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## Phenyl Substituted Dipyrazoles:

## 1,3-Dipole Addition Reactions of Sydnones and Nitrilimines (I)

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A series of phenyl substituted phenylene dipyrazoles has been synthesized by the 1,3-dipole addition reactions of phenylenedisynone and phenylenedinitrilimines on phenyl acetylene as well as the reactions of phenylsydnone and phenylnitrilimine on diethynylbenzenes. A preliminary study of solvents for the sydnone reaction has been made.

In the course of an investigation aimed at the synthesis of polymers via 1,3-dipole addition reactions (2) as the mode of propagation, it was necessary to investigate the synthesis of several bis-dipoles, study the reaction conditions which favored optimum yields of products, and synthesize the corresponding model compounds whose structures could be related to the polymer recurring unit. On the basis of synthetic feasibility and the conversions in dipole addition reactions which had been reported, the sydnones (3,4), nitrilimines (5-8), and nitrile oxides seemed to be the most promising dipoles for the polymer-forming reaction. The reactions of iso- and terephthalonitrile oxides with various dipolarophiles in fact have been investigated in this respect (9-11).

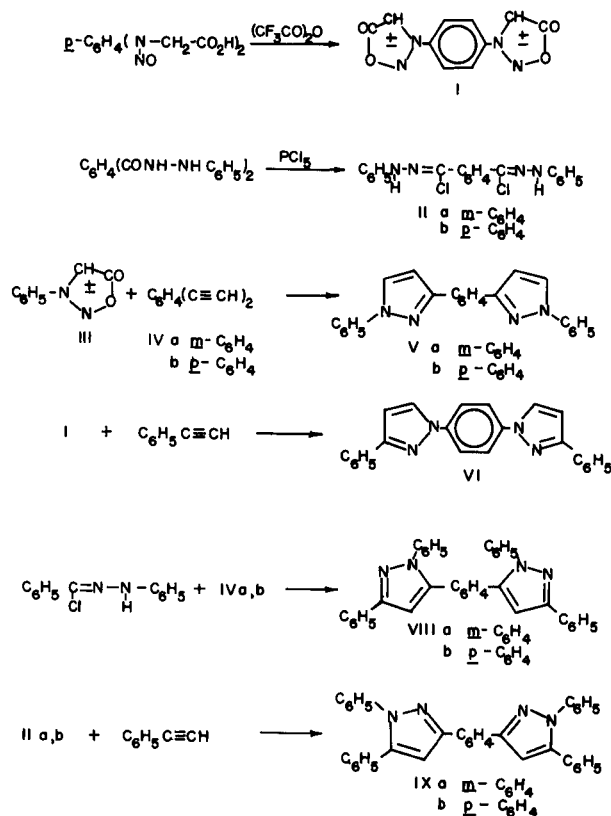
The synthesis of *p*-phenylene-3,3'-disynone (I) by the nitrosation of phenylene-*p*-diglycine and dehydration of the nitrosation product has been reported (12). Modification of the nitrosation procedure and the use of trifluoroacetic anhydride as the dehydrating reagent improves the yields significantly. The reactions of iso- and terephthaloylphenylhydrazides with phosphorous pentachloride afforded the corresponding iso- and terephthaloylphenylhydrazide chlorides (IIa,b).

The sydnone dipoles are known to undergo addition reactions with acetylenes, presumably through an intermediate Diels-Alder type adduct, with the subsequent loss of carbon dioxide to form pyrazoles (3,4). The nitrilimine, which is usually generated in the presence of a dipolarophile, can be obtained by the action of a tertiary amine on a phenylhydrazide chloride *in situ*. The products of the 1,3-dipole addition are also pyrazoles. In each case, the cycloaddition reactions afford only one isomer when the possibility of formation of several isomers exists, and the direction of the addition usually can be predicted from a consideration of the polar sites in both the dipole and dipolarophile.

The reaction of 3-phenylsydnone (III) (13) with *m*- and *p*-diethynylbenzene (IVa,b) (14) in refluxing xylene gave the *m*- and *p*-phenylenedipyrazoles (Va,

b) respectively. A study of reaction solvents for this reaction as followed both by the evolution of carbon dioxide and the yield of dipyrazole (Table I), showed that nitrobenzene and xylene gave higher yields of product than diglyme, while *m*-dichlorobenzene gave an oil. Similarly, the reaction of I with phenylacetylene provided 3,3'-diphenyl-1,1'-*p*-phenylenedipyrazole (VI).

The reaction of benzoylphenylhydrazide chloride (VII) with triethyl amine in refluxing benzene gene-



rated the corresponding nitrilimine which reacted with *m*- and *p*-diethynylbenzene to afford the 1,1',-3,3'-tetraphenyl-5,5'-*m*- and *p*-phenylenedipyrzoles (VIIIa, b) respectively. The 1,1',5,5'-tetraphenyl-3,3'-*m*- and *p*-phenylenedipyrzoles (IXa, b) were obtained from the bis-nitrilimine precursors, IIa, b, and phenyl acetylene.

The high melting points of these phenylated phenylenedipyrzoles is a reflection of the polarity of the pyrazole ring. The melting points of these polyaromatic structures can be compared with the polyphenyl analogs by replacing the pyrazole ring with a *m*-phenylene ring. Thus, 1,1':3', 1'':4'', 1''':3''', 1''''-quinquephenyl, m.p. 233-234° (15) corresponds to Vb and VI, m.p. 223-224° and 225-227°, respectively. The quinquephenyl containing three *m*-phenylene units is low melting, 97-98° (16) and this low melting point is also reflected in the dissymmetry of Va, m.p. 150°.

## EXPERIMENTAL

### *N,N'*-Dinitroso-*p*-phenylenediglycine.

The nitrosation of *p*-phenylenediglycine (17) was carried out as described (12) except that the following modifications were made: After the slow addition of a solution of 12.75 g. (0.15 mole) of potassium nitrite in 20 ml. of water to 18.0 g. (0.8 mole) of *p*-phenylenediglycine in 45 ml. of water at 0° and 2 hours of stirring at 0°, the mixture was filtered. The filtrate was then made acidic by the addition of 10% hydrochloric acid until a black semi-solid layer formed on the top. The black material was removed by filtration, and the deep yellow filtrate was further acidified until red-brown crystals appeared. The crystals were filtered, washed with ice water and dried under reduced pressure to afford 10 g. (47.3%) of crude product. Recrystallization from 4:1 ethanol-water using decolorizing charcoal afforded 2.25 g. (10.7%) of white product, m.p. 139-140° (d), reported (12) 138-139° (d). A positive Liebermann's test was obtained. Infrared maxima were observed at 1733, 1509, 1416 and 1402 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>O<sub>6</sub>: C, 42.55; H, 3.57; N, 19.85. Found: C, 42.90; H, 3.92; N, 19.00.

### *p*-Phenylene-3,3'-disydnone (I).

Acetic anhydride dehydration: The dehydration of *N,N'*-dinitroso-phenylene-*p*-diglycine with acetic anhydride at room temperature for 5 days followed by a treatment at 75-80° for 1.5 hours was carried out as described (12). From 6.0 g. (0.024 mole) of dinitroso compound was obtained 1.01 g. (17.7%) of crude product which was recrystallized from water and carefully dried over a long period to afford pure product m.p. 255-256° (d), reported (12) 360°. Infrared maxima were observed at 1760 and 733 cm<sup>-1</sup>.

*Anal.* Calcd. for C<sub>10</sub>H<sub>6</sub>N<sub>4</sub>O<sub>4</sub>: C, 48.78; H, 2.45; N, 22.76. Found: C, 48.92; H, 3.20; N, 21.93.

Trifluoroacetic anhydride dehydration: To a solution of 6.0 g. (0.024 mole) of *N,N'*-dinitroso-phenylene-*p*-diglycine in 36 ml. of anhydrous methylene chloride at 0° was added slowly 22.5 ml. of trifluoroacetic anhydride. After the initial reaction subsided, the mixture was heated at the reflux temperature for 1 hour, cooled, and then poured into 300 ml. of ice water. The yellow precipitate was filtered, washed with cold ethanol, and dried to yield 4.05 g. (71%) of disydnone, m.p. 255-256° (d).

Found: C, 48.84; H, 2.79; N, 23.00.

Pure dinitroso compound was not necessary in this reaction; equally good yields were obtained from the crude material.

### Isophthaloylphenylhydrazide.

To a cooled solution of 108 g. (1.0 mole) phenylhydrazine in 150 ml. anhydrous ether was slowly added a solution of 50.7 g. (0.25 mole) isophthaloyl chloride in 200 ml. of anhydrous ether. The resulting precipitate was filtered, triturated with water, and recrystallized from ethanol to afford 59 g. (61.7%) of product, m.p. 260-262°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>: C, 69.36; H, 5.20; N, 16.18. Found: C, 69.11; H, 5.23; N, 16.19.

### Terephthaloylphenylhydrazide.

The preparation of terephthaloylphenylhydrazide was carried out as described for the *m*-isomer to afford 66 g. (68.9%) of product, m.p. 260-262°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>: C, 69.36; H, 5.20; N, 16.18. Found: C, 69.61; H, 5.34; N, 16.37.

### Isophthaloylphenylhydrazide chloride (IIa).

A mixture of 20 g. (0.057 mole) isophthaloylphenylhydrazide and 24 g. (0.114 mole) phosphorus pentachloride in 100 ml. anhydrous ether was heated under reflux for 24 hours. To the mixture was added 80 g. of phenol in 60 ml. ether, followed by the slow addition of 80 ml. of methanol. The solution was evaporated to low volume and allowed to cool. The dark brown precipitate which formed was filtered and recrystallized from acetone-water to afford 12.4 g. (58.3%) of product, m.p. 165-166°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>4</sub>: C, 62.66; H, 4.20; N, 14.62. Found: C, 62.58; H, 4.42; N, 14.49.

### Terephthaloylphenylhydrazide chloride (IIb).

The preparation of terephthaloylphenylhydrazide chloride was carried out as described for the *m*-isomer to afford 10.7 g. (50.3%) of product, m.p. 205-206°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>4</sub>: C, 62.66; H, 4.20; N, 14.62. Found: C, 62.67; H, 4.17; N, 14.63.

### *m*-Diethynylbenzene (IVa).

This compound was prepared by the bromination of pure *m*-divinylbenzene (18) and the subsequent dehydrobromination of this intermediate according to the known procedure (14).

### 1,1'-Diphenyl-3,3'-*m*-phenylenedipyrzole (Va).

To a solution of 0.81 g. (0.005 mole) of 3-phenylsydnone (III) in 5 ml. of *o*-xylene was added 0.315 g. (0.0025 mole) of *m*-diethynylbenzene (IVa). The mixture was heated at the reflux temperature for 20 hours and allowed to cool. During this period, 75 ml. (67%) of carbon dioxide was evolved. The red solid which precipitated was removed and recrystallized from ethanol to yield 0.272 g. (30%) of a light yellow compound, m.p. 150-152°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>: C, 79.54; H, 5.00; N, 15.46. Found: C, 79.17; H, 5.22; N, 15.27.

### 1,1'-Diphenyl-3,3'-*p*-phenylenedipyrzole (Vb).

To a solution of 0.81 g. (0.005 mole) of 3-phenylsydnone (III) in 10 ml. of *o*-xylene was added 0.315 g. (0.0025 mole) of *p*-diethynylbenzene (IVb) (14). The mixture was heated at the reflux temperature for 20 hours during which time 112 ml. (100%) of carbon dioxide was evolved. Upon cooling, yellow crystals formed which were removed and recrystallized from pyridine. There was obtained 0.687 g. (75.88%) of light yellow product, m.p. 233-234°.

*Anal.* Calcd. for C<sub>24</sub>H<sub>18</sub>N<sub>4</sub>: C, 79.54; H, 5.00; N, 15.46. Found: C, 79.54; H, 5.30; N, 15.31.

This reaction was carried out in four different solvents--xylene, *m*-dichlorobenzene, nitrobenzene, and diglyme as follows: In 50 ml. of each solvent was dissolved 0.81 g. (0.005 mole) of 3-phenylsydnone. In some cases, warming was necessary. The reaction flasks, connected to gas burettes, were then immersed in oil baths at 155° and 0.315 g. (0.0025 mole) of *p*-diethynylbenzene was added. After 30 hours, the amount of carbon dioxide which had evolved was measured by allowing the flasks to cool to 25°, the temperature at which the burettes had been leveled prior to the start of the reaction. The reaction solvent was removed under reduced pressure, the products were washed with pentane and recrystallized from pyridine. All reactions were carried out at 155°, except the reaction in xylene, which was carried out at the reflux temperature, nearly 15° lower.

TABLE 1

Solvent	% CO <sub>2</sub> Evolved	% Yield Product
Nitrobenzene	89	78
Xylene	80	75
Diglyme	66	56
Dichlorobenzene	74	(a)

(a) Solvent reacted to afford an oil.

3,3'-Diphenyl-1,1'-*p*-phenylenedipyrazole (VI).

To a solution of 0.615 g. (0.0025 mole) of *p*-phenylene-3,3'-disydnone (I) in 5 ml. of nitrobenzene was added 0.510 g. (0.005 mole) of phenyl acetylene. The mixture was heated at 190° for 20 hours and allowed to cool; 90 ml. (80%) of carbon dioxide had been collected. The yellow crystals which formed were removed and recrystallized from pyridine to give 0.561 g. (62%) of light yellow product, m.p. 225-227°.

*Anal.* Calcd. for  $C_{24}H_{18}N_4$ : C, 79.54; H, 5.00; N, 15.46. Found: C, 79.59; H, 5.29; N, 15.27.

1,1',3,3'-Tetraphenyl-5,5'-*m*-phenylenedipyrazole (VIIIa).

To a mixture of 0.252 g. (0.002 mole) of *m*-diethynylbenzene and 0.920 g. (0.004 mole) of benzoylphenylhydrazide chloride (5) in 10 ml. of benzene at the reflux temperature was added 3 ml. of triethylamine. After the addition was complete, the mixture was heated under reflux for 2 hours. The dark brown precipitate which formed was filtered, washed with ethanol to remove triethylamine hydrochloride, and recrystallized from pyridine to afford 0.740 g. (72.1%) of light yellow product, m.p. 232-234°.

*Anal.* Calcd. for  $C_{38}H_{28}N_4$ : C, 84.01; H, 5.09; N, 10.89. Found: C, 83.73; H, 5.26; N, 10.82.

1,1',3,3'-Tetraphenyl-5,5'-*p*-phenylenedipyrazole (VIIIb).

The preparation of 1,1',3,3'-tetraphenyl-5,5'-*p*-phenylenedipyrazole was carried out as described for the *m*-isomer to afford 0.798 g. (77.6%) of light yellow product, m.p. 242-244°.

*Anal.* Calcd. for  $C_{38}H_{28}N_4$ : C, 84.01; H, 5.09; N, 10.89. Found: C, 84.34; H, 5.01; N, 10.66.

1,1',5,5'-Tetraphenyl-3,3'-*m*-phenylenedipyrazole (IXa).

To a mixture of 0.766 g. (0.002 mole) isophthaloylphenylhydrazide chloride and 5 ml. of phenyl acetylene in 8 ml. of benzene at the reflux temperature was added 3 ml. of triethylamine. After the addition was complete, the mixture was heated under reflux for 4 hours. The solution was then evaporated to low volume and allowed to cool overnight. The dark brown precipitate which formed was filtered, washed with ethanol to remove triethylamine hydrochloride, and recrystallized from pyridine to afford 0.520 g. (50.5%) of light yellow product, m.p. 205-206°.

*Anal.* Calcd. for  $C_{38}H_{28}N_4$ : C, 84.01; H, 5.09; N, 10.89. Found: C, 83.98; H, 5.25; N, 10.87.

1,1',5,5'-Tetraphenyl-3,3'-*p*-phenylenedipyrazole (IXb).

The preparation of 1,1',5,5'-tetraphenyl-3,3'-*p*-phenylenedipyrazole was carried out as described for the *m*-isomer to afford 0.576 g. (56%) of light yellow product, m.p. 256-258°.

*Anal.* Calcd. for  $C_{38}H_{28}N_4$ : C, 84.01; H, 5.09; N, 10.89. Found: C, 84.12; H, 5.27; N, 10.71.

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