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# NUCLEOPHILIC SUBSTITUTION IN THE 10,11-DIHYDRODIBENZ[*b,f*]IODEPINIUM CATION

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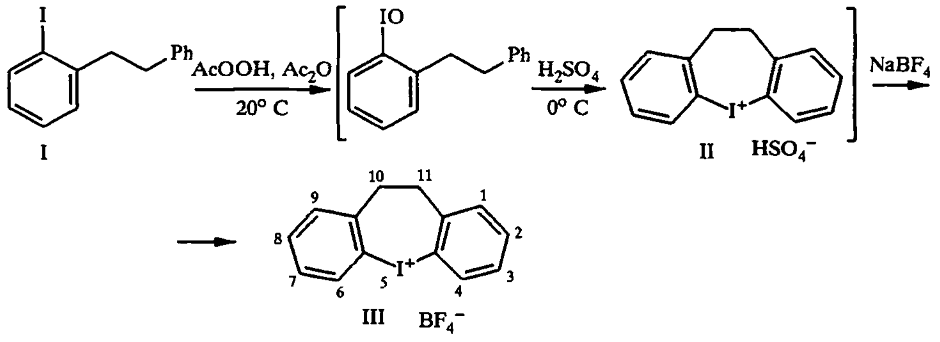
*10,11-Dihydrodibenz[b,f]iodepinium tetrafluoroborate gave only 1-(2-azidophenyl)-2-(2-iodophenylethane with the* $N_3^-$ *in aqueous DMSO, while with* $NO_2^-$ *it gave 1-(2-nitrophenyl)-2-(2-iodophenyl)ethane (93%), 9,10-dihydrophenanthrene (5%), and traces of phenanthrene. Both in pure and aqueous DMSO this cation with the* $Br^-$ *ion was converted into phenanthrene (80% and 68% respectively) and 1-(2-bromophenyl)-2-(2-iodophenyl)ethane (10 and 20%), while in water it gave 9,10-dihydrophenanthrene (75%) and phenanthrene (5%). A new route for the synthesis of 1-(2-aminophenyl)-2-phenylethane starting from this tetrafluoroborate has been proposed.*

In the preceding paper [1] we showed that iodonium salts with an iodine atom in five or eight membered rings reacted with a series of anionic nucleophiles to give different products depending on the size of the ring. While the five membered dibenz[*b,d*]iodolium cation reacted with $NO_2^-$, $N_3^-$, and $Br^-$ to give diphenyl, 2-iododiphenyl, 2,2′-diiododiphenyl along with the corresponding products of nucleophilic substitution - 2-nitro-, 2-azido-, or 2-bromo-2′-iododiphenyl, the eight membered 11,12-dihydro-10H-dibenz[*b,g*]iodosium cation gave a single product in each case – 1-(2-nitrophenyl)-, 1-(2-bromophenyl)-, or 1-(2-azidophenyl)-3-(2-iodophenyl)propane.

It seemed possible to explain these results only in terms of the Budylin-Kost mechanism [4], the essence of which is the formation of a hypervalent intermediate, similar in structure to five-coordinate compounds of phosphorus, from the iodonium cation and the nucleophile. By analogy with the phosphorus compounds, reductive elimination of the reaction product from the intermediate is symmetry forbidden [3]. To overcome this barrier to reaction it is necessary to construct an intermediate with a different conformation. It is difficult to do this in a cyclic iodonium ion with a small ring and the reaction principally takes an alternate route with electron exchange from the nucleophile to the iodonium center with normal conversion to pairs of free radicals of this type [4, 5]. It was much less difficult to construct an eight membered cyclic iodonium cation, and, like the acyclic iodonium salt, it gave the expected products of nucleophilic substitution [1].



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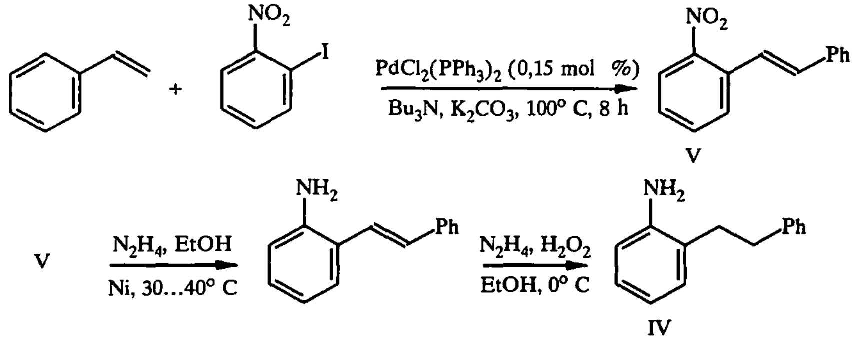
The 10,11-dihydrobenzo[*b*,*f*]iodepenium seven membered cation occupies an intermediate position in this series. Consequently we were interested to study its behavior with a range of nucleophiles. With this object in mind 10,11-dihydrobenz[*b*,*f*]iodenium hydrogen sulfate was obtained from 1-(2-iodophenyl)-2-phenylethane (I) using the method from [6]. By treatment of an aqueous solution of II, saturated with $NaBF_4$, with a mixture of nitromethane and chloroform, the previously unknown 10,11-dihydrobenz[*b*,*f*]iodenium tetrafluoroborate (III) was extracted.

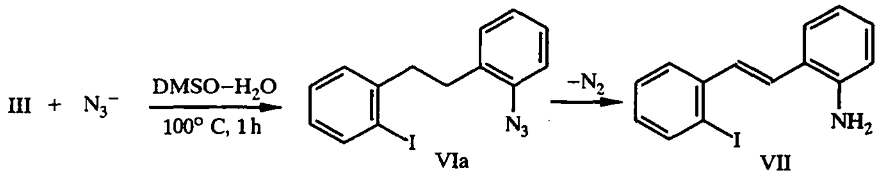
The initial iodide I was obtained in 60% yield by normal diazotisation of the corresponding amine (IV) [7] which we obtained by a simpler method:



In the first step (the Heck reaction [8]) styrene was arylated with 2-iodonitrobenzene in 97% yield to give the nitrostilbene (V), the nitro group of which was reduced in the second stage with hydrazine hydrate and Raney nickel (by analogy with [9]), but the double bond was reduced by the diimide generated from hydrazine hydrate and hydrogen peroxide by a known method [10]. The intermediate 2-aminostilbene was not isolated: it was only necessary before addition of $H_2O_2$ to filter off the nickel catalyst.

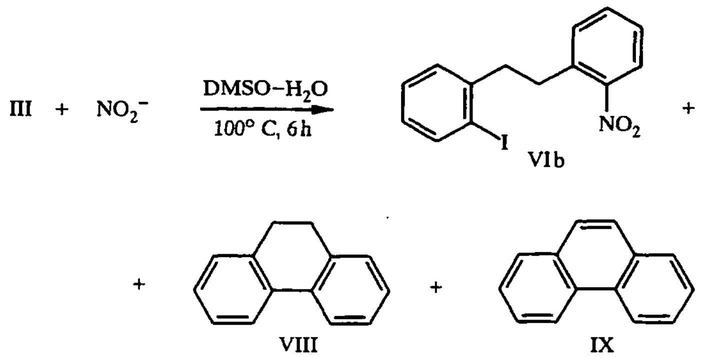
Investigations of the tetrafluoroborate III with nucleophiles were carried out under standard conditions [1] using a solution of the salt in pure DMSO, aqueous DMSO, or water with 10 equivalents of $NaN_3$, $NaNO_2$, or NaBr at 100-140°C with subsequent chromato-mass spectrometric analysis of the reaction mixture.

Salt III gave a single compound with the strongest nucleophile, $N_3^-$ in aqueous DMSO: 1-(2-azidophenyl)-2-(2-iodophenyl)ethane, the product of nucleophilic substitution:

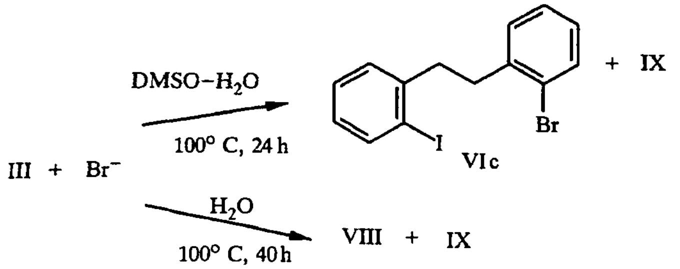


The azide VIa lost $N_2$ in the ionization chamber of the mass spectrometer to form a nitrene which partially isomerized to 2-amino-2′-iodostilbene (VII).

Under the same conditions salt III reacted with $NO_2^-$ to give the product of nucleophilic substitution, 1-(2-nitrophenyl)-2-(2-iodophenyl)ethane (VIb, 93%), together with 9,10-dihydrophenanthrene (VIII, 5%), and traces of phenanthrene (IX). Unexpectedly, the latter was the main product of the reaction of salt III with $Br^-$ (DMSO, 120-140°C) (80% yield), with a 10% yield of 1-(2-bromophenyl)-2-(2-iodophenyl)ethane (VIc). In aqueous DMSO the same compounds were obtained in yields of 68 and 20% respectively. The product of nucleophilic substitution VIc



was not obtained when the reaction was carried out in water: only compounds VIII (75%) and IX (5%) were observed in the reaction mixture:



All of the reaction products were characterized by mass spectrometry. Compounds VIII and IX were identified by the US National Standards Institute Data Bank, while the structures of the remaining compounds agreed with the characteristic fragmentation of the molecular ions.

The results obtained indicate that the seven membered ring including the iodonium atom is sufficiently flexible that reconstruction of the T-shaped conformation of the intermediate in the three-rayed star is not prohibited (this question is discussed in the preceeding paper [1]). Consequently, of the possible routes for further reaction of the intermediate, corresponding to reactions with the azide and nitrite ions, the energetically more suitable is the ejection of the iodoarene with formation of the nucleophilic substitution products, while with the bromide ion the IBr molecule is lost to give the dihydrophenathrene VIII which is dehydrogenated to phenanthrene IX under the influence of DMSO. We have previously observed analogous reaction (elimination of $I_2$ with formation of phenantrene structures) on thermolysis of 10-carboxydibenz[*b,f*]iodepinium iodide [11] and 2-bromo- or 3-bromo-10-carboxydibenz[*b,f*]iodepedinium iodides [12].

## EXPERIMENTAL

$^1$H NMR Spectra were recorded with a Varian VXR-300. GLC analysis used a LKhM-8MD apparatus with a flame ionization detector, nitrogen carrier gas, 3% SP-2100 on Chromatron N-Super (1000 × 2 mm) column, temperature program 100-190°C, 16°/min, with tolan as internal standard. Chromato-mass spectrometry was carried out with a Kratos-MS-25-RFA, 25 m × 0.32 mm capillary column, liquid phase CP-Sil 8 CB, helium carrier gas. Ionizing voltage 50 eV, source temperature 250°C. Temperature program 170-250°C, 4°/min.

**2-Nitrostilbene (V).** Tri(*n*-butyl)amine (1.85 g, 2.4 ml, 0.01 mole) and $PdCl_2(PPh_3)_2$ (0.108 g, 0.15 mmole) were added to a mixture of 2-iodonitrobenzene (24.9 g, 0.10 mole) and styrene (20.8 g, 22.9 ml, 0.20 mole) in an argon atmosphere. The mixture was stirred with gentle heating for 10 min and then a solution of $K_2CO_3$ (41.4 g, 0.30 mole) in water (200 ml) was added. Stirring was continued for 8 h at 100°C until the 2-iodonitrobenzene starting material had disappeared (monitored by GLC). The excess styrene and tri(*n*-butyl)amine were steam distilled from the flask, the residue was filtered off, washed with water, dilute hydrochloric acid, and again with

TABLE 1. Mass Spectrometric Data for the Compounds Synthesized

| Compound | $m/z$ ($I_{rel}$, %) | | |
|---|---|---|---|
| VIa | 321 (10)<br>$[M-N_2]^+$ | 217 (10)<br>$[C_6H_5ICH_2]^+$ | 194 (100)<br>$[321-I]^+$ |
| VIb | 353 (36)<br>$[M]^+$ | 336 (88)<br>$[M-OH]^+$ | 323 (2)<br>$[M-NO]^+$ |
| | 209 (52)<br>$[336-I]^+$ | 208 (19)<br>$[209-H]^+$ | 179 (28)<br>$[306-I]^+$ |
| VIc | 386 + 388 (17)<br>$[M]^+$ | 307 (3)<br>$[M-Br]^+$ | 259 + 261 (4)<br>$[M-I]^+$ |
| | 169 + 171 (38)<br>$[M-217]^+$ or<br>$[307-C_7H_6]^+$ | 90 (94)<br>$[C_7H_6]^+$ | |
| VII | 321 (74)<br>$[M]^+$ | 194 (35)<br>$[M-I]^+$ | 193 (26)<br>$[M-HI]^+$ |

| Compound | $m/z$ ($I_{rel}$, %) | | | |
|---|---|---|---|---|
| VIa | 167 (9)<br>[194-HCN]+ | 90 (39)<br>$[217-I]^+$ | | |
| VIb | 306 (5)<br>[336-NO]+ | 233 (21)<br>$[323-C_7H_6]^+$ | 231 (15)<br>$[M-C_6H_4NO_2]^+$ | 217 (100)<br>$[C_7H_6I]^+$ |
| | 178 (45)<br>[179-H]+ | 136 (14)<br>$[M-C_7H_6I]^+$ | | |
| VIc | 217 (100)<br>$[C_7H_6I]$+ | 203 (9)<br>$[C_6H_4I]^+$ | 180 (49)<br>$[M-I-Br]^+$ | 179 (36)<br>$[180-H]^+$ |
| VII | 118 (100)<br>$[M-C_6H_4I]$+ | 117 (53)<br>$[118-H]^+$ | 91 (34)<br>$[117-CN]^+$ | 90 (34)<br>$[C_7H_6]^+$ |

water, and was then dissolved in benzene. The solution was filtered through a layer of silica gel (15 mm diameter, 5-7 mm thick) and the filtrate was evaporated to dryness and the residue dried in vacuum over $P_2O_5$ and praffin to give 2-nitrostilbene (21.76 g, 97%), m.p. 71-72°C (from ethanol). Lit. data [13]: m.p. 72°C.

**1-(2-Aminophenyl)2-phenylethane (IV).** 2-Nitrostilbene V (11 g, 0.049 mole) was dissolved in ethanol (75 ml) by gentle heating on a water bath. Raney nickel (1 g) was added to the warm solution and then 85% hydrazine hydrate (7.5 ml, 7.6 g, 0.13 mole) was added dropwise at 30-40°C. The mixture was kept at this temperature until the starting material V had disappeared (monitoring by GLC). At the end of the reaction the nickel catalyst was filtered off. 85% Hydrazine hydrate (25.9 ml, 26.25 g, 0.80 mole) was added to the filtrate, which contained 2-aminostilbene, and then 30% $H_2O_2$ (32 ml, 35.6 g, 0.30 mole) was added in small portions with ice cooling. The mxture was then stirred at 20°C until the 2-aminostilbene had disappeared (GLC monitoring). The reaction mass was poured into water and the reaction product extracted with ether. The ether extract was washed with FeSO4 solution, water, and saturated NaCl solution, and then dried over $MgSO_4$. The residue after removal of the ether crystallized completely on cooling with ice to give compound IV (7.1 g, 75%), m.p. 30-32°C. Lit. data [14]: m.p. 33°C.

**1-(2-Iodophenyl)-2-phenylethane (I)** was obtained in 70% yield by diazotization of IV as described elsewhere [6] and was used without further purification.

**10,11-Dihydrobenz[*b,f*]iodepinium tetraflouroborate (III).** A solution of compound (I) (4.35 g, 14 mmole) in acetic anhydride (10 ml) was added to 28% peracetic acid (25 ml) and the mixture was kept at 20°C for a day. Conc. $H_2SO_4$ (5 ml) was added to the solution of the iodoso compound at 0-2°C over 2 h and the mass was kept at room temperature for about 16 h, then poured onto ice and extracted with benzene. An excess of a saturated aqueous solution of $NaBF_4$ was added to the aqueous layer, which contained the hydrogen sulphate II, and the salt III was extracted with a 3:1 (by volume) mixture of nitromethane and chloroform until a test with $NaHgBr_3$ was negative (absence of cloudiness resulting from a precipitate of the corresponding tribromomercurate). Removal of the solvent in vacuum gave the crude salt III (5.25 g, 95%). It was purified further by filtering an acetone solution precipitating salt III with an excess of ether. Precipitation of salt III from acetone solution with ether was repeated through a layer of $Al_2O_3$ diameter 15 mm, depth 5-7 mm), evaporating the solvent to a volume of 1-2 ml and three times more. The solid was then dried at 80°C in vacuum to give pure III (2.9 g, 53%), m.p. 177.5-178.5°C. Found, %: C 42.99, H 2.99. Calc for $C_{14}H_{12}BF_4I$, %: C 42.68, H, 3.07. $^1$H NMR Spectrum ($CF_3COOH$): 3.57 (4H, s, 10- and 11-H), 7.29-7.36 (2H, m, 2- and 8-H), 7.53-7.57 (2H, m, 1- and 9-H), 7.60-7.66 (2H, m, 3- and 7-H), 8.0-8.4 ppm (2H, m, 4- and 6-H).

**Reaction of Salt III with $NaN_3$.** A solution of salt III (0.394 g, 1 mmole) and $NaN_3$ (0.65 g, 10 mmole) in a mixture of DMSO (6 ml) and water (2.5 ml) was boiled until salt III was completely decomposed (1 h). The mixture was diluted to 5-6 times its volume with water and then treated with ether (5 x 15 ml). The extract was carefully washed with water and then dried over $MgSO_4$. According to GLC, the extract contained VIa as the lone reaction product. It was characterized by its mass spectrum (Table 1).

**Reaction of Salt III with $NaNO_2$.** A solution of salt III (0.394 g, 1 mmole) and $NaNO_2$ (0.788 g, 11 mmole) in a mixture of DMSO (3 ml) and water (1 ml) until the iodonium salt had completely decomposed. The reaction mixture was worked up as in the reaction with sodium azide. According to GLC-MS data, the ether extract contained VIb (93%), VIII (5%), and IX (traces).

**Reaction of Salt III with $NaNO_2$ in DMSO.** A solution of salt III (0.394 g, 1 mmole) and NaBr (1.03 g, 10 mmole) in DMSO (10 ml) was boiled until the iodonium salt was completely destroyed (1 h). The reaction mixture was worked up as in the reaction with sodium azide. According to GLC-MS data, the ether extract contained IX (80%) and VIc (10%).

**Reaction of Salt III with $NaNO_2$ in aqueous DMSO.** A solution of salt III (0.194 g, 0.5 mmole) and NaBr (0.5 g, 4.9 mmole) in a mixture of DMSO (10 ml) and water (1.5 ml) was boiled until salt III had disappeared (24 h). The reaction mixture was worked up as in the reaction with sodium azide. According to GLC-MS data, the ether extract contained IX (68%) and VIc (20%).

**Reaction of Salt III with $NaNO_2$ in Water.** A solution of salt III (0.197 g, 0.5 mmole) and NaBr (0.5, 4.9 mmole) in water (10 ml) was boiled until the iodonium salt was completely destroyed (35-40 h). The reaction products were extracted from the cooled reaction mixture with ether (3 x 10 ml). The ether extract, after drying over $CaCl_2$, contained VIII (75%) and IX (5%) according to GLC-MS data.

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