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

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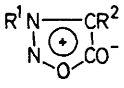
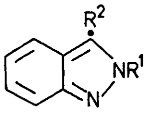
Summary During the preparation of benzo-condensed five-membered heterocycles by cycloaddition–extrusion reaction of benzyne with mesoionic compounds, a cycloadduct with a thiazol-4-one was isolated, which behaved differently on pyrolysis and photolysis.

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-aminobenzotriazole[3] with 3-phenyl-, 3-phenyl-4-methyl-, and 3-benzyl-4-phenyl-sydnone (**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.



(1)



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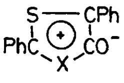
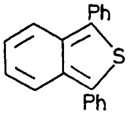


(3)

a; R^1 = Ph, R^2 = H
b; R^1 = Ph, R^2 = Me
c; R^1 = PhCH$_2$, R^2 = Ph

(a) X = S
(b) X = PhN



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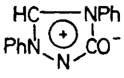

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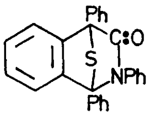
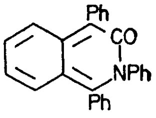


(6)



(7)

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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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[1] M. Ohta and H. Kato, 'Nonbenzenoid Aromatics,' vol. 1, ed. J. P. Snyder, Academic Press, New York, 1969, p. 117.

[2] A. Y. Lazaris, *Zhur. org. Khim.*, 1966, **2**, 1322 (*Chem. Abs.*, 1967, **66**, 65,426); H. Gotthardt, R. Huisgen, and R. Knorr, *Chem. Ber.*, 1968, **101**, 1056.

[3] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742.

[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 I*, 1972, 305; D. H. R. Barton, E. H. Smith, and B. J. Willis, *Chem. Comm.*, 1970, 1226.