

## NUCLEOPHILIC SUBSTITUTION IN DIBENZ[b,d]IODOLIUM AND 11,12-DIHYDRO-10H-DIBENZ[b,g]IODOCINIUM CATIONS

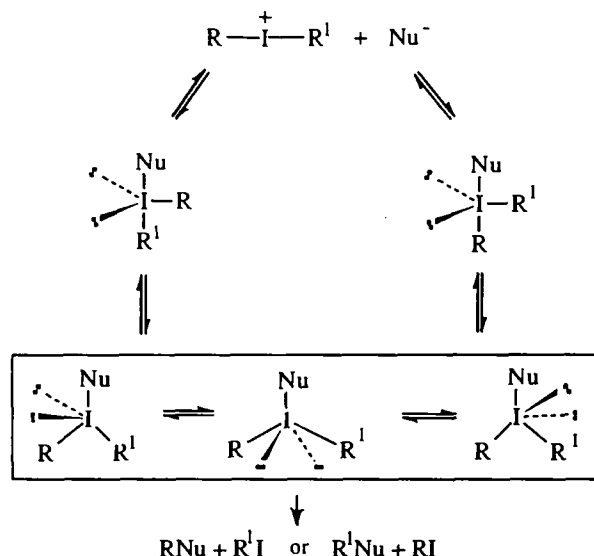
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*Treatment of dibenz[b,d]iodolium tetrafluoroborate with  $\text{NO}_2^-$ ,  $\text{Br}^-$ , and  $\text{N}_3^-$  ions gave, along with nucleophilic substitution products, 2-nitro-, 2-bromo-, and 2-azido-2'-iododiphenyls, diphenyl, 2-iododiphenyl, and 2,2'-diiododiphenyl (products of one electron reduction), whereas 11,12-dihydro-10H-dibenz[b,g]-iodocinium tetrafluoroborate underwent nucleophilic substitution with all three nucleophiles to give a single product in each case: 1-(2-nitrophenyl)-, 1-(2-bromophenyl)-, or 1-(2-azidophenyl)-3-(2-iodophenyl)propane.*

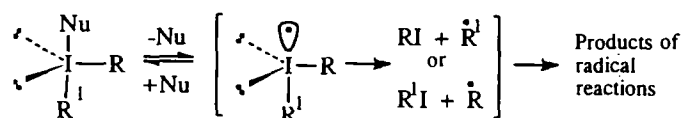
The chemistry of aromatic iodonium compounds, which were discovered more than a century ago [1], has not yet been exhausted and indeed continues to be vigorously developed [2-5]. An important property of these compounds, frequently used in syntheses, is their great reactivity with nucleophiles, with which they may react, depending on the conditions and the reagents, via ionic ( $\text{S}_{\text{N}}$ ) or free radical routes, i.e., by one electron reductions [5] via a 9-I-2 intermediate\* [7,8] with subsequent decomposition to an aryl iodide and an aromatic radical which then undergoes normal reactions. Both these routes are frequently observed to take place simultaneously [4-6]. The mechanism of the ionic reactions of diaryliodonium salts with nucleophiles has been frequently discussed (for a complete analysis of this question see [9]). Most investigators favor the  $\text{S}_{\text{N}}\text{Ar}$  mechanism [4, 5] since electron withdrawing substituents activate the diaryliodonium cation to nucleophilic attack whereas electron donating substituents deactivate it. However it is not possible to explain some experimental facts in terms of this mechanism, particularly the so-called *ortho* effect, the preference of the nucleophile to attack an *ortho* substituent ligand even when the latter is an electron donating group.

A mechanism for the reaction of iodonium salts with nucleophiles was proposed in 1981 [10] which permitted the explanation of many characteristics of the reaction. The authors proposed that the nucleophile first attacked the iodonium iodine to give hypervalent 10-I-3 intermediate, T-shaped complexes of iodine(III) [5], in which, as in the iodonium salts, the angle between the aromatic ligands was close to  $90^\circ$  and the nucleophile was generally placed opposite the more bulky substituent. In these complexes loss of an iodoarene can occur [10], similarly to the reductive elimination of an iodoarene from a triaryliodine [6]. If it is considered that the two unshared pairs play the role of substituents (phantom ligands), then the T-shaped structure of the 10-I-3 complex can be discussed as a trigonal bipyramid [5]. In this structure apical-equatorial interactions are symmetry forbidden [11]. In solution compounds of iodine(III) are fluxional (stereochemically nonrigid) [12]. Consequently 10-I-3 complexes may undergo pseudorotation similarly to pentacoordinate compounds of phosphorus via the so-called turnkey rotation via a tetragonal pyramid in which the iodine and all three substituents lie in a single plane, not in the form of a letter T but in the form of an almost symmetrical three-rayed star. In this configuration interaction between any two of the substituents bound to iodine is symmetrically allowed [11]. In nonsymmetrical 10-I-3 intermediates the nucleophile bonds predominantly to the ligand which gives the lower transition state energy for elimination. This may be the more electron deficient ligand, elimination of which reduces the positive charge on the iodine atom, or, much more likely, the more bulky ligand, loss of which would lower the steric hindrance in the base of the tetragonally pyramidal 10-I-3 complex.

\*Here and in what follows the first number indicates the number of electrons in the outer electron shell of the central atom of the complex (iodine in this case), while the second shows the number of ligands bonded to the central atom.



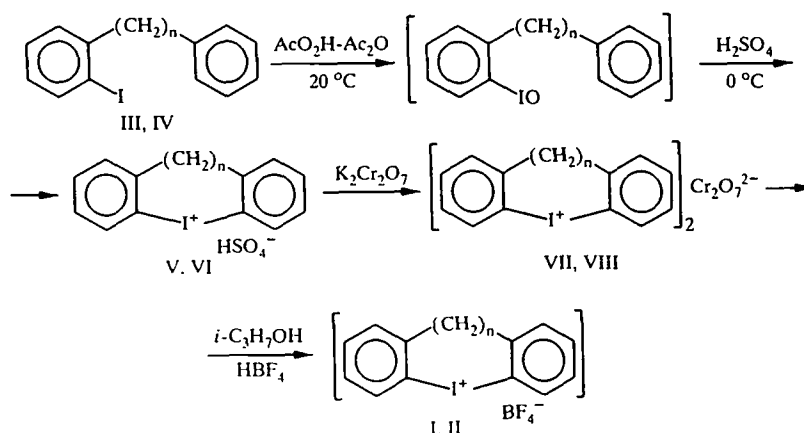
If the permutation of the 10-I-3 intermediate is hindered in any way, formation of nucleophilic substitution products is disrupted and the reaction occurs by homolytic decomposition of the 10-I-3 complex via a 9-I-2 intermediate.



We suggested that a carbon bridge between the aromatic radicals in the iodonium salt should hinder permutation of the 10-I-3 intermediate. The shorter the bridge the greater the hindrance to permutation and consequently the larger the fraction of radical reaction products in comparison with nucleophilic substitution products.

In order to test this suggestion (assuming the reaction mechanism proposed previously [10]) we synthesized two cyclic iodonium salts: dibenz[*b,d*]iodolium tetrafluoroborate (I) with a firmly fixed five-membered ring including the iodine atom (the shortest bridge) and 11,12-dihydro-10H-dibenz[*b,g*]iodocinium tetrafluoroborate (II) in which the iodine atom is included in a nonplanar flexible eight-membered ring. We then investigated the reactions of these salts with nucleophiles ( $\text{NO}_2^-$ ,  $\text{Br}^-$ , and  $\text{N}_3^-$ ).

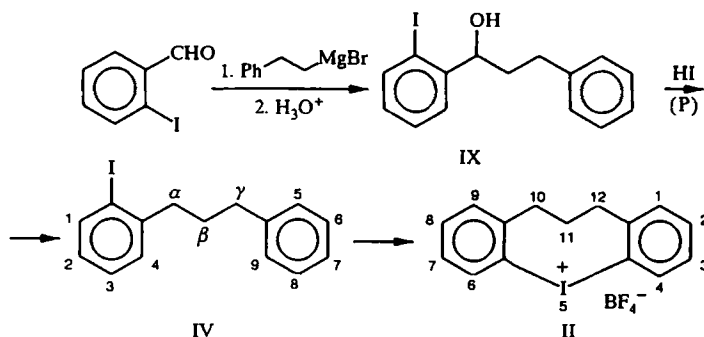
We obtained the hydrogen sulfates of both iodonium cations (V and VI) by oxidative cyclization of the 2-iodo derivatives of the corresponding binuclear arenes III and IV by a known method [13]. The hydrogen sulfate anion was replaced by tetrafluoroborate by a new method for onium salts. The dichromates (VII and VIII), which were poorly soluble in water, were precipitated and then reduced with an alcohol (isopropanol was best) in the presence of a stoichiometric amount of the corresponding acid, in this case  $\text{HBF}_4$ .



I, III, V, VII  $n = 0$ ; II, IV, VI, VIII  $n = 3$

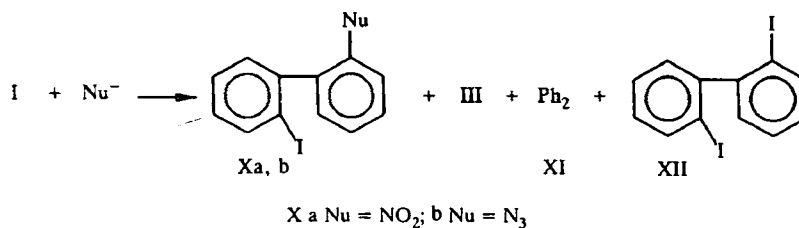
The reagents used in this method are cheap and available, and the reaction and separation of products are not difficult. However, although both reactions can occur quantitatively we did not optimize the conditions for the reaction and for the isolation of the products so the yield of salt II was comparatively small.

2-Iododiphenyl (III), the precursor of salt V, was synthesized by a known method. To prepare 1-(2-iodophenyl)-3-phenylpropane (IV), the precursor of salt (VI), which was first described in 1956 [3], we developed a shorter and more suitable method of synthesis which consisted of the reaction of  $\beta$ -phenylethylmagnesium bromide with 2-iodobenzaldehyde, followed by reduction of carbinol IX with hydroiodic acid in the presence of red phosphorus. The structures of compounds II and IV were confirmed by  $^1\text{H}$  NMR spectroscopy (numbering of the protons is given in the reaction scheme).

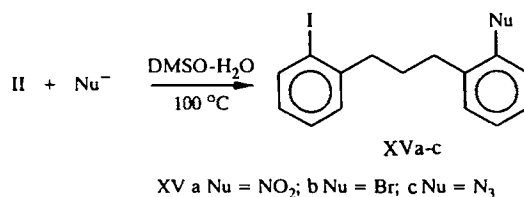


Reactions of salts I and II with nucleophiles were carried out under standard conditions: solutions of the iodonium salts in DMSO or DMSO-water (2:1) were heated with 10 equivalents of NaBr, NaNO<sub>2</sub>, or NaN<sub>3</sub> at 100-140°C followed by chromato-mass spectrometric analysis of the reaction mixtures.

Salt I reacted with NO<sub>2</sub><sup>-</sup> and N<sub>3</sub><sup>-</sup> to give multicomponent mixtures which contained products of the S<sub>N</sub> reactions together with a number of compounds — 2-iododiphenyl (III), diphenyl (XI), 2,2'-diiododiphenyl (XII) — which clearly arose from free radicals. The cation of salt I did not react with Br<sup>-</sup> at 120-140°C in DMSO-water in 30 h, however as described elsewhere [14] for the thermal decomposition of dibenz[*b,d*]iodolium bromide, 2-bromo-2'-iododiphenyl (Xc, 76%) was formed together with iododiphenyl (III, 1%), diiododiphenyl (XII, 14%), 2-bromodiphenyl (1%), and 2,2'-dibromodiphenyl (10%), products arising from free radicals.



Reaction of salt II with nucleophiles gave a high yield of single compound (XVa-c) — the product of nucleophilic substitution, in each case.



The substances cited in Tables 1 and 2 were characterized by mass spectroscopy. Compounds III and XI were identified by mass spectroscopy using the Data Bank of the US National Standards Institute. The structures of the remaining compound are in excellent agreement with the characteristic fragments of their molecular ions (Table 3).

TABLE 1. Conditions and Products of the Reaction of Salt I with Nucleophiles in Aqueous DMSO (100°C) and Product Yields

Nu	Reaction time, h	Reaction products, % yield (based on GLC)			
		Xa, b	III	XI	XII
NO <sub>2</sub> <sup>-</sup>	4	26,5	22,5	9,0	42,5
N <sub>3</sub> <sup>-*</sup>	3	55,0	8,0	—	15,0

\*The mixture contained 2-azidodiphenyl (XIII, 18%) and 2-amino-2'-iododiphenyl (XIV, 4%).

TABLE 2. Reaction Conditions, Products and Yields for Reactions of Salt with Nucleophiles

Nu	Reaction conditions		Reaction product (XV), yield, %
	T, °C	time, h	
NO <sub>2</sub> <sup>-</sup>	100	1,5	88 (a)
Br <sup>-*</sup>	120...140	11,5	87 (b)
N <sub>3</sub> <sup>-</sup>	100	0,75	Quantitative (c)

\*In DMSO.

Hence the eight-membered rings containing the iodonium atom are, as expected, sufficiently large to allow pseudorotation in the hypervalent 10-I-3 intermediate similar to that which occurs in the analogous intermediate in reactions of acyclic diaryliodonium salts. In the 10-I-3 intermediate with the iodine atom in a five-membered ring pseudorotation is hindered, as the low yield of the products of nucleophilic substitution Xa and Xb (Table 1) compared to the yields of the analogous substances XVa-c (Table 2) shows, as also does the appearance of compounds III, XI, and XII which are clearly products of free radical reactions.

Literature data pertaining to the thermal decomposition of halides of cyclic iodonium salts are in good agreement with our results. For example, while thermolysis of diphenyliodonium bromide and iodide gave quantitative yields of iodo-, bromo-, and chlorobenzenes [15], thermolysis of the corresponding dibenz[*b,d*]iodolium halides occurred with ring opening of the onium ring to only 75% of 2-halogeno-2'-iododiphenyl and about 25% of a mixture of all possible 2-mono- and 2,2'-dihalogenodiphenyls [14, 16]. Thermolysis of dibenz[*b,e*]iodinium chloride with the onium atom in a six-membered ring the yield of 2-chloro-2'-iododiphenylmethane reached 93% [14]. Finally, thermolysis of 4,2'-iodonio-3-phenyl-1,2-benzisoxazole, in which the iodonium atom is in an almost planar six-membered ring of a very rigid heterocyclic system [17], occurs exclusively by a free radical pathway to give all possible isomers of 4-halogeno-3-(2-halogenophenyl)-1,2-benzisoxazole [18]. Apart from the thermolyses of the halides, ring opening of the six-membered dibenz[*b,e*]iodinium cation under the influence of the nitrite anion has been described to give 2-iodo-2'-nitrodiphenylmethane and the products of radical reactions, 1-iodofluorene and 2-iododiphenylmethane [19].

Our results confirm the mechanism proposed by V. A. Budylin and co-workers for reaction of iodonium salts with nucleophiles [10]. This mechanism has recently been confirmed in another way by the analysis of the results of the interaction of aryl-B-carboranyliodonium salts with nucleophiles [9].

## EXPERIMENTAL

IR spectra of films were recorded with a UR-20 spectrometer. <sup>1</sup>H NMR Spectra were measured with Varian XL-400 and Bruker WP-200SY machines. GLC analyses were carried out with Biochrom-1 machine with a flame ionization detector and a glass capillary column (50 m × 0.22 mm, XE-60 liquid phase) and temperature programming from 100-190°C, 16°/min. Chlorobenzene was the internal standard. Chromato-mass spectrometry was carried out with a Finnigan MAT 2125S with a Labkom-2 data acquisition system, a capillary column (30 m × 0.25 mm, OV-101 liquid phase), temperature programming from 40° (5 min) to 260°C at 12°/min, an ionization energy of 80 eV, temperature of the ionization chamber 250-280°C, and a mass spectrum scanning rate of 1 sec/decade.

TABLE 3. Mass Spectrometric Data for Compounds Xa-XVc

Compound	$m/z$ ( $I_{rel}$ , %)
Xa	325(11) [M] <sup>+</sup> ; 198(100) [M-I] <sup>+</sup> ; 168(35) [198-NO]; 152(31) [198-NO <sub>2</sub> ] <sup>+</sup> ; 139(22) [168-CHO] <sup>+</sup>
Xb	293(100) [M-N <sub>2</sub> ] <sup>+</sup> ; 166(83) [293-I] <sup>+</sup> ; 139(33) [166-HCN] <sup>+</sup>
XII	406(87) [M] <sup>+</sup> ; 279(100) [M-I] <sup>+</sup> ; 152(90) [279-I] <sup>+</sup> ; 151(50) [152-H] <sup>+</sup> ; 150(31) [151-H] <sup>+</sup> ; 139,5(58) [M-I] <sup>2+</sup> ; 76(83) [C <sub>6</sub> H <sub>4</sub> ] <sup>+</sup>
XIII	167(100) [M-N <sub>2</sub> ] <sup>+</sup> ; 166(34) [167-H] <sup>+</sup> ; 140(12) [167-HCN] <sup>+</sup> ; 139(18) [140-H] <sup>+</sup>
XIV	295(47) [M] <sup>+</sup> ; 168(100) [M-I] <sup>+</sup> ; 167(73) [M-HI] <sup>+</sup> ; 140(7) [167-HCN] <sup>+</sup> ; 139(16) [140-H] <sup>+</sup>
XVa	367(23) [M] <sup>+</sup> ; 231(36) [M-C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )CH <sub>2</sub> ] <sup>+</sup> ; 222(61) [M-I-H <sub>2</sub> O] <sup>+</sup> ; 217(86) [C <sub>7</sub> H <sub>6</sub> I] <sup>+</sup> ; 194(14) [222-CO] <sup>+</sup> ; 118(100) [C <sub>9</sub> H <sub>10</sub> ] <sup>+</sup> ; 104(43) [231-I] <sup>+</sup> ; 103(21) [104-H] <sup>+</sup> ; 91(86) [C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup> ; 90(70) [C <sub>7</sub> H <sub>6</sub> ] <sup>+</sup>
XVb	400*(14) [M] <sup>+</sup> ; 273*(1) [M-I] <sup>+</sup> ; 231(19) [M-C <sub>6</sub> H <sub>4</sub> (Br)CH <sub>2</sub> ] <sup>+</sup> ; 217(12) [C <sub>7</sub> H <sub>6</sub> I] <sup>+</sup> ; 196*(11) [M-C <sub>6</sub> H <sub>4</sub> I-H] <sup>+</sup> ; 195*(13) [196-H] <sup>+</sup> ; 183*(7) [M-C <sub>6</sub> H <sub>4</sub> (I)CH <sub>2</sub> ] <sup>+</sup> ; 169*(15) [M-C <sub>6</sub> H <sub>4</sub> (I)CH <sub>2</sub> CH <sub>2</sub> ] <sup>+</sup> ; 117(22) [C <sub>9</sub> H <sub>9</sub> ] <sup>+</sup> ; 104(38) [231-I] <sup>+</sup> ; 91(100) [C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup>
XVc	335(19) [M-N <sub>2</sub> ] <sup>+</sup> ; 217(13) [C <sub>7</sub> H <sub>6</sub> I] <sup>+</sup> ; 208(51) [335-I] <sup>+</sup> ; 132(77) [335-C <sub>6</sub> H <sub>4</sub> I] <sup>+</sup> ; 118(100) [C <sub>9</sub> H <sub>10</sub> ] <sup>+</sup> ; 91(85) [C <sub>7</sub> H <sub>7</sub> ] <sup>+</sup>

\*Ions containing <sup>79</sup>Br.

$\beta$ -Phenylethyl bromide was prepared from  $\beta$ -phenylethanol by a known method [20]. 2-Iodobenzaldehyde was prepared from 2-iodotoluene [21].

**1-(2-Iodophenyl)-3-phenylpropane (IV).** A solution of  $\beta$ -phenylethylmagnesium bromide, prepared from magnesium (5 g, 0.21 mol) and  $\beta$ -phenylethyl bromide (18.85 g, 0.1 mole) in absolute ether (250 ml) in the presence 1,2-dibromoethane (6 ml, 0.04 mol) (reaction with assistance), was treated with 1,2-dibromoethane (11 ml) in absolute ether (35 ml) until all the unreacted magnesium was consumed. After boiling for 1.5 h, a solution of 2-iodobenzaldehyde (15.77 g, 0.07 mol) in absolute ether (50 ml) was added to the Grignard reagent at 0°C. The mixture was boiled for 30 min, kept for 12 h, and then decomposed with excess 30% AcOH. Carbinol IX, which was obtained after normal work up (IR spectrum: 3700-3100 ( $\nu_{OH}$ ), 1500 ( $\nu_{Ar}$ ), 700 cm<sup>-1</sup> (*o*-substituted arene)) was dissolved without further purification in glacial acetic acid (27 ml), added to a solution of red phosphorus (12.77 g), iodine (8.2 g), and conc. HI (40 ml) and the mixture was boiled for 11 h (monitored by TLC). The hot reaction mixture was filtered, washed twice with water, the oil was separated, and the water layer was extracted with benzene (3  $\times$  50 ml). The benzene extract was added to the oil and the mixture was washed until colorless with NaHSO<sub>3</sub>, then with water and then dried over MgSO<sub>4</sub>. After evaporation of the benzene the oily residue was distilled in vacuum to give 1-(2-iodophenyl)-3-phenylpropane (IV) (17.42 g, 76%), b.p. 125-140°C (1.5-2  $\cdot$  10<sup>-2</sup> mmHg) (lit. data [13] b.p. 210°C/2 mmHg). <sup>1</sup>H NMR Spectrum (CD<sub>2</sub>Cl<sub>2</sub>/CCl<sub>4</sub> 4:1): 7.74 (1H, m, 1-H), 7.28-7.06 (7H, m, 2-, 3-, 5-, 9-H), 6.84-6.76 (1H, m, 4-H), 1.96-1.84 (2H, m,  $\beta$ -H), 2.78-2.64 ppm (4H, m,  $\alpha$ - and  $\alpha'$ -H).

**11,12-Dihydro-10H-dibenz[*b,g*]iodocinium Tetrafluoroborate (II).** Iodoarene (IV) (16.09 g, 0.05 mole) in Ac<sub>2</sub>O (30 ml) was added dropwise to peracetic acid (30%, 95 ml) and the mixture was kept at 20°C for 12 h. Then conc. H<sub>2</sub>SO<sub>4</sub> (28 ml) was added dropwise at 0°C with stirring to the solution in which 1-(2-iodosophenyl)-3-phenylpropane was forming. The mixture was kept at 20°C until the initial iodoarene had disappeared (monitored by TLC). The solution of 11,12-dihydro-10H-dibenz[*b,g*]iodocinium hydrogen sulfate (VI) was cooled with ice and poured with stirring into saturated K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution (0.5 liter). The precipitated 11,12-dihydro-10H-dibenz[*b,g*]iodocinium dichromate (VIII) was washed with ice water and with an ether-*n*-heptane mixture (1:3), and then dissolved without further purification in a mixture of 40% aqueous HBF<sub>4</sub> (77.5 ml) and propanol-2 (100 ml) and boiled for 1 h. Most of the solvent was evaporated and the residue was washed with a minimum amount of water to remove the Cr(III) salts, recrystallized from water and precipitated from nitromethane solution with ether to give 11,12-dihydro-10H-dibenz[*b,g*]iodocinium tetrafluoroborate (II) (8.75 g, 44% based on iodoarene (IV)), m.p. 221-222°C. Found, %: C 44.04, H 3.66. Calc. for C<sub>15</sub>H<sub>14</sub>BF<sub>4</sub>I, %: C 44.16, H 3.46. <sup>1</sup>H NMR Spectrum (acetone-D<sub>6</sub>): 8.5-8.3 (2H, d, 4- and 6-H), 7.7-7.5 (4H, m, 2-, 3-, 7-, 8-H), 7.4-7.2 (2H, m, 1- and 9-H), 3.7-3.4 (4H, m, 10- and 12-H), 3.3-3.1 ppm (2H, m, 11-H).

**Dibenz[*b,d*]iodolium Dichromate (VII).** A hot solution of dibenz[*b,d*]iodolium hydrogen sulfate V\* (9.4 g, 25 mmole) in water (0.5 ml) was added with stirring to a saturated solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.2 ml). The yellow precipitate was washed with water, acetone–ether mixture (1:2), and ether and dried to give dichromate (VII) (9.5 g, 98%). T<sub>decomp</sub> 210°C. Found, %: C 37.05, H 2.25, Cr 13.15. Calc. for C<sub>24</sub>H<sub>16</sub>Cr<sub>2</sub>I<sub>2</sub>O<sub>7</sub>, %: C 37.24, H 2.08, Cr 13.43.

**Dibenz[*b,d*]iodolium Tetrafluoroborate (I).** A mixture of salt VII (9 g, 12 mmole), HBF<sub>4</sub> (40% aqueous, 25 ml), and propanol-2 (50 ml) was boiled for 1 h. After evaporation of the solvent the precipitated salt I was filtered off and washed with water. The filtrate and washing water were diluted three fold with water and the remaining salt I extracted with a mixture of nitromethane and chloroform (3:1). The solution was evaporated to dryness in vacuum. All of salt I was precipitated from nitromethane with ether (yield 8.17 g, 96%), mp 247–249°C. Found, %: C 39.54, H 2.18. Calc. for C<sub>12</sub>H<sub>8</sub>BF<sub>4</sub>I, %: C 39.39, H 2.20.

**Reaction of Salt I with NaNO<sub>2</sub>.** A solution of salt I (0.2 g, 0.55 mmole) and NaNO<sub>2</sub> (0.4 g, 5.7 mmole) in DMSO (2 ml) and water (1 ml) was boiled for 4 h to complete decomposition of the iodonium salt, diluted with twice the volume of water, and extracted with ether (4 × 20 ml). The ether solution was washed with water and dried over CaCl<sub>2</sub>. GLC results showed that the residue contained diphenyl (XI, 9%), 2-iododiphenyl (III, 26%), 2,2'-diiododiphenyl (XII, 40%) and 2-nitro-2'-iododiphenyl (Xa, 21%).

**Reaction of Salt I with NaN<sub>3</sub>.** A mixture of salt I (0.2 g, 0.55 mmole), NaN<sub>3</sub> (0.35 g, 5.4 mmole), DMSO (3 ml) and water (1.5 ml) was boiled for 3 h to complete decomposition of the iodonium salt. The mixture was treated as in the previous experiment. The residue after evaporation of the ether was dissolved in 1:1 benzene–petroleum ether and the solution was passed through a layer of silica gel of height 2 cm and diameter 1.5 cm (none of the reaction products were adsorbed irreversibly on the silica gel), and the eluate was concentrated to about 10 ml. According to GLC data, the eluate contained 2-azido-2'-iododiphenyl (Xb, 55%), 2-azidodiphenyl (XIII, 18%), 2-amino-2'-iododiphenyl (XIV, 4%), and also compounds III (8%) and XII (15%), the mass spectra of which were identical with those from the previous experiment.

**Reaction of Salt II with NaNO<sub>2</sub>.** A solution of salt II (1 g, 2.45 mmole) and NaNO<sub>2</sub> (1.8 g, 26 mmole) in a mixture of DMSO (18 ml) and water (9 ml) was boiled for 1.5 h until salt II was completely reacted. The mixture was then worked up as for the reaction of salt I with NaNO<sub>2</sub>. The residue after evaporation of ether from the extract was chromatographed on a column (2 × 25 cm) packed with 40/100 silica gel with 1:1 benzene–heptane eluant to give 1-(2-iodophenyl)-3-(2-nitrophenyl)propane (XVa) (0.79 g, 88%), n<sub>D</sub><sup>20</sup> 1.6220, and no other product was observed.

**Reaction of Salt II with NaBr.** A mixture of salt II (0.2 g, 0.49 mmole) and NaBr (0.5 g, 4.9 mmole) in DMSO (7 ml) was heated at 120–140°C until salt had completely reacted (11.5 h) and the reaction mixture was treated as described above to give 1-(2-bromophenyl)-3-(2-iodophenyl)propane (XVb) (0.17 g, 86%), mp 68–71°C.

**Reaction of Salt II with NaN<sub>3</sub>.** A solution of salt II (0.2 g, 0.49 mmole) and NaN<sub>3</sub> (0.32 g, 4.9 mmole) in a mixture of DMSO (3 ml) and water (1 ml) was boiled for 45 m until salt II had reacted completely. The reaction mixture was worked up as described above. The ether extract contained a single product — 1-(2-iodophenyl)-3-(2-azidophenyl)propane (XVc).

## REFERENCES

1. C. Hartmann and V. Meyer, *Ber.*, **27**, 426 (1894).
2. R. B. Sandin, *Chem. Rev.*, **32**, 249 (1943).
3. D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).
4. G. A. Olah, *Halonium Ions*, Wiley Interscience, New York (1975).
5. G. F. Koser, *Chemistry of Functional Groups*, Suppl. D, Ch. 25, Wiley Interscience, Chichester (1983), 1265.
6. R. M. Moriarity and R. K. Vaid, *Synthesis*, No. 6, 431 (1990).
7. C. W. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Alegria, and J. K. Kochi, *J. Am. Chem. Soc.*, **102**, 7753 (1980).
8. D. D. Tanner, D. W. Reed, and B. P. Setiloane, *J. Am. Chem. Soc.*, **104**, 3917 (1982).
9. V. V. Grushin, I. I. Demkina, and T. P. Tolstaya, *J. Chem. Soc. Perkin Trans. II*, No. 3, 505 (1992).
10. V. A. Budylin, M. S. Ermolenko, F. A. Chugtai, and A. N. Kost, *Khim. Geterotsikl. Soedin.*, No. 11, 1494 (1981).

\*Obtained by the sequence diphenyl → 2-nitrodiphenyl [22] → 2-aminodiphenyl (analogously to [23]) → 2-iododiphenyl [24] → V [13].

11. R. Hoffman, J. M. Howell, and E. L. Muetteries, *J. Am. Chem. Soc.*, **94**, 3047 (1972).
12. H. J. Reich and C. S. Cooperman, *J. Am. Chem. Soc.*, **95**, 5077 (1973).
13. J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Am. Chem. Soc.*, **78**, 3819 (1956).
14. T. Sato, K. Shimizu, and H. Moriya, *J. Chem. Soc. Perkin Trans. I*, No. 13, 1537 (1974).
15. Y. Yamada, K. Kashima, and M. Okawara, *Bull. Chem. Soc. Jpn.*, **47**, 3179 (1974).
16. T. Sato, S. Shimada, K. Shimuzu and K. Hato, *Bull. Chem. Soc. Jpn.*, **43**, 1918 (1970).
17. A. S. Batsanov, V. N. Petrov, Yu. T. Struchkov, L. D. Egorova, I. N. Lisichkina, and T. P. Tolstaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 10, 2309 (1985).
18. T. P. Tolstaya, L. D. Egorova and I. N. Lisichkina, *Khim. Geterotsikl. Soedin.*, No. 4, 474 (1985).
19. L. D. Egorov, I. N. Lisichkina, T. P. Tolstaya and N. N. Kostitsyna, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1347 (1985).
20. K. H. Slotta and W. Altner, *Ber.*, **64**, 1510 (1931).
21. C. J. Angial, in: *Organic Reactions*, Pt. 8, R. Adams (ed.) [Russian translation], Inostr. Lit., Moscow (1956), p. 263.
22. F. Bell, J. Kenyon, and P. H. Robinson, *J. Chem. Soc.*, No. 6, 1239 (1926).
23. Byung Hce Han, Dae Hyun Shin, and Sung Yun Cho, *Tetrah. Lett.*, **26**, 6233 (1985).
24. H. Gilman, J. E. Kirby, and C. R. Kinney, *J. Am. Chem. Soc.*, **51**, 2252 (1929).