

Cycloadditions of *anhydro*-2,3-Diphenyl-4-hydroxythiazolium Hydroxides: Reaction with Dimethyl acetylenedicarboxylate

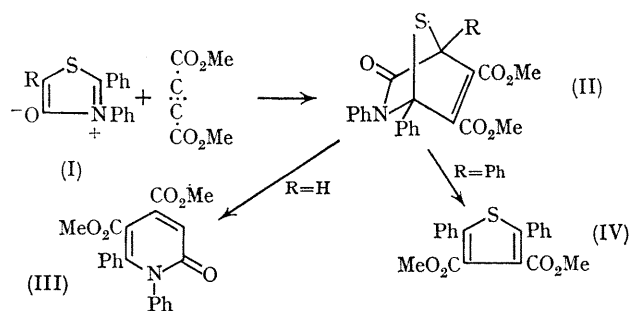
By K. T. POTTS,* E. HOUGHTON, and U. P. SINGH

(Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181)

Summary *anhydro*-2,3-Diphenyl-4-hydroxythiazolium hydroxide readily underwent cycloaddition with dimethyl acetylenedicarboxylate to dimethyl 1,6-diphenyl-2-pyridone-4,5-dicarboxylate with extrusion of sulphur, whereas *anhydro*-4-hydroxy-2,3,5-triphenylthiazolium hydroxide under the same conditions gave dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate with elimination of phenyl isocyanate.

CYCLOADDITION reactions of mesoionic ring systems studied¹ to date may be interpreted in terms of 1,3-dipolar type intermediates except for the reaction of dimethyl azodicarboxylate with *anhydro*-2,3-diphenyl-5-mercapto-1,3,4-thiadiazolium hydroxide and its 2-*p*-chlorophenyl analogue.² The formation of *anhydro*-1,6-diaryl-3-mercapto-1,2,4,5-tetrazinium hydroxides indicated that a 1,4-addition of the dipolarophile occurred. Particularly noteworthy was the complete inertness of the mesoionic 1,3,4-thiadiazole system to other dipolarophiles such as dimethyl acetylenedicarboxylate and tetracyanoethylene.³

We now report an extremely ready 1,4-type cycloaddition of *anhydro*-2,3-diphenyl- and 2,3,5-triphenyl-4-hydroxythiazolium hydroxide⁴ (I; R=H and Ph, respectively) with dimethyl acetylenedicarboxylate in benzene



at reflux temperatures. Thus from (I; R=H), the hypothetical, primary cycloadduct (II; R=H) underwent

spontaneous elimination of sulphur and electron rearrangement to form dimethyl 1,6-diphenyl-2-pyridone-4,5-dicarboxylate (III) [colourless prisms† (70%), m.p. 180—

181°; ν_{\max} (KBr) 1710 (CO₂Me), 1660 (—CO·N—Ph) cm.⁻¹; λ_{\max} (MeOH) 205 (log ϵ 4.65), 250 (3.99), 355 nm. (3.82); M^+ , m/e 363 (100%); n.m.r. (CDCl₃) τ 6.53 (s, 3H, 4-CO₂CH₃), 6.08 (s, 3H, 5-CO₂CH₃), 2.83 (m, 11H, ArH). Alkaline hydrolysis of this ester gave the corresponding acid as colourless needles, m.p. 257—258° [ν_{\max} (KBr) 3320 (OH), 1700, 1625 (CO) cm.⁻¹].

However, from (I; R = Ph) and the dipolarophile, dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate (IV; R = Ph) [colourless needles (90%), m.p. 167—168° (lit.⁵ 166—167.5°); ν_{\max} (KBr) 1710 (CO) cm.⁻¹; λ_{\max} (MeOH) 206 (log ϵ 4.49), 240 (4.34), 295 nm. (4.12); n.m.r. (CDCl₃) τ 6.22 (s, 6H, CO₂CH₃), 2.50 (m, 10H, ArH); M^+ , m/e 352

(100%)] and phenyl isocyanate were obtained. Alkaline hydrolysis of the ester gave the corresponding acid as colourless needles, m.p. 200° [ν_{\max} (KBr) 3300 (OH), 1700 (CO) cm.⁻¹; M^+ , m/e 324 (5%)] which, on decarboxylation with copper-quinoline, formed 2,5-di-phenylthiophen, m.p. 153—154°, identical with an authentic sample.⁶ This cycloaddition is a particularly attractive route to thiophens of type (IV).

These cycloadditions are noteworthy for the ease with which sulphur is eliminated to yield the pyridone and also for the elimination of phenyl isocyanate from the primary cycloadduct. Several canonical forms can account for the reactivity of the mesoionic system, the first one of this type in which a 1,4-type cycloaddition has been observed.⁷

We thank the U.S. Public Health Service, National Cancer Institute for financial assistance.

(Received, July 21st, 1969; Com. 1084.)

† Satisfactory analytical data were obtained for all products whose mass spectra were consistent with the assigned structures.

¹ R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, 1968, **101**, 536; H. Gotthardt and R. Huisgen, *ibid.*, 552; H. Gotthardt, R. Huisgen, and R. Knorr, 1056; R. Huisgen and H. Gotthardt, 1059; R. Huisgen, R. Grashey, and H. Gotthardt, *ibid.*, 829; R. Huisgen and H. Gotthardt, *ibid.*, 839; H. Gotthardt, R. Huisgen, and F. C. Schaefer, *Tetrahedron Letters*, 1964, 487; J. K. Stille, F. W. Harris, and M. A. Bedford, *J. Heterocyclic Chem.*, 1966, **3**, 155; G. Singh and S. Singh, *Tetrahedron Letters*, 1964, 3789; H. Gotthardt and B. Christl, *Tetrahedron Letters*, 1968, 4747, 4751; K. T. Potts and D. N. Roy, *Chem. Comm.*, 1968, 1061, 1062; K. T. Potts and U. P. Singh, *Chem. Comm.*, 1969, 66.

² R. M. Moriarty, J. M. Kliegman, and R. B. Desai, *Chem. Comm.*, 1967, 1045.

³ K. T. Potts and C. Sapino, jun., unpublished observations.

⁴ K. T. Potts, U. P. Singh, and E. Houghton, previous communication.

⁵ H. Gotthardt and B. Christl, *Tetrahedron Letters*, 1968, 4747.

⁶ S. Kapf and C. Paal, *Ber.*, 1888, **21**, 3053; E. Fromm, P. Fantl, and E. Leibsohn, *Ann.*, 1927, **457**, 267.

⁷ R. Huisgen, *Z. Chem.*, 1968, **8**, 290; *Angew. Chem. Internat. Edn.*, 1968, **7**, 321.