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3-Aryliodonio-1,4-naphthoquinone-2-imides: A New Class of Aryliodonium 1,4 Dipoles

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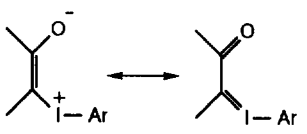
Abstract: The synthesis of a new class of zwitterionic aryliodonium compounds from 2-amino-1,4-naphthoquinone and [(hydroxy) (tosyloxy)iodo]arenes is described. These dipoles exhibit an interesting reactivity under thermal and photochemical conditions.

The chemistry of hypervalent iodine organic compounds has undergone a great expansion during the last two decades[1] and a variety of them are currently used as valuable reagents in organic synthesis.[2] Zwitterionic iodonium compounds, with the positive charge on iodine compensated by the negative charge within the molecule, constitute a fairly large class of interesting compounds; their most important members are 1,2 dipoles (ylides) and 1,4 dipoles.

Aryliodonio 1,4 dipoles are usually phenolates bearing electron withdrawing substituents on the aromatic ring; they exhibit an interesting and some times unexpected reactivity.[1] Recently we reported the preparation and reactivity of aryliodonio 1,4 dipoles from 1,3-dihydroxybenzene derivatives,[3] 8-hydroxyquinoline derivatives[4] and 2-hydroxy-1,4-benzoquinones.[5] In all cases the negative charge is localized on oxygen giving stable dipoles of the general type **1**.



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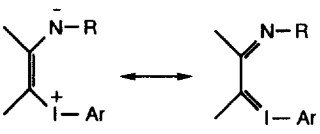
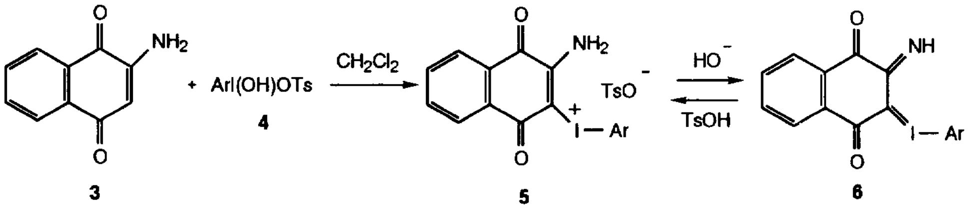


2

Analogous nitrogen 1,4 dipoles **2** are not known in the literature with the exception of the unstable zwitterionic phenyliodonium compounds derived from indole[6] and enamino-dimethyl-cyclohexanone.[7] In order to avoid writing localized dipole structures , the double bond notation for all such compounds has been adopted in this paper.

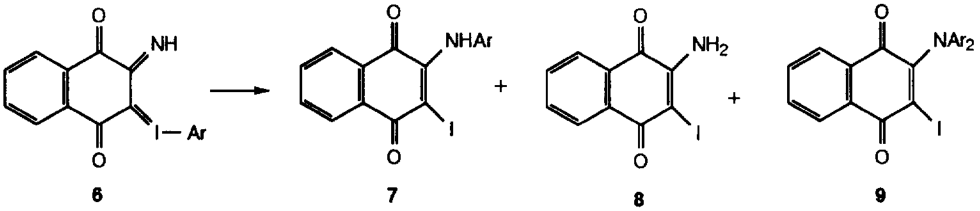
In continuation of our studies on oxido-iodonium zwitterions, we have turned our attention to their aza-analogs, choosing as a suitable substrate 2-amino-1,4-naphthoquinone, **3**. This particular compound was selected because its phenyliodonium dipole **6a**, would bear analogy to the iodonium zwitterion derived from 2-hydroxy-1.4-naphthoquinone. This was previously studied by us[8] and a comparison of the reactivity of these related 1,4 dipoles would be possible.Further, aminonaphthoquinone derivatives are of current interest in view of their pharmacological properties.[9]

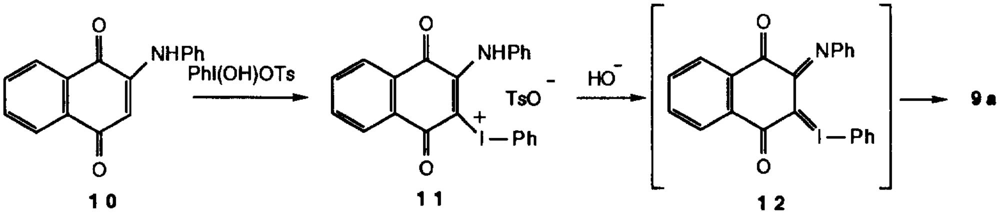
The reaction of 2-amino-1,4-naphthoquinone **3** with [(hydroxy)(tosyloxy)iodo]arenes, **4**, gave readily[10] the iodonium salts **5** in high yield (80-90%). Their spectral data were consistent with the proposed structure. When treated with dilute NaOH, iodonium salts **5** were converted to the corresponding zwitterions **6** in reasonable yield (65-80%). The trifluoroacetate analogue of **5a** was also obtained from **3** and $PhI(OCOCF_3)_2$ in 93% yield and, in a similar way, converted to **6a** with alkali; the acetate analogue of **5a** was not obtained from **3** and $PhI(OCOCH_3)_2$.



4,5,6 Ar **a** = C_6H_5 , **b**= p-MeC_6H_4 , **c** = p-$MeOC_6H_4$, **d** = m-$O_2NC_6H_4$

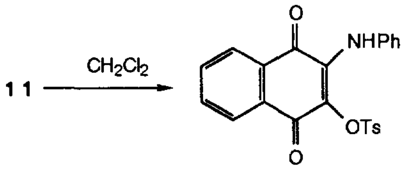
The characterization of **6** was based on their conversion back to the salts **5** upon reaction with p-toluenesulfonic acid (or the corresponding aryliodonium chlorides, with HCl). Their spectral data (NMR , MS) were also consisted with their structure. All zwitterions **6** are microcrystalline compounds which upon attempted recrystallization rearrange thermally to 2-arylamino-3-iodo-1,4-naphthoquinone **7**. In boiling acetonitrile this isomerization was quantitative in one hour.





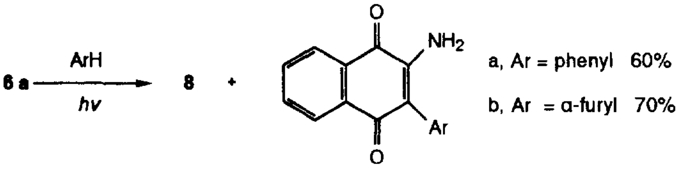
The rearrangement **6** to **7** constitutes probably an example of the Smiles rearrangement. The substituents on the phenyl ring, however, do not have a powerful effect on the rate of rearrangement. In the presence of catalytic amounts of $Cu(acac)_2$, compounds **6** rearrange at room temperature in acetonitrile but the formation of **7** is now accompanied by small amounts of 2-amino-3-iodo-1,4-naphthoquinone **8** and 2-diarylamino-3-iodo-1,4-naphthoquinone **9**, in equal proportions. It seems that under these conditions **7** disproportionates to **8** and **9**. In fact, 2-phenylamino-1,4-naphthoquinone **10** was separately converted to its phenyliodonium salt **11** and this with NaOH did not afford **12** but it was converted directly to **9a**.It is interesting to note the difference in reactivity between the oxido and imido iodonium zwitterions; in the case of 2-oxido-3-phenyliodonio-1,4-naphthoquinone no migration of the phenyl group was observed but ring contraction led to indanedione in 91% yield.[8] The same ring contraction, possibly through carbenes, was observed in the case of 2-oxido-3-phenyliodonio-1,4-benzoquinones.[5]

Although iodonium tosylates **5** are fairly stable, the phenylamino derivative **11** in CH_2Cl_2 solution is quantitatevely converted to 2-phenylamino-2-tosyloxy-1,4-naphthoquinone **13** in one day at room temperature.The reaction is an internal nucleophilic substitution common in iodonium salts, which however do not generally react with such weak nucleophiles.[1]



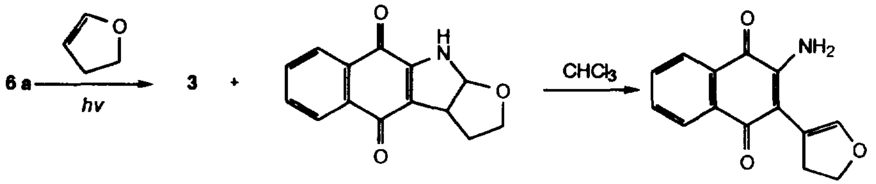
1 3

Since zwitterions **6** under thermal conditions are converted mainly to aryl migration products, some reactions of **6** under photochemical conditions were tried. 3-Phenyliodonio-1,4-naphthoquinone-3-imide **6a** under irradiation in benzene and furan afforded the corresponding phenyl **14a** and α-furyl **14b** substitution products (yield 60 and 70% respectively), along with some 3-iodo-2-amino-1,4-naphthoquinone **8**.



14a,b

The photochemical reaction of zwitterion **6a** with an enol ether (dihydrofuran) led to the cyclization product **15** (yield 15%).



15 16

The latter, although stable when solid, was rapidly transformed to the tautomeric amino enol ether **16** in chloroform solution at room temperature.

This reactivity of zwitterions **6** offers strong indications that this new class of iodonium dipoles may find application for the synthesis of compounds bearing the pharmacologically interesting aminoquinone moiety.

REFERENCES AND NOTES

1. Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*, VCH, New York, 1992.
2. Varvoglis, A. *Chimika Chronika, New Series* **1995**, 24 , 3-55.
3. Spyroudis, S. ; Tarantili, P. *Tetrahedron* **1994**, 50, 11541-11552.
4. Spyroudis, S. ; Georgantji, A. *Tetrahedron Lett.* **1995**, 36, 443-446 .
5. Papoutsis, I. ; Spyroudis, S. ; Varvoglis, A. *Tetrahedron Lett.* **1994**, 35, 8449-8452.
6. Moriarty, R.M. ; Ku, Y.Y. ; Sultana, M. ; Tuncay, A. *Tetrahedron Lett.* **1987**, 28, 3071-3075.
7. Arena, B.E. ; Neiland, O., Ya. ; Kampare, R. B. *Zh.Org. Khim.* **1982**,18, 995-1000.
8. Hatzigrigoriou, E. ; Spyroudis, S. ; Varvoglis, A. *Liebigs Ann. Chem.* **1989**, 167-170.
9. Marcos, A. ; Pedregal, C. ; Avendano, C. *Tetrahedron* **1994**, 50 , 12941-12952 and references cited therein.
10. In a typical procedure [(hydroxy)(tosyloxy)iodo]benzene **4a** (1 mmol) was added to a stirred solution of 2-amino-1,4-naphthoquinone **3** (1 mmol) in CH_2Cl_2 (15 ml). After two hours the resulting solid was filtered and washed several times with CH_2Cl_2 to afford the iodonium salt **5a** in 90% yield.

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