



Title	A SUCCESSFUL PREPARATION OF 2-ARYL-2,3-DIHYDRO-2,3-IMINO-1,4-NAPHTHOQUINONES
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A SUCCESSFUL PREPARATION OF  
2-ARYL-2,3-DIHYDRO-2,3-IMINO-1,4-NAPHTHOQUINONES

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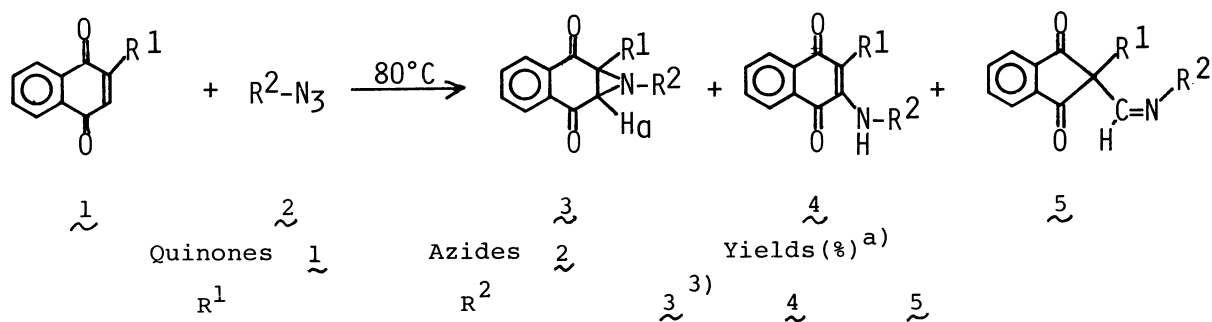
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A new class of compounds, 2-aryl-2,3-dihydro-2,3-imino-1,4-naphthoquinones 3, was synthesized for the first time by heating 2-aryl-1,4-naphthoquinones with aryl azides. The yields were 30-50% when p-methoxy-phenyl azide was used.

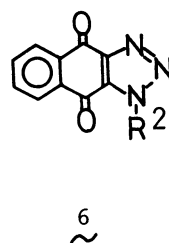
This is the first successful preparation of new class of compounds 2-aryl-2,3-dihydro-2,3-imino-1,4-naphthoquinones 3. Though compounds 3 have a simple structure, the syntheses to our knowledge have not yet been accomplished despite of a lot of trials.<sup>1)</sup>

A typical procedure of iminodihydronaphthoquinone preparation is as follows; a mixture of 1 mmol of 1a, 3 mmol of 2a, and 200 mg of Na<sub>2</sub>CO<sub>3</sub> (added to suppress acid catalyzed isomerization of 3) was heated at 80°C without using any solvent. When almost the starting quinone was consumed after about 4 days, the reaction products were separated by passing the CH<sub>2</sub>Cl<sub>2</sub> solution of the mixture through a column of silica gel with hexane-ether as eluents. Three products were isolated; 2,3-dihydro-2,3-(N-p-anisidino)imino-2-phenyl-1,4-naphthoquinone 3a, 2-p-anisidino-3-phenyl-1,4-naphthoquinone 4a, and 2-(p-anisidinoiminomethyl)-2-phenyl-1,3-indandione 5a. Their yields are tabulated in Table. Electron donating substituent at phenyl azide tended to increase the yields of 3. The structure of 3a was confirmed by the following spectral data and by the acid catalyzed isomerization to 4a. The spectral data of 3a; <sup>1</sup>HNMR(CDCl<sub>3</sub>) δ 3.56(s, 3H, OCH<sub>3</sub>), 3.96(s, 1H, NCH), 6.45(d, J=9Hz, 2H, aromatic), 6.66(d, J=9Hz, 2H, aromatic), 7.2-7.4(m, 5H, aromatic), 7.4-7.6(m, 2H, aromatic), 7.8-8.0(m, 2H, aromatic); IR(KBr) cm<sup>-1</sup> 1690(CO), 1590, 1510, 1245, 1030, 860, 820, 755, 700; MS(10 eV) m/e(rel. intensity) 355(M<sup>+</sup>, 100). Anal. Calculated for C<sub>23</sub>H<sub>17</sub>O<sub>3</sub>N: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.45; H, 4.68; N, 3.86. Mp. 139-140°C. The analytical data exclude a possibility of triazoline derivative. The <sup>1</sup>HNMR signal at δ 3.96 was assigned as the proton attaching to the carbon adjacent to the nitrogen on aziridine ring(H<sub>a</sub>), which exhibited a reasonable value compared with that of other aziridine derivative.<sup>2)</sup> Other naphthoquinone derivatives than 2-aryl-1,4-naphthoquinones failed to afford iminodihydronaphthoquinones under similar conditions. 1,4-Naphthoquinone and its 2-methoxy- or 2-amino-derivatives gave the corresponding triazole derivatives 6 and 1,3-indandione derivatives. 2,3-Disubstituted 1,4-naphthoquinones gave no adducts and the starting quinones were recovered.

Table. Reactions of Quinones and Azides



	Quinones R <sup>1</sup>	Azides R <sup>2</sup>	3 <sup>3)</sup>	4	5
a.	Ph	p-MeOC <sub>6</sub> H <sub>4</sub>	52	trace	40
b.	Ph	Ph	28	6	38
c.	Ph	p-ClC <sub>6</sub> H <sub>4</sub>	22	13	31
d.	Ph	p-BrC <sub>6</sub> H <sub>4</sub>	19	3	29
e.	p-ClC <sub>6</sub> H <sub>4</sub>	p-MeOC <sub>6</sub> H <sub>4</sub>	38	8	34
f.	p-ClC <sub>6</sub> H <sub>4</sub>	p-ClC <sub>6</sub> H <sub>4</sub>	19	9	41
g.	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	p-MeOC <sub>6</sub> H <sub>4</sub>	34	8	43
h.	p-MeOC <sub>6</sub> H <sub>4</sub>	p-MeOC <sub>6</sub> H <sub>4</sub>	20	10	32



a) Isolated yields.

## References and Notes

- (1) a) L. Wolff, *Ann. Chem.*, **394**, 68 (1912); *ibid.*, **399**, 274 (1913). b) A. Korczynski reported that hydrazoic acid reacted with 1,4-naphthoquinone to give 2,3-imino-1,4-naphthoquinone (A. Korczynski and St. Namylslowski, *Bull. Soc. Chim. Fr.*, **35**, 1186 (1924)). However, it was found to be erroneous and the product was 2-amino-1,4-naphthoquinone in fact (L. F. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, **57**, 1482 (1935)). c) Other trials done by us ended in failure: i) The Gabriel reaction of brominated naphthoquinone (2,3-dibromo-2,3-dihydro-1,4-naphthoquinone) with several kinds of amines afforded 2-(N-substituted)-amino-1,4-naphthoquinones. 2,3-Dibromo-2,3-dimethyl-naphthoquinone with amines afforded 2,3-dimethyl-1,4-naphthoquinone. ii) 1,4-Naphthoquinone was treated with bromoazide or iodoazide but 2-azido-1,4-naphthoquinone was afforded.
- (2) A. Padwa and L. Hamilton, *J. Am. Chem. Soc.*, **89**, 102 (1967).
- (3) The melting points of products 3; 3a: 139-140°C, 3b: 169-170°C, 3c: 207-209°C, 3d: 201-202°C, 3e: 134-135°C, 3f: 210-212°C, 3g: oil, 3h: 159-160°C.

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