Ring Expansion of Heteroaromatic Betaines with Cyclopropene Derivatives

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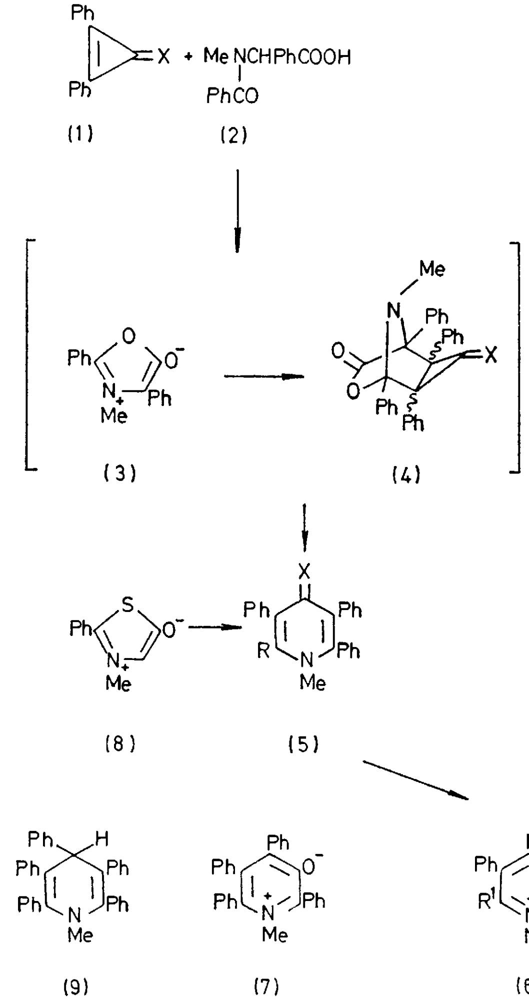
Summary Reaction of diphenylcyclopropenone, diphenylcyclopropenethione, and triphenylcyclopropene with *N*-benzoyl-*N*-methyl-*C*-phenylglycine in acetic anhydride provides a convenient route to 4-pyridones, pyridine-4-thiones, and 1,4-dihydropyridines, respectively; the *anhydro*-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide system also reacts readily with diphenylcyclopropenethione.

SMALL, strained rings have recently been shown to be effective substrates in a variety of cycloadditions[1] and, when treated with the 'masked' 1,3-dipole present in mesoionic ring systems,[2] should provide a simple approach to some interesting heterocyclic systems. We have found that substituted 4-pyridones, pyridine-4-thiones, and 1,4-dihydropyridines may be readily prepared from appropriate cyclopropene derivatives and several mesoionic ring systems or, preferably, from their precursors.[3]



Reaction of diphenylcyclopropenone (**1**; X = O), *N*-benzoyl-*N*-methyl-*C*-phenylglycine[4] (**2**), and acetic anhydride at 85° for 10 min gave the pyridone (**5**; R = Ph; X = O),† needles from $CHCl_3$–Et_2O, m.p. 309—310° [i.r. (KBr) ν_{CO} 1620 cm^{-1}; λ_{max} (MeOH) 276 nm (log ϵ 4·12) and 236sh (4·36); n.m.r. ($CDCl_3$) δ 7·23 (s, 10H, ArH), 7·07 (s, 10H, ArH), and 3·03 (s, 3H, *N*Me); M^+ 413 (58%)], characterized further by conversion with Meerwein's reagent into the tetrafluoroborate (**6**; R^1 = Ph; R^2 = OEt), needles from EtOH, m.p. 275—278° (decomp.) [i.r. (KBr) $\nu_{C=N}$ 1610 cm^{-1}; λ_{max} (MeOH) 290sh (log ϵ 3·94), and 243 nm (4·41); n.m.r. ($CDCl_3$) δ 7·00—7·73 (m, 20H, ArH), 3·63 (s, 3H, *N*Me), 3·55 (qt, 2H, CH_2), and 0·67 (t, 3H, Me)]. A likely intermediate in this reaction is (**4**), formed from (**1**) and the hydroxide (**3**), similar intermediates having been isolated recently from cyclopropenone and diphenylisobenzofuran as well as 9,10-dimethylanthracene.[5] However, alternative modes of addition are possible,[6] resulting in the formation of the hydroxide (**7**). The above spectral data were more consistent with (**5**) than with (**7**) and we have now confirmed this by direct comparison with a sample prepared from 2,3,5,6-tetraphenyl-4-pyrone and methylamine.[7]

Diphenylcyclopropenethione (**1**; X = S) gave with (**2**) and Ac_2O at 40° in 5 min orange-yellow irregular prisms of the thione (**5**; R = Ph; X = S), m.p. 320—322° (decomp.) [i.r. (KBr) $\nu_{C=C}$ 1560 cm^{-1}; λ_{max} (MeOH) 360 (log ϵ 4·18), 272sh (3·80), and 238 nm (4·18); n.m.r. ($CDCl_3$) δ 7·10, 7·23, and 7·27 (3×s, 20H, ArH), and 3·05 (s, 3H, *N*Me); M^+ 429 (60%), M^{2+}, 214·5 (5)] also obtained from the corresponding pyridone and P_2S_5 in refluxing pyridine, and converted into the corresponding methiodide (**6**; R^1 = Ph; R^2 = SMe), m.p. 240—242° (decomp.) with methyl iodide. This is the first example of addition to the C=C bond of diphenylcyclopropenethione, insertion between C(1)–C(2) being the usual mode of addition.[2,8]

Reaction of (**1**); (X = S) with the hydroxide[9] (**8**) in benzene at room temperature for 12 h gave the thione (**5**; R=H; X=S), yellow needles from $CHCl_3$–light petroleum m.p. 240—245° (decomp.) [i.r. (KBr) $\nu_{C=C}$ 1610 cm^{-1}; λ_{max} (MeOH) 360 (log ϵ 3·96), 267 (3·71), and 226 nm (4·13); n.m.r. ($CDCl_3$) δ 7·00—8·00 (m, 16H, ArH and 6-H), 3·40 (s, 3H, *N*Me); M^+ 353 (58%), M^{2+} 176·5 (5)], likewise readily converted into a methiodide (**6**; R^1 = H; R^2 = SMe) with methyl iodide, m.p. 207—210° (decomp.) Analogous products were obtained using the 2-*p*-chlorophenyl analogue of (**8**).

The dihydropyridine (**9**) is also readily available from (**2**) and triphenylcyclopropene, forming yellow prisms, m.p. 206—207°. It has recently been prepared[10] directly from (**3**).

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† All new compounds gave satisfactory analytical results.

[1] For some recent applications see: R. Grigg, R. Hayes, J. L. Jackson, and T. J. King, *J.C.S. Chem. Comm.*, 1973, 349; M. L. Deem, *Synthesis*, 1972, 675; A. Steigel, J. Sauer, D. A. Kleier, and G. Binsch, *J. Amer. Chem. Soc.*, 1972, **94**, 2770; R. W. La Rochelle and B. M. Trost, *Chem. Comm.*, 1970, 1353; G. Heinrichs, H. Krapf, B. Schroder, A. Steigel, T. Troll, and J. Sauer, *Tetrahedron Letters*, 1970, 1617; W. Dittmar, G. Heinrichs, A. Steigel, T. Troll, and J. Sauer, *ibid.*, 1970, 1623; E. E. Nunn and R. N. Warrener, *Synthetic Comm.*, 1970, **2**, 67; K. T. Potts and J. Baum, *Chem. Rev.*, in press.

[2] *E.g.* K. T. Potts, A. J. Elliott, and M. Sorm, *J. Org. Chem.*, 1972, **37**, 3838 and references therein.

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