

Synthesis of Phenylated Phthalimides.  
The Diels-Alder Reaction of Tetraphenylcyclopentadienone with Maleimides

Frank W. Harris and Steve O. Norris

Department of Chemistry, Wright State University, Dayton, Ohio 45431

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A series of phenylated dihydrophthalimides has been synthesized by the Diels-Alder reaction of tetraphenylcyclopentadienone with maleimide, *N*-phenylmaleimide, and *N,N'*-*o*-, *m*-, and *p*-phenylenedimaleimide. Subsequent dehydrogenation of these compounds yielded the corresponding phenylated phthalimides. These phthalimides were also obtained in one step when the initial reactions were carried out in refluxing nitrobenzene.

In the course of a study aimed at the synthesis of polymers *via* Diels-Alder addition reactions (1), the reaction of tetraphenylcyclopentadienone (tetracyclone) with maleimides was investigated as a possible mode of propagation in the synthesis of phenylated polyimides. The Diels-Alder reaction of tetracyclone (I) with several substituted alkenes (II) had previously been carried out to afford a series of bridged carbonyl compounds (III) (2,3). These compounds lost carbon monoxide upon heating with the temperature needed depending upon the structure of the compound. The reaction of tetracyclone and alkene had also been carried out under conditions in which the carbonyl bridge was lost. The dihydrobenzene intermediates (IV) were aromatized thermally or with chemical dehydrogenating agents. In fact, aromatic products (V) were obtained when the initial reactions were run at high temperature or when an oxidizing agent or palladium on charcoal was used (4).

The reaction of tetracyclone with maleimide (VIa) and *N*-phenylmaleimide (VIb) in refluxing  $\alpha$ -chloronaphthalene for 2 hours or refluxing 1,2,4-trichlorobenzene

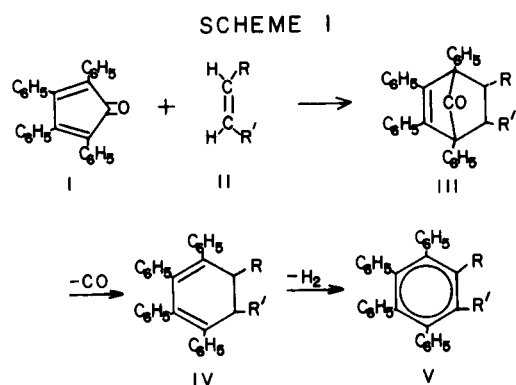
for 18 hours afforded quantitative yields of 1,2-dihydro-3,4,5,6-tetraphenylphthalimide (VIIa) and *N*-phenyl-1,2-dihydro-3,4,5,6-tetraphenylphthalimide (VIIb), respectively. Similarly, the reaction of I with *N,N'*-*o*-, *m*-, and *p*-phenylenedimaleimide (IXa-c) provided the bisdihydrophthalimides Xa, b, and c.

The dihydrophthalimides VIIa,b, and Xa-c were dehydrogenated by treatment with bromine in trichlorobenzene to afford high yields (88-92%) of the phthalimides VIIa,b and XIa-c, respectively. These phthalimides were also obtained in one step when the initial reaction of I with the appropriate maleimide was carried out in refluxing nitrobenzene for 12 hours. The yields of phthalimides prepared in this manner ranged from 90 to 95%.

Attainment of aromaticity upon dehydrogenation of the dihydrophthalimides was evidenced by large increases in melting point (Tables I and II). Although aromatization also resulted in a decrease in solubility in hydrogen-bonding solvents, the phenylated phthalimides were very soluble in chloroform, dioxane, and aromatic solvents. All of these high-melting compounds (332-479°) were white and crystalline.

Dehydrogenation of the dihydrophthalimides also produced marked changes in their ultraviolet spectra (Tables II and III). The high intensity absorption band at 225-235 m $\mu$  was shifted to 252-263 m $\mu$  with an increase in intensity while the absorption band at 320-322 m $\mu$  decreased in intensity. This demonstrates the large effect of the benzene nucleus of the phthalimide residue on the absorption spectra. This effect was noted previously by Arcoria and Passerini (5) who found that the introduction of substituents in the 3 and 4 positions dramatically affected the ultraviolet spectrum of phthalimide.

In the infrared region the strong carbonyl absorption band at 1780-1790 cm<sup>-1</sup> was shifted to 1765-1780 cm<sup>-1</sup>



## SCHEME 2

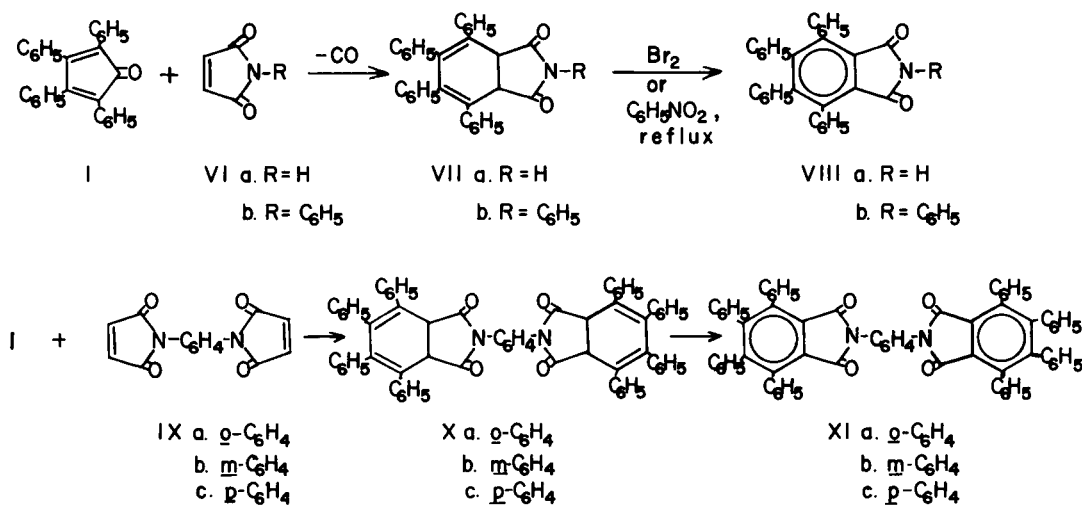


TABLE I

## Phenylated Dihydrophthalimides

Compound Number	M.p., °C	Empirical Formula	C	Analyses				
				Calculated	H	N	C	Found
VIIa	290-292	C <sub>32</sub> H <sub>23</sub> NO <sub>2</sub>	84.74	5.11	3.09	84.47	5.02	3.22
VIIb	236-238	C <sub>38</sub> H <sub>27</sub> NO <sub>2</sub>	86.17	5.14	2.65	85.85	4.98	2.66
Xa	300-301	C <sub>70</sub> H <sub>48</sub> N <sub>2</sub> O <sub>4</sub>	85.69	4.93	2.86	85.82	5.07	2.68
Xb	306-308	C <sub>70</sub> H <sub>48</sub> N <sub>2</sub> O <sub>4</sub>	85.69	4.93	2.86	85.76	4.98	2.79
Xc	340-342	C <sub>70</sub> H <sub>48</sub> N <sub>2</sub> O <sub>4</sub>	85.69	4.93	2.86	85.49	5.13	2.82

TABLE II

## Phenylated Phthalimides

Compound Number	M.p., °C	Empirical Formula	C	Analyses				
				Calculated	H	N	C	Found
VIIIa	332-334	C <sub>32</sub> H <sub>21</sub> NO <sub>2</sub>	85.12	4.69	3.10	85.34	4.81	3.07
VIIIb	351-352 (a)	C <sub>38</sub> H <sub>25</sub> NO <sub>2</sub>	86.50	4.78	2.65	86.38	4.70	2.75
XIa	411-413	C <sub>70</sub> H <sub>44</sub> N <sub>2</sub> O <sub>4</sub>	86.04	4.53	2.86	86.34	4.83	2.52
XIb	478-479	C <sub>70</sub> H <sub>44</sub> N <sub>2</sub> O <sub>4</sub>	86.04	4.53	2.86	85.77	4.50	2.83
XIc	462-463	C <sub>70</sub> H <sub>44</sub> N <sub>2</sub> O <sub>4</sub>	86.04	4.53	2.86	85.85	4.50	2.90

(a) Lit. (7) m.p. 348-353°.

with the increase in conjugation. The second carbonyl absorption band at 1710-1730 cm<sup>-1</sup>, characteristic of 5-membered cyclic imides (6), was not affected. The conversion to phthalimide could also be followed with nmr by the disappearance of the singlet peak at 4.34 ppm due to the loss of the fusion hydrogens.

## EXPERIMENTAL

Melting points were determined on Mel-temp and Thomas-Hoover Capillary Melting Point Apparatus and are uncorrected. Infrared, ultraviolet, and nuclear magnetic resonance spectra were recorded on Perkin-Elmer 457, Cary-14, and Varian HA-60 spectrophotometers, respectively. Analyses were performed by A. Bern-

TABLE III  
Spectral Data for Dihydrophthalimides

Compound Number	Uv (a)		Ir (b) C=O
	$\lambda_1$ ( $\epsilon \times 10^{-3}$ )	$\lambda_2$ ( $\epsilon \times 10^{-3}$ )	
VIIa	232 (20.0) sh	320 (12.0)	1780, 1710
VIIIb	230 (34.0)	322 (11.1)	1780, 1710
Xa	228 (50.3) sh	320 (21.6)	1790, 1730
Xb	230 (56.4) sh	320 (21.4)	1780, 1710
Xc	235 (60.4)	322 (21.3)	1780, 1715

(a) Determined in 1,4-dioxane with absorption maxima reported in  $\mu$ . (b) Determined in potassium bromide pellets with carbonyl absorption bands reported in  $\text{cm}^{-1}$ .

TABLE IV  
Spectral Data for Phthalimides

Compound Number	Uv (a)		Ir (b) C=O
	$\lambda_1$ ( $\epsilon \times 10^{-3}$ )	$\lambda_2$ ( $\epsilon \times 10^{-3}$ )	
VIIIa	252 (26.7) sh	322 (5.3)	1765, 1710
VIIIb	253 (47.5)	320 (4.5) sh	1770, 1710
XIa	252 (77.7)	325 (7.7)	1780, 1730
XIb	253 (87.4)	320 (9.1)	1775, 1720
XIc	263 (74.8)	322 (10.2) sh	1775, 1720

(a) Determined in 1,4-dioxane with absorption maxima reported in  $\mu$ . (b) Determined in potassium bromide pellets with carbonyl absorption bands reported in  $\text{cm}^{-1}$ .

hardt, Mikroanalytisches Laboratorium, 5251 Elbach über Engelkirchen, Fritz-Pregl Strasse 14-16, West Germany.

Maleimide, *N*-phenylmaleimide, and *N,N'*-*o*- and -*p*-phenylenedimaleimide were obtained from Aldrich Chemical Company. *N,N'*-*o*- and -*p*-phenylenedimaleimide were recrystallized from peroxide-free dioxane prior to use.

Tetraphenylcyclopentadienone (Tetracyclone) (I).

Tetracyclone was prepared by the base-catalyzed condensation of 1,3-diphenyl-2-propanone and benzil according to the known procedure (8).

*N,N'*-*m*-Phenylenedimaleimide (IXb).

Condensation of *m*-phenylenediamine with maleic anhydride according to the known procedure gave *N,N'*-*m*-phenylenedimaleamic acid which upon elimination of water yielded the dimaleimide (9).

Preparation of Dihydrophthalimides (VIIa and b).

A mixture of 0.002 mole maleimide or *N*-phenylmaleimide and 0.002 mole tetracyclone was stirred in refluxing  $\alpha$ -chloronaphthalene for 4 hours or refluxing 1,2,4-trichlorobenzene for 18 hours. Approximately two-thirds of the solvent was removed under reduced pressure and the residue added to hexane. The light yellow precipitate which formed was collected by filtration and recrystallized from absolute ethanol to afford a quantitative yield of white needles.

Preparation of Bisdihydrophthalimides (Xa-c).

The bisdihydrophthalimides Xa-c were prepared by the procedure described for VIIa,b with a 2:1 molar ratio of tetracyclone to dimaleimide. Recrystallization from benzene-ethanol afforded quantitative yields of the white products.

General Procedure for the Dehydrogenation of Dihydrophthalimides (10).

To a solution of 0.010 mole of dihydrophthalimide in 20 ml. of warm 1,2,4-trichlorobenzene was slowly added 0.011 mole of bromine. After the addition was complete, the solution was refluxed for 3 hours with considerable evolution of hydrogen bromide. Upon cooling the white product precipitated from solution and was collected by filtration. Recrystallization from benzene-ethanol afforded a high yield (88-92%) of the white, crystalline phthalimide.

Direct Preparation of Phthalimides (VIIIa,b, and XIa-c).

The phthalimides VIIIa,b and XIa-c were obtained by the procedures described for VIIa,b and Xa-c when the initial reactions were carried out in refluxing nitrobenzene for 12 hours (yields 90-95%).

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