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REACTIONS OF BICYCLOALKENYLDIIODONIUM SALTS WITH NUCLEOPHILES

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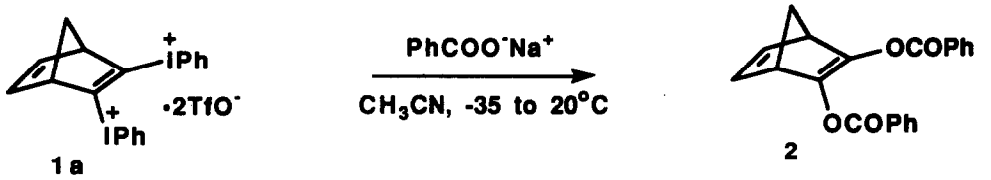
Summary. *Alkenyldiiodonium salts 1 react with a number of anionic nucleophiles to give the corresponding products of the vinylic nucleophilic substitution of the iodobenzene moiety. However, analogous reaction with Ph_3P leads to the formation of tetraphenylphosphonium salt and diiodoalkene.*

In recent years a large variety of alkynyl- and alkenyl(phenyl)iodonium salts have become readily available and are employed as versatile reagents in organic synthesis.[1] Both these types of iodonium salts are highly reactive toward nucleophiles due to the excellent leaving group properties of iodonium. Of special synthetic and research interest are the reactions of alkynyliodonium salts with anionic nucleophiles leading to previously unknown alkynyl esters.[1b,2] However, only two examples of the analogous reactions of alkenyl(phenyl)iodonium species, namely for phenyl(4-*tert*-butyl-cyclohexenyl)iodonium tetrafluoroborate[3a] and phenyl(2,2-dimethyl-4(diethylphosphono)-2,5-dihydro-3-furyl)iodonium perchlorate,[3b] have been reported in the literature. Recently we have reported a general approach to the synthesis of novel bicycloalkenybis(phenyliodonium) triflates by the Diels-Alder cycloaddition reaction of bis(phenyliodonium)acetylene and various dienes.[4] The goal of the present communication is to investigate the scope of the reactions of this new class of bicyclic bisiodonium salts with nucleophiles.

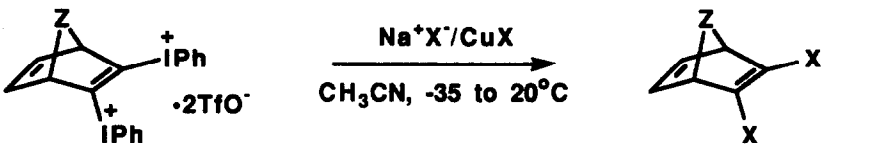
As model substrates for this research we have chosen the readily available Diels-Alder adducts of bis(phenyliodonium)acetylene with cyclopentadiene and furan (**1a,b**).[4] First we have studied the reactions of anionic nucleophiles, such as sodium phenolate, thiophenolate, bromide, cyanide, and benzoate in acetonitrile or methylene chloride. All of these reactions except the last one are non selective and lead to a wide spectrum of unidentified products as determined by NMR data on the crude product mixture. However, in the reaction of compound **1a** with sodium benzoate we were able to isolate the corresponding product of nucleophilic substitution **2**[5] in low yield along with the products of its hydrolysis.



1a

2

However, carrying out the same reactions in the presence of copper(I) salts leads to a dramatic improvement. The reactions of **1a,b** with sodium bromide, iodide, and cyanide and the corresponding copper(I) salts lead to exclusive formation of the desired substitution products 3 and the expected iodobenzene according to the NMR data. Although the reactions appear to be quantitative by NMR the isolated yields for some of these products (**3a,d**) are low due to their volatility; the remainder are good (63-83%). Products 3 were identified by the IR, NMR and mass-spectral data.[6]

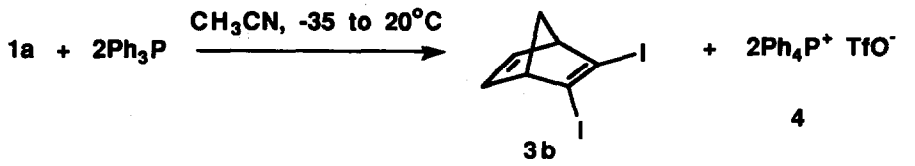


1a, Z = CH_2
b, Z = O

3a, Z = CH_2, X = Br
b, Z = CH_2, X = I
c, Z = CH_2, X =CN
d, Z = O, X = Br
e, Z = O, X = I
f, Z = O, X = CN

*General procedure for the reaction of alkenyldiiodonium salts **1a,b** with nucleophiles in the presence of copper(I) salts.* The carefully dried sodium salt (2 mmoles) and the corresponding copper(I) salt (2 mmoles) are mixed with 50 ml of dry acetonitrile at room temperature under nitrogen. The suspension is cooled to -35 - -40°C and the iodonium salt **1** (1 mmole) is added under stirring. The mixture is gradually warmed to room temperature and stirred for an additional 10-15 hours. The precipitate of inorganic salts is filtered off, the resulting solution evaporated and the residue dissolved in methylene chloride. The solution in methylene chloride is filtered through silicagel and evaporated to give a colorless or slightly yellow oil, which, according to NMR data consists of only iodobenzene and the corresponding product 3. The pure products 3 can best be obtained by blowing nitrogen through the mixture for 1-2 hours to remove the volatile iodobenzene.

The reaction of iodonium salt **1a** with a neutral soft nucleophile, triphenylphosphine in acetonitrile, gives a different outcome. In this case the major isolated products are diiodide **3b** and tetraphenylphosphonium triflate **4**.[7]



3b **4**

This result can be explained by the nucleophilic substitution of the iodine moiety in the phenyl ring of the iodonium salt by triphenylphosphine. Such a reaction path differs from the usual reactions of alkynyliodonium salts with triphenylphosphine leading to alkynylphosphonium salts,[4,8] however, it is similar to the analogous reaction of phenyl(2,2-dimethyl-4(diethylphosphono)-2,5-dihydro-3-furyl)iodonium perchlorate.[3b]

In conclusion, reactions of the bicycloalkenyldiiodonium salts with anionic nucleophiles in the presence of copper(I) salts result in a selective nucleophilic substitution of the iodobenzene moiety and can be used for synthetic purposes. However, the analogous reaction with triphenylphosphine leads to the cleavage of the Ph-I bond giving tetraphenylphosphonium salt as the major product.

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3. a) M. Ochiai, K. Sumi, Y. Takaoka, M. Kunishima, Y. Nagao, M. Shiro, E. Fujita, *Tetrahedron* **1988**, *44*, 4095; b) N.S. Zefirov, A.S. Koz'min, T. Kasumov, K.A. Potekhin, V.D. Sorokin, V.K. Brel', E.V. Abramkin, V.V. Zhdankin, P.J. Stang, *J. Org. Chem.* **1992**, *57*, 2433.
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5. For **2**: oil (25 %); ^{1}H NMR ($CDCl_3$): δ 8.1 (m, 4H), 7.6 (m, 2H), 7.4 (m, 4H, 2Ph), 6.6 (br. s, 2H,

CH=CH), 4.9 (br. s, 2H, 2CH), 2.5 and 2.3 (2m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, ^1H-decoupled): δ 180.1 (C=O), 145.4 (-OCH=CHO-), 141.9 (CH=CH), 138.1, 137.5, 131.6, 129.3 (all Ph), 74.0 (CH_2), 55.1 (2CH); CI HRMS m/z 333.1137 $[M+H]^+$, calcd for $C_{21}H_{17}O_4$: 333.1127.

6. For **3a**: oil (30 %); ^1H NMR ($CDCl_3$): δ 6.7 (br. s, 2H, CH=CH), 3.65 (br. s, 2H, 2CH), 2.45 and 2.2 (2m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, ^1H-coupled): δ 138.4 (d, J = 177 Hz, CH=CH), 127.3 (s, BrC=CBr) 70.3 (t, J = 137 Hz, CH_2), 58.5 (d, J = 156 Hz, 2CH); EI HRMS m/z 247.882564 $[M]^+$, calcd for $C_7H_6Br_2$: 247.883646. **3b**: oil (65 %); ^1H NMR ($CDCl_3$): δ 6.83 (br. s, 2H, CH=CH), 3.76 (br. s, 2H, 2CH), 2.45 and 2.05 (2m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, ^1H-coupled): δ 140.8 (d, J = 180 Hz, CH=CH), 115.4 (s, IC=CI) 72.8 (t, J = 137 Hz, CH_2), 62.6 (d, J = 156 Hz, 2CH); CI HRMS m/z 343.85436 $[M]^+$, calcd for $C_7H_6I_2$: 343.855654. **3c**: oil (66 %); IR (cm^{-1}): 2217 (CN); ^1H NMR ($CDCl_3$): δ 6.9 (br. s, 2H, CH=CH), 4.1 (br. s, 2H, 2CH), 2.5 and 2.4 (2m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, ^1H-coupled): δ 141.4 (s, NC-C=C-CN), 141.2 (d, J = 177 Hz, CH=CH), 113.0 (s, CN), 74.9 (t, J = 137 Hz, CH_2), 55.4 (d, J = 160 Hz, 2CH); CI HRMS m/z 143.061656 $[M]^+$, calcd for $C_9H_7N_2$: 143.060923. **3d**: oil (25 %); ^1H NMR ($CDCl_3$): δ 7.2 (br. s, 2H, CH=CH), 5.2 (br. s, 2H, 2CH); ^{13}C NMR ($CDCl_3$, ^1H-coupled): δ 142.3 (d, J = 184 Hz, CH=CH), 127.4 (s, BrC=CBr), 88.2 (d, J = 173 Hz, 2CH); EI HRMS m/z 249.862580 $[M]^+$, calcd for $C_6H_4Br_2O$: 249.862911. **3e**: oil (63 %); ^1H NMR ($CDCl_3$): δ 7.2 (br. s, 2H, CH=CH), 5.35 (br. s, 2H, 2CH); ^{13}C NMR ($CDCl_3$, ^1H-coupled): δ 141.9 (d, J = 184 Hz, CH=CH), 115.4 (s, IC=CI), 91.1 (d, J = 175 Hz, 2CH); EI HRMS m/z 345.835979 $[M]^+$, calcd for $C_6H_4I_2O$: 345.834919. **3f**: (83 %), slightly yellow solid, dec. above 210°C (lit. dec. at 240°C);[9] IR (cm^{-1}): 2223 (CN); ^1H NMR ($CDCl_3$): δ 7.2 (br. s, 2H, CH=CH), 5.8 (br. s, 2H, 2CH); ^{13}C NMR ($CDCl_3$, ^1H-coupled): δ 143.1 (d, J = 187 Hz, CH=CH), 142.2 (s, NC-C=C-CN), 111.3 (s, CN), 85.9 (d, J = 176 Hz, 2CH).

7. For **4**: white crystals (52%), m.p. 220°C (dec); ^1H NMR (CD_3CN): δ 7.9-7.7 (m); ^{13}C NMR (CD_3CN): δ 136.2-135.5 (m), 121.2 (d, J_{C-P} = 12.7) 70.3 (t, J = 137 Hz, CH_2), 118.3 (q, J = 318 Hz, $CF_3SO_3^-$); ^{31}P NMR (CD_3CN): δ 24.4. FAB MS m/z 339 $[M - OTf^-]^+$.

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