

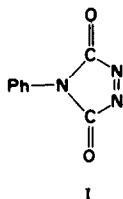
4-PHENYL-1,2,4-TRIAZOLIN-3,5-DIONE: A POWERFUL DIENOPHILE

R.C. Cookson, S.S.H. Gilani and I.D.R. Stevens

Department of Chemistry, University of Southampton

(Received 17 May 1962)

DIENOPHILIC reactivity rises in the series fumaric acid, maleic acid, maleic anhydride¹ and the well recognized dienophilic properties of azodicarboxylic ester² place it last in this series ahead of maleic anhydride. However, it fails to react (or reacts by allylic addition) with some dienes with which the latter reacts, a result which may be ascribed to the trans configuration of the nitrogen-nitrogen double bond. Constraining this bond into a cis configuration ought, therefore, to enhance the dienophilic reactivity; a prediction borne out by a study of 4-phenyl-1,2,4-triazolin-3,5-dione (I).



The preparation of I (the N-phenylimide of azodicarboxylic acid) was reported as long ago as 1894 by Thiele³ and more recently by Stolle.⁴ Both obtained it by oxidation of 4-phenylurazole; but the yields were rather low, probably due to the sensitivity of I to both acid and base.

¹ W.E. Bachman and L.B. Scott, *J. Amer. Chem. Soc.* **70**, 1458 (1948); W.R. Vaughan and K.S. Andersen, *J. Org. Chem.* **21**, 673 (1956).

^{2a} O. Diels, J.H. Blom and W. Kohl, *Liebigs Ann.* **443**, 243 (1925);

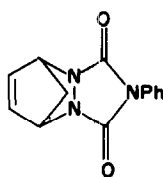
^b K. Alder and H. Niklas, *Ibid.* **585**, 81; 97 (1954).

³ J. Thiele and O. Stange, *Liebigs Ann.* **283**, 1 (1894).

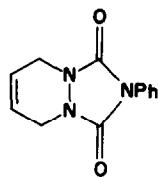
⁴ J. Stolle, *Ber. Dtsch. Chem. Ges.* **45**, 273 (1912).

We now wish to report that I may be conveniently prepared in 80 per cent yield by oxidizing 4-phenylurazole with t-butylhypochlorite in dry acetone at -50° to -78°C and may be used as a dienophile without isolation. By careful removal of solvent, followed by sublimation at reduced pressure, I may be obtained as carmine-red needles, which are quite stable in the absence of light and moisture; but are decomposed instantly by alkali and more slowly by acid, water or alcohol. Solid I decomposes without melting at $160\text{-}180^{\circ}$; but its solutions decompose at room temperature. The infra-red spectrum (Nujol) shows a strong carbonyl doublet at 1780 and 1760 cm^{-1} (cf. 4-phenylurazole singlet at 1682 cm^{-1}).

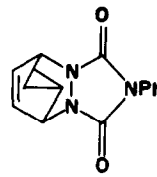
In acetone solution, I reacts instantaneously with cyclopentadiene at -78° and with butadiene and cycloheptatriene at -50° as evidenced by the immediate discharge of the red colour. The adducts II, III and IV, respectively, are formed in high yield. With bicycloheptadiene, I reacts



II



III



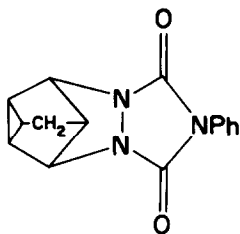
IV

rapidly at reflux, in acetone, to form the "anomalous" adduct V m.p. $173\text{-}174^{\circ}$, whose structure has been assigned on the basis of analysis (1:1 adduct), I.R. spectrum, absence of olefinic unsaturation and by analogy with the adducts of bicycloheptadiene with acrylonitrile,⁵ tetracyanoethylene⁶ and maleic anhydride.⁷

⁵ H.K. Hall, *J. Org. Chem.* **25**, 42 (1960).

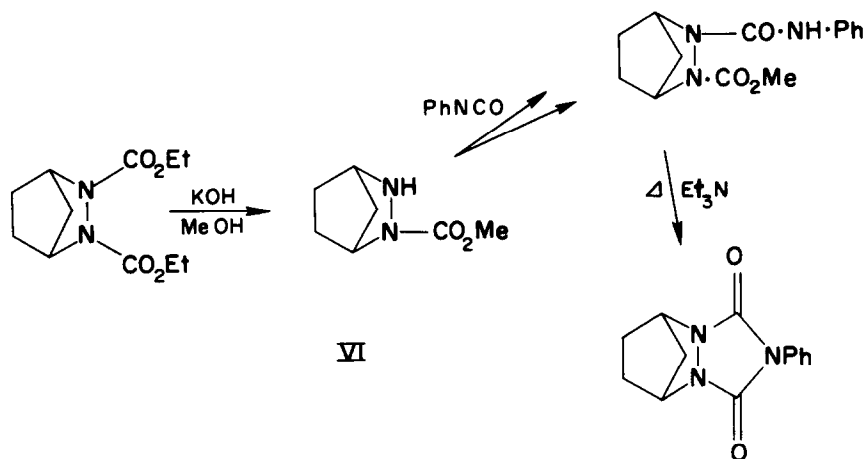
⁶ A.T. Blomquist and Y.C. Meinwald, *J. Amer. Chem. Soc.* **81**, 667 (1959).

⁷ E.F. Ullman, *Chem. & Ind.* 1173 (1958).



V

The structure of II, m.p. 143-145^o, has been confirmed by transforming the dihydro adduct of cyclopentadiene with ethyl azodicarboxylate, ^{2a,8} VI, into dihydro II by the reactions shown.

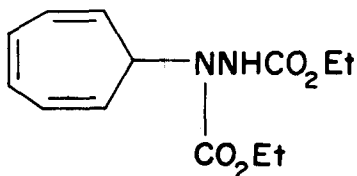


VI

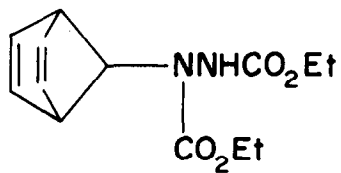
The structure of IV m.p. 186-188^o has been deduced from the analysis (1:1 adduct), I.R. spectrum, catalytic hydrogenation (1 double bond with Pd/C and 5 double bonds with Pt/HOAc) and N.M.R. spectrum (multiplet centred on "τ" 9.4 confirming the presence of the cyclopropane ring).

⁸ S.G. Cohen, R. Zand and C. Steel, J. Amer. Chem. Soc. **83**, 2895 (1961).

The formation of Diels-Alder adducts IV and V is in marked contrast to the behaviour of ethyl azodicarboxylate, which reacts slowly with cycloheptatriene⁹ to give VII and very slowly (even at elevated temperatures) with bicycloheptadiene to give a complex mixture of adducts probably formed via VIII.¹⁰



VII



VIII

This greatly enhanced dienophilic reactivity of a cis azo linkage flanked by either one or two carbonyl functions is also exemplified by the recent reports of Ullman and Barktus¹¹ on indazolone and by those of Clement¹² and of Kealy¹³ on diazaquinones.

Our thanks are due to Dr. J.C.D. Brand for measuring NMR spectra and to Dr. J. Hudec for much helpful discussion.

⁹ J.M. Cinnamon and K. Weiss, J. Org. Chem. **26**, 2644 (1961).

¹⁰ J. Hudec and S.S.H. Gilani, Unpublished observations.

¹¹ E.F. Ullman and E.A. Barktus, Chem. & Ind. 93 (1962).

¹² R.A. Clement, J. Org. Chem. **25**, 1724 (1960); **27**, 1115 (1962).

¹³ T.J. Kealy, J. Amer. Chem. Soc. **84**, 966 (1962).