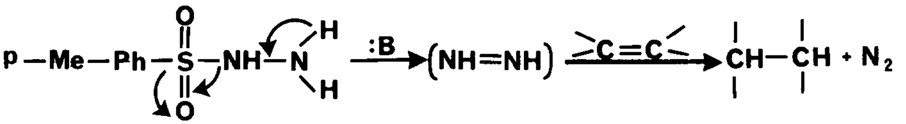
Tetrahedron Letters No. 15, pp 1333 - 1336.		0040-4039/79/0408-1333$02.00/0

# PERICYCLIC REACTIONS OF DIIMINE

F. Gaviña*, P. Gil and B. Palazón
Departamento de Química Orgánica, Facultad de Ciencias
Universidad de Zaragoza, Zaragoza, Spain

Diimine ($H_2N_2$) has been implicated as an intermediate in a variety of reduction reactions. Kinetic[1], as well as spectroscopic[2] and stereochemical[3] evidences have been used to support the intermediacy of $H_2N_2$. Thus, p-toluenesulfonylhydrazine is believed to generate diimine, through decomposition in presence of olefinic compounds[4]. Because decomposition can be accelerated by the addition of hydroxide ion, it may involve a β-elimination (eq. 1).



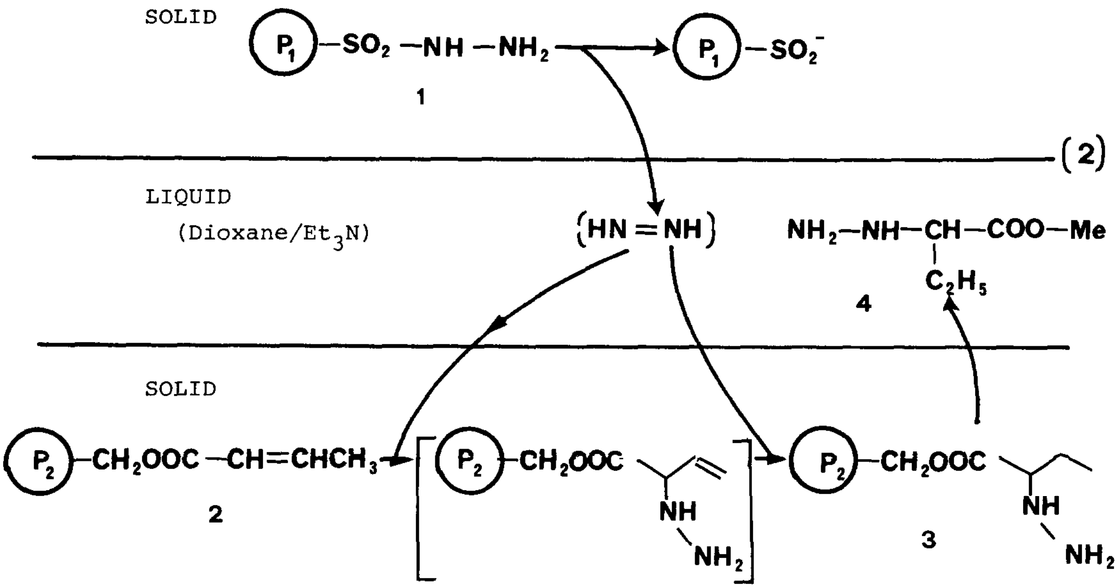
(1)

Attemps have been made to trap $H_2N_2$ by means of a Diels-Alder reaction[5], but, so far, there was no evidence of such reactions in diimine. We found that $H_2N_2$ can, in fact, be the subject of some pericyclic reactions. Additional evidence for free diimine in reactions like (1) was provided generating such active intermediate from a suitable polymer-bond precursor and trapping it as a pericyclic adduct on a second solid phase. This is the "Three-Phase Test", that has been succesfully used in the detection of several reactive intermediates[6].

Recently[7] it has been noticed that a variety of azo dienophiles give ene-Alder with preference to the Diels-Alder adduct with dienes. Accordingly, we performed the three-phase test for detection of free diimine, as follows:

Macroreticular, cross-linked polystyrene (Rohm & Haas, XE 305) was converted to the polymeric tosyl chloride[6a], then to the polymeric tosyl hydrazine <u>1</u>[8] (eq. 2). The trapping agent <u>2</u> (I.R., 1725, 1661 $cm^{-1}$) was prepared by treatment of chlorometylated 2% cross-linked (microreticular) Merrifield's resin with crotonic acid and triethylamine.

A suspension of the two solid phases in $Et_3N$ containing dioxane was heated under reflux for 6 hours. The resins were separed by flotation and the adduct resin 3 (eq. 2) was transesterified ($Me_2N(CH_2)_2OH/MeOH$) to give a mixture of methyl esters, from which compound 4[9] could be isolated by preparative TLC[10]:

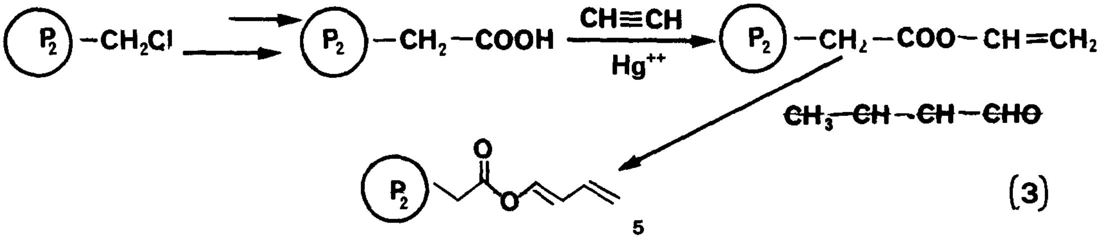


The isolation of that compound in the three phase experiment, unambiguously support the conclusion that tosyl hydrazine generates free diimine which add to trapping resin 2 by an ene-Alder reaction, as direct reaction of the two polymers is physically precluded. First adduct resin would be reduced to 3 by more free diimine.

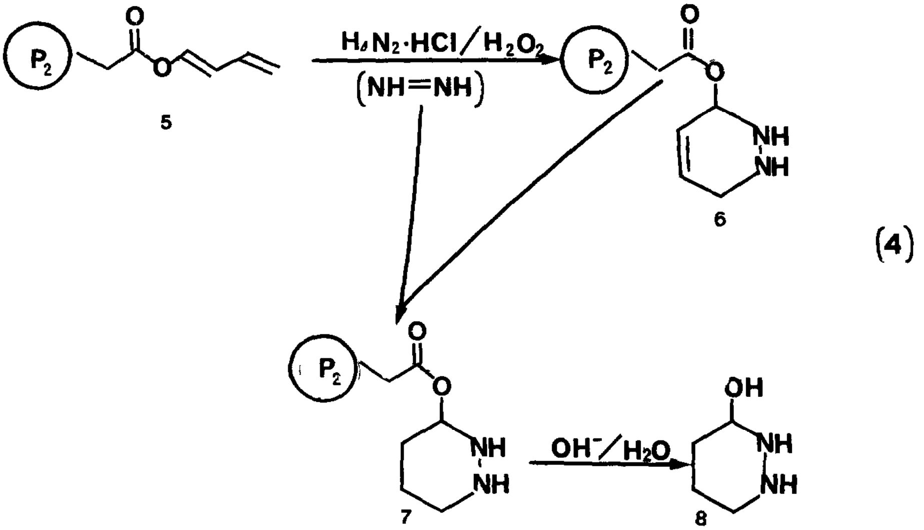
We felt that Diels-Alder reaction of diimine would take place provided "ene" reaction would be disallowed. Thus, trapping resin 5[11] (eq. 3) was prepared by succesive treatment of chloromethylated Merrifield's resin with KCN, hydrolysis and acetylene in presence of mercury salts[12], followed by crotonaldehyde in the presence of $Cu^{++}$ salts. This reaction has several non-resin counterparts[13].

First attemps to trap $H_2N_2$ on 5 using three phase were unsuccesful. Nevertheless, 5 showed to be able to trap diimine from other sources than polymeric tosyl hydrazine. Thus, when a mixture of $H_2O_2$ and $H_4N_2$.HCl was shaken at room temperature in the presence of 5 (eq. 4) it gave polymeric adduct 6, which was reduced to 7. Hydrolysis of 7 led to compound 8[14], isolated by preparative

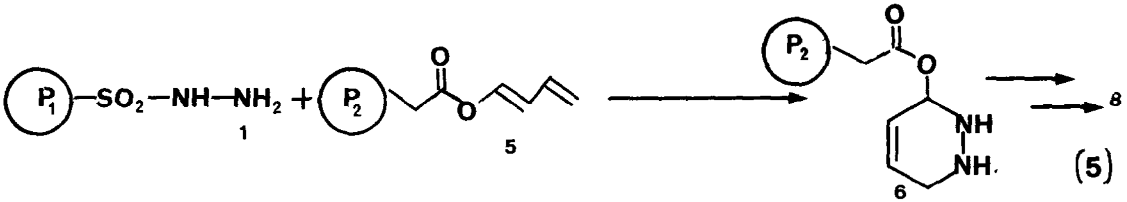
TLC.



These results are consistent with the concept of diimine being an intermediate in reductions with hydrazine and suggest that $H_2N_2$ is able to give Diels-Alder adduct with dienes.



More recently, we were able to make reaction (5), to give 8, identical with an authentic sample from reaction (4). Yields were lower than in reaction (2) (11%). We can conclude that Diels-Alder reaction of diimine is less favourable than ene-Alder one (at least with open dienes). Diels-Alder adduct yield is so low, that in three-phase conditions it was hard to identify:



Experiments starting from other polymeric diimine sources are underway.

## REFERENCES AND NOTES

1.- H. Paulsen and D. Stoye, *Chem. Ber.*, *99*, 908 (1966); R. Buyly, *Helv. Chim. Acta*, *47*, 2449 (1964)

2.- E. Blau, F. Hochheimer and H.J. Unger, *J. Chem. Phys.*, *34*, 1060 (1961)

3.- S. Hunig, H.R. Müller and W. Thier, *Tetrahedron Letters*, *1961*, 353

4.- R.S. Dewey and E.E. Van Tamelen, *J. Am. Chem. Soc.*, *83*, 3729 (1961)

5.- E. Corey, W.L. Mock and D.J. Pasto, *Tetrahedron Letters*, *1961*, 347

6.- (a) J. Rebek and F. Gaviña, *J. Am. Chem. Soc.*, *97*, 3453 (1975); (b) *ibid.* *97*, 1591 (1975); (c) *ibid.*, *97*, 3221 (1975); (d) J. Rebek, F. Gaviña and C. Navarro, *Tetrahedron Letters*, *35*, 3021 (1977)

7.- B.M. Jacobson, A.C. Feldstein and J.I. Smallwood, *J. Org. Chem.*, *42*, 2849 (1977)

8.- I.R., 3260, 3200, 1325, 1160 $cm^{-1}$; combustion analysis indicated 3.94 mequiv of hydrazine/g. Resin behaves as the already known donors of $H_2N_2$. Thus, reductions of oleic acid and cyclohexene were carried out by heating under reflux a suspension of resin 1 in a solution of the olefinic component.

9.- I.R. (KBr), 3220, 1740, 1200 $cm^{-1}$. $^1H$ NMR ($(CD_3)_2CO$) $\delta$, 0.9 (t, 3H), 1.4-1.6 (m, 2H), 2.5 (s, 3H), 3.6 (t, 1H), 3.8 (s, 3H). Elemental analysis gave expected results.

10.- Yield (on basis of polymeric tosyl hydrazine): 32%

11.- I.R., 1735, 1600, 1150, 1000, 950 $cm^{-1}$; by hydrolysis it gives free crotonaldehyde (0.5 mequiv/g. resin)

12.- R.H. Wiley, *O. S. coll. vol. III*, 853 (1955)

13.- W.J. Bayley and R. Barclay Jr., *J. Org. Chem.*, *21*, 328 (1956); J. Castells and J. Fernández Sánchez, *Anales Química*, *70*, 367 (1974)

14.- Yield (on basis of $H_4N_2.HCl$): 18%. Spectral data: $^1H$ NMR ($(CD_3)_2CO$) $\delta$, 1.8 (m, 4H), 2.3 (t, 2H), 4.7 (broad s, 3H), 4.9 (t, 1H); I.R. (KBr), 3350, 3250, 1450, 1150 $cm^{-1}$; MS, m/e 102, 84 ($M^+$- 18). Elemental analysis gave expected results.

(Received in UK 23 January 1979)