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Direct Nitration of 3-Arylamino-2-Chloro-1,4 Naphthoquinones; Novel Quinone derivatives

[A015]

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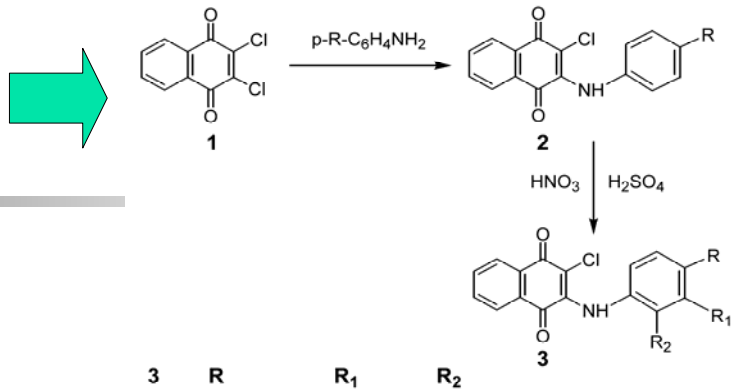
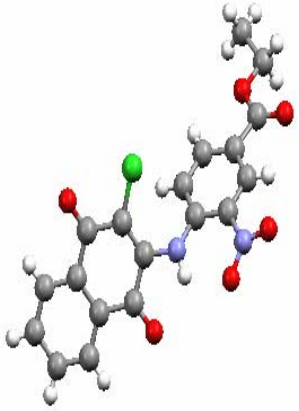
The Michael type addition of aromatic amines to 2,3-dichloro-1,4-naphtho quinone does not work with nitroanilines. We developed a convenient method for the direct mono- and dinitration of 3-arylamino-2-chloro-1,4 naphtho quinones. A series of new quinone derivatives, unattainable before, of potential biological importance were prepared. The strong electron withdrawing nature of 2,4-dinitrophenylamino group when attached to chloro-naphthoquinone (**3**) enhances the

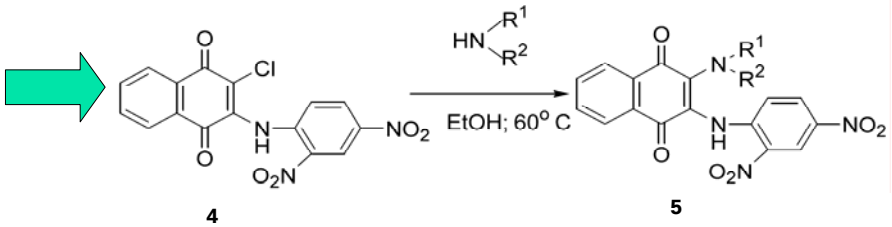




Single crystal structure of **3f**

3	R	R_1	R_2
a	NO_2	H	H
b	CH_3	NO_2	H
c	$(CH_2)_{13}CH_3$	NO_2	H
d	OCH_3	NO_2	H
e	F	NO_2	H
f	COOEt	H	NO_2
g	NO_2	H	NO_2
h	OCH_3	NO_2	NO_2

Various primary and secondery aliphatic amines, cyclic and aromatic amines could substitute the chlorine and yield a novel series of 2-amino-3-(2,4-dinitrophenyl amino) derivatives of 1,4-naphthoquinone (**5**). Synthetic parameters and spectral data of both the mono- and the dinitro derivatives will be presented.



UV-Vis data of 4 and 5a-h in $CHCl_3$

Compds	λ1 (log ε)	λ2 (log ε)	λ3 (log ε)
4	264(4.09)	334(4.03)	440(3.70)
5a	266(4.14)	342(4.21)	452(3.49)
5b	274(4.49)	352(4.28)	488(3.61)
5c	266(4.32)	342(4.17)	508(3.23)
5d	284(4.33)	352(4.13)	498(3.73)
5e	294(4.33)	360(4.22)	524(3.77)
5f	292(4.29)	360(4.15)	522(3.70)
5g	286(4.23)	380(3.99)	542(3.48)
5h	286(4.41)	384(4.16)	540(3.54)

Entry	R^1	R^2	Compd	Ratio [4:Amine]	yield (%)
1	H	H	**5a**	excess NH_3	52
2	H	$CH_3(CH_2)_4CH_2$	**5b**	1:6	63
3	CH_3CH_2	CH_3CH_2	**5c**	1:5	58
4			**5d**	1:2	65
5			**5e**	1:3	63
6		N	**5f**	1:3	77
7	H	*p*-HO-C_6H_4	**5g**	1:4	78
8	H	*p*-CH_3O-C_6H_4	**5h**	1:9	75

It was shown that the very strong electron withdrawing nature of the 2,4-dinitrophenylamino group allowed the easy displacement of the second chlorine atom by various aliphatic, cyclic and aromatic amines. These new quinones have of two acceptors and one donor and might be expected to show unusual spectroscopic, electrochemical and other properties.