Tetrahedron Letters, Vol.31, No.34, pp 4871-4872, 1990
Printed in Great Britain

0040-4039/90 $3.00 + .00
Pergamon Press plc

OXIDATION OF PHENOLS TO QUINONES BY BIS(TRIFLUOROACETOXY)IODOBENZENE.

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Summary : Bis (trifluoroacetoxy) iodobenzene oxidizes phenols into quinones in good yield.

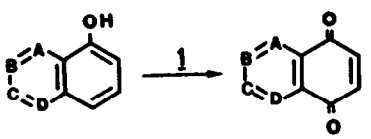
In connection with work on the Diels-Alder reaction, we needed some derivatives of quinones to synthesize aza-anthraquinones.[1] The Fremy salt is the best known reagent for the oxidation of phenols into quinones but this reaction leads to a mixture of ortho and para isomers,[2] or to dimeric compounds.[3]

Recently, we have shown that quinone imines are synthesized from heterocyclic amines by iodylbenzene in the presence of vanadyl acetylacetonate,[4] but we have found this reagent does not lead to quinones from phenols in good yield. Thus, we chose to investigate the oxidation of phenols with different hypervalent iodine derivatives.

In this paper, we described a mild and efficient method for the oxidation of phenols to quinones using bis(trifluoroacetoxy) iodobenzene 1.

In a typical experiment, a solution of 1-naphthol (1.0 equiv.) in acetonitrile-water (2/1, v/v) is added dropwise to 1 (2.2 equiv.) in acetonitrile-water (2/1, v/v) under nitrogen and cooling to 0°C. The solution is stirred for 2h. Naphthoquinone is obtained after chromatographic purification (yield : 73 %). Other phenols are oxidized and give quinones in good yield (58-88 %) (Table I).

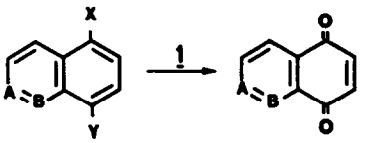
TABLE I



A	B	C	D	%
CH	CH	CH	CH	73
CH	CH	CH	N	88
CH	CH	C-CH_3	N	82
CH	CH	N	CH	80[5]
CH	CH	CH	C-OH	58
CH	CH	CH	C-OCH_3	80
N	C-CH_3	C-CH_3	N	70

At last aromatic amines lead to the formation of quinones ; the yields are less important than phenols (Table II).

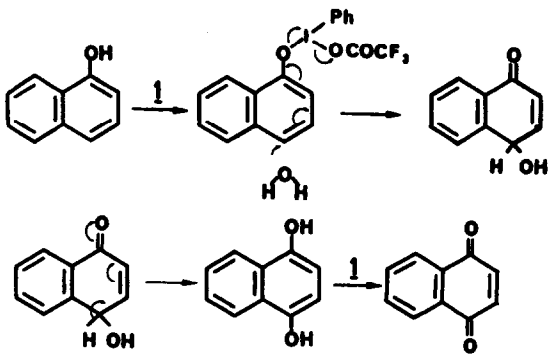
TABLE II



A	B	X	Y	%
CH	CH	NH_2	H	57
CH	N	NH_2	H	85
CH	N	H	NH_2	87
N	CH	NH_2	H	46

The mechanism of this reaction can be rationalized assuming an intermediate 2 is obtained by nucleophilic addition of hydroxy group to hypervalent iodine ; 2 breaks down into hydroquinone 3 which is oxidized into quinones. The oxidation of amines leads to the formation of quinone imines which are hydrolyzed into quinones (Scheme I).

SCHEME I



In conclusion, this reaction is an attractive and efficient way to synthesize quinones.

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(Received in France 20 June 1990)