

## Cycloaddition Reactions of the Mesoionic Dehydrodithizone Incorporating a New 1,3-Dipolar Species

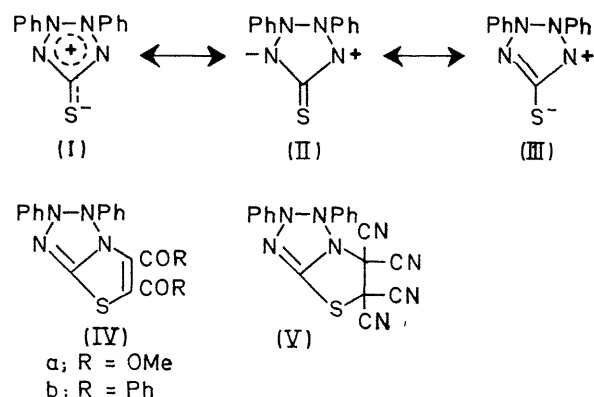
By P. RAJAGOPALAN\* and P. PENEV

(Endo Laboratories Inc., Garden City, New York, 11530)

**Summary** The mesoionic dehydrodithizone (I) reacts readily, in 1,3-dipolar fashion, with activated alkenes and alkynes to furnish cycloadducts and with ethoxycarbonylmethylenetriphenylphosphorane to yield the betaine (IX).

1,3-DIPOLAR cycloaddition reactions of a few mesoionic ring systems have been described<sup>1</sup> but all of these were accompanied by the spontaneous extrusion of either carbon dioxide or carbon oxysulphide from the transient primary adducts leading to the isolated products. We now report on the reactions of dehydrodithizone which conform to the classical 1,3-dipolar addition pattern involving no loss of fragments.

The communication on the X-ray crystal structure analysis of dehydrodithizone by Kushi and Fernando<sup>2</sup> has established that it is mesoionic in nature as suggested by Grammaticakis<sup>3</sup> and Ogilvie and Corwin.<sup>4</sup> The structure of dehydrodithizone, according to them,<sup>2</sup> is best represented by (I).



We examined the likelihood of (I) behaving as a 1,3-dipole in its reactions with dipolarophiles. Of the several possible canonical forms of (I), those represented by (II) and

(III) are worth considering from the point of view of 1,3-dipolar cycloaddition. The probability of structure (II) being invoked by dehydrodithione for its reactions becomes inconsequential because of the presence of a residual negative charge on its sulphur atom as indicated by the X-ray studies<sup>2</sup> and also because of the ease with which it undergoes S-alkylation.<sup>4</sup> It seems logical, then, to assume that structure (III) would be the one involved in the cycloadditions.

(I) was prepared by the oxidation of dithione<sup>5</sup> with potassium ferricyanide in aqueous alkaline medium.<sup>4</sup> It reacted readily and rapidly with electron-deficient alkynes exemplified by dimethyl acetylenedicarboxylate and dibenzoylacetylene and with the alkene tetracyanoethylene, affording, respectively, (IVa), m.p. 168—170°, 90%,† (IVb), m.p. 161—163° (decomp.), 95%,† (V), m.p. 140—145° (decomp.), 79%.†

With the electron-rich enamine double bond, the reaction was equally smooth and the compounds (VI), m.p. 115—117° (decomp.), 79%,† (VII), m.p. 85—90° (decomp.), 80%,† and (VIII), m.p. 150—155° (decomp.), 81%,† were obtained from the corresponding enamines.

The reaction of (I) with ethoxycarbonylmethylenetriphenylphosphorane also led to a 1:1 adduct [m.p. 112—116° (decomp.)†] in 72% yield which, however, exists as the betaine (IX) and not as the cycloadduct (X) as borne out by its <sup>31</sup>P n.m.r. spectrum‡ which carries a signal at -27.2 p.p.m. relative to 85% H<sub>3</sub>PO<sub>4</sub> as external standard. Phosphonium salts<sup>6</sup> and betaines,<sup>7</sup> in general, have negative values for <sup>31</sup>P chemical shifts while the cyclic pentacovalently bound phosphorus atom usually exhibits a positive <sup>31</sup>P chemical shift value.<sup>8</sup>

† Satisfactory analytical and spectral data have been obtained for this compound which did not possess any significant biological activity.

‡ Determined at 40.5 MHz on a Varian HA-100 instrument. We thank Dr. V. A. Engelhardt of the Central Research Department, E. I. duPont de Nemours and Co., Wilmington, Del., for obtaining this spectrum for us.

<sup>1</sup> R. Huisgen, H. Gotthardt, H. O. Bayer, and F. C. Schaefer, *Angew. Chem. Internat. Edn.*, 1964, **3**, 136; R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, 1968, **101**, 552; K. T. Potts and D. N. Roy, *Chem. Comm.*, 1968, 1061; H. Gotthardt and B. Christl, *Tetrahedron Letters*, 1968, 4747.

<sup>2</sup> Y. Kushi and Q. Fernando, *Chem. Comm.*, 1969, 1240.

<sup>3</sup> P. Grammaticakis, *Compt. rend.*, 1952, **234**, 528.

<sup>4</sup> W. Ogilvie and A. Corwin, *J. Amer. Chem. Soc.*, 1961, **83**, 5023.

<sup>5</sup> J. H. Billman and E. S. Cleland, *Org. Synth.*, 1955, **3**, 360.

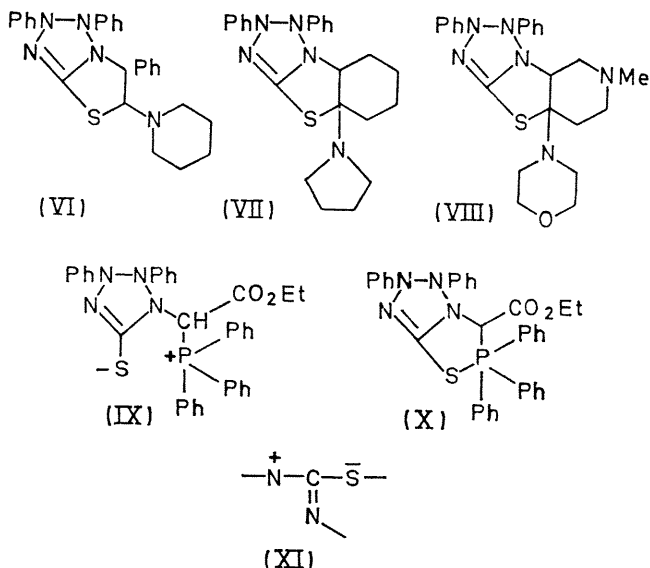
<sup>6</sup> A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, 1963, **85**, 2790.

<sup>7</sup> F. Ramirez, J. F. Pilot, N. B. Desai, and C. P. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 6273.

<sup>8</sup> G. Birum and C. N. Matthews, *J. Org. Chem.*, 1967, **32**, 2554; R. Huisgen and J. Wulff, *Chem. Ber.*, 1969, **102**, 746.

<sup>9</sup> R. Huisgen, *Angew. Chem. Internat. Edn.*, 1969, **2**, 565.

An interesting aspect of these reactions of (I) is the nature of the 1,3-dipolar species (XI) involved. With its nitrogen, carbon, and sulphur atoms it is unique in not having been



encountered so far and in not falling into any of the classifications of known and unknown dipoles according to Huisgen.<sup>9</sup>

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