Cycloaddition—Double Fragmentation Reactions of Mesoionic Compounds with Dimethyl 7-Oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate: Synthesis of Aromatic Heterocycles

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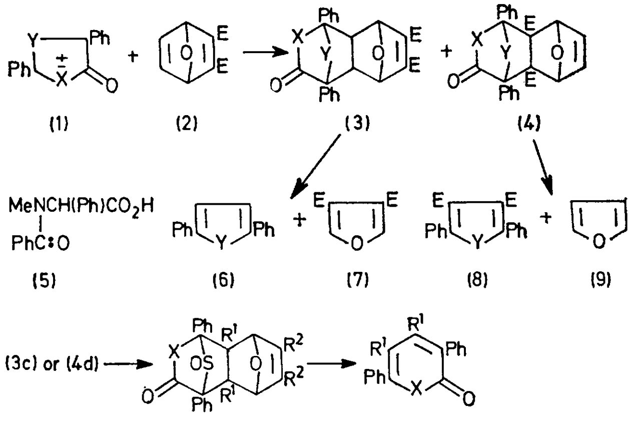
Summary Cycloaddition–double fragmentation reactions of five-membered mesoionic compounds with an oxabicycloheptadiene afford a convenient synthetic route to five- and six-membered conjugated heterocycles.

RETRO Diels-Alder fragmentation has been used for the preparation of some heterocyclic systems.[1] Resonance stabilisation in the transition state is believed to facilitate such fragmentations.[2] The energy required to pass over the transition state may be lowered further by generating an unstable intermediate, possibly by using a five-membered mesoionic compound. The intermediate ylides formed by cycloaddition–extrusion of mesoionic compounds with olefins would then fragment into stable compounds.

We report that the cycloaddition–double fragmentation of an oxabicycloheptadiene takes place with mesoionic compounds having a readily extrudable group, and that some mesoionic compounds give isolable primary cycloadducts, from which either of the two potentially extrudable groups may be extruded to give five- and six-membered heterocycles by appropriate modification of the intermediates. Reactions of mesoionic compounds with bridged olefins generally give poorly defined products[3] except one example of a cycloadduct and its decomposition at high temperature.[4]

The reaction of the mesoionic oxazalone (**1a**) with dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**2**) in benzene at room temperature for 15 min gave the pyrroles (**6a**)[5] (16%) and (**8a**)[5] (24%).† The n.m.r. spectrum of the crude reaction mixture (δ 7·81, 3·82 and 6·20) showed that the furans (**7**) and (**9**) were also formed, but they were not isolated. N.m.r. spectroscopy showed that



E = CO_2Me

a; X = O, Y = NMe

b; X = S, Y = NMe

c; X = Y = S

d; X = NPh, Y = S

c, R^1 = H, R^2 = CO_2Me

d, R^1 = CO_2Me, R^2 = H

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† All compounds were identified by elemental analyses, and i.r., n.m.r., and mass spectroscopy.

the main reaction was complete within a few minutes. The pyrroles (**6a**) and (**8a**) could also be obtained in 24 and 16% yields respectively by the treatment of (**2**) with (**5**) in acetic anhydride at 50—55 °C. These results indicate that the cycloaddition of (**1a**) proceeded *via* the cycloadducts (**3a**) and (**4a**). The reaction became more selective with the less reactive thiazolone (**1b**), which afforded, *via* the unisolable cycloadducts (**3b**) and (**4b**), the pyrroles (**6a**) and (**8a**) in 79 and 7% yields respectively when it was heated with (**2**) in benzene for 13 h.

When the mesoionic dithiolone (**1c**) and (**2**) were heated in CH_2Cl_2, the cycloadduct (**3c**) was isolated [82%, m.p. 165—166 °C, ν (C=O) 1750 and 1713 cm^{-1}, δ 5·00, 4·85 (each 1H, d, J 1Hz), 3·80, 3·34 (each 1H, dd, J 6 and 1 Hz), and 3·80 (6H, s)]. Pyrolysis of the adduct (**3c**) in boiling xylene resulted in a double fragmentation to give the thiophen (**6c**)[6] (92%) and the furan (**7**)[7] (91%). Photolysis of the adduct (**3c**) in benzene through a Pyrex filter also gave (**6c**) (71%). The sulphoxide (**10c**) (94%), m.p. 201—202 °C, was formed by the *m*-chloroperbenzoic acid oxidation of the adduct (**3c**). Pyrolysis of (**10c**) in refluxing xylene resulted in clean extrusion of sulphur monoxide accompanied by fragmentation to give the thiopyranone (**11c**) (81%), m.p. 187 °C. The reaction of the mesoionic thiazolone (**1d**) with (**2**) in benzene under reflux gave, besides the thiophen (**8d**)[8] (3%), two cycloadducts (**3d**) [42%, m.p. 202—204 °C, ν (C=O) 1745 and 1708 cm^{-1}, δ 5·06, 5·03 (each 1H, d, $J < 1$ Hz), 3·82, 3·78 (each 3H, s), 3·72 and 3·31 (each 1H, dd, J 6 and <1 Hz)] and (**4d**) [40%, m.p. 180—182 °C (decomp.), ν (C=O) 1749 and 1715 cm^{-1}, δ 6·77, 6·57 (each 1H, ABq, J 6 Hz), 5·27 (2H, s, br.), 3·13 and 3·07 (each 3H, s)]. The adduct (**4d**) gave the thiophen (**8d**) (84%) when heated in xylene for 4·5 h, but the adduct (**3d**) was recovered unchanged under similar conditions. The crude sulphoxide (**10d**), derived from the adduct (**4d**), underwent double fragmentation in boiling benzene to give the pyridone (**11d**)[3b] (70%).

These results show that by use of suitable mesoionic compounds, the cycloaddition–double fragmentations readily take place, possibly *via* an unstable intermediate ylide, though a concerted fragmentation of X=C=O and furan may not be ruled out completely. Moreover, these reactions provide not only a source of activated masked acetylenes for cycloadditions but also a novel method of preparation of six-membered aromatic heterocycles from mesoionic compounds.

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