzene-methanol through a Pyrex filter resulted in extrusion of sulphur to give 1,2,4-triphenyl-3-isoquinolone (**7**) [55%, m.p. 279–281° ν (C=O) 1620 cm⁻¹], and the



presence of (**4**) or methyl phenylcarbamate in the reaction mixture could not be detected by t.l.c. Such complete selectivity in thermal and photochemical fragmentation of a compound bearing two potentially extrudable group, though not without precedent,⁴ is unique.

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† All new compounds gave satisfactory analyses and spectra. M.p.s: (**2b**), 88.5–89.8°; (**2c**), 105.2–107°.

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⁴ R. M. Kellog and S. Wassenaar, *Tetrahedron Letters*, 1970, 1987; D. H. R. Barton and B. J. Willis, *Chem. Comm.*, 1970, 1225; *J.C.S. Perkin 1*, 1972, 305; D. H. R. Barton, E. H. Smith, and B. J. Willis, *Chem. Comm.*, 1970, 1226.