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Abstract

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SALTS OF DIPHENYL-o,o'-DIPHENYLENAMMONIUM

Fully aromatic onium compounds are known for all elements of group V (main subgroup) of the periodic system, with the exception of nitrogen. In the present work we describe the preparation and properties of the first representatives of previously unknown tetraarylammonium compounds—salts of diphenyl-o,o'-diphenylenammonium.

By decomposition of phenyldiazonium fluoroborate in the presence of bromobenzene and chlorobenzene, we obtained diphenylbromonium (^{1}) and diphenylchloronium (^{2}) compounds. Similarly, starting from diphenyl ether, triphenyloxonium compounds (^{3}) were obtained. However, triphenylamine under these conditions, and also upon decomposition in it of diphenyliodonium fluoroborate (^{4}), is not arylated. It had previously been shown that cyclic aromatic onium compounds of this type are formed more readily and in better yield (^{5}). In the present case we found that, already on heating diazotized o-amino-o'-diphenylaminodiphenyl in acetic acid, diphenyl-o,o'-diphenylenammonium acetate is formed in 43% yield:

$$[\ \text{diazotized } o\text{-amino-}o'\text{-diphenylaminodiphenyl}\ ]\ CH_3COO^- \xrightarrow[\text{in aqueous } CH_3COOH]{\text{heating}} [\ \text{diphenyl-}o,o'\text{-diphenyle}$$

from which, by double-exchange reactions, its other salts were also obtained. The structure of the diphenyl-o,o'-diphenylenammonium cation was proved by thermal decomposition of its hydroxide (in aqueous solution), which led to the formation of N-phenylcarbazole, diphenyl ether, and a small amount of phenol (the last two substances were identified chromatographically):

$$[(C_6H_4)_2\overset{+}{N}(C_6H_5)_2]\ OH^- \xrightarrow{\text{heating}} C_6H_5N(C_6H_4)_2 + C_6H_5OH,$$

$$[(C_6H_4)_2\overset{+}{N}(C_6H_5)_2]\ OH^- + C_6H_5OH \xrightarrow{\text{heating}} C_6H_5N(C_6H_4)_2 + (C_6H_5)_2O + H_2O.$$

The salts of diphenyldiphenylenammonium described in this article are crystalline substances, resistant to acids and alkalis, melting with decomposition above 200°, soluble in polar solvents (nitromethane, acetone, chloroform), insoluble in nonpolar solvents (ether, benzene), and poorly soluble in water. They readily exchange the anion and, unlike other fully aromatic onium compounds ([3,6]), do not decompose on boiling with aqueous solutions of NaN_3, $NaNO_2$, $(C_2H_5)_2NH$, or with 20% NaOH solution. Diphenyldiphenylenammonium iodide decomposes only on boiling with 50% KOH solution, forming N-phenylcarbazole, iodobenzene, and an insignificant amount of diphenyl ether. In the absence of alkali, the salt is unchanged at the boiling temperature of 50% KOH.

Experimental Part

1. *o′*-Nitro-*o*-diphenylaminodiphenyl. A finely ground mixture of 15 g (0.07 mole) of *o′*-nitro-*o*-aminodiphenyl*, 13 g (0.09 mole) of K_2CO_3, 45 ml (0.40 mole) of iodobenzene, and 1 g of copper powder was heated for 20 h (with removal of the water formed) at 210–215° (thermometer in the bath). The iodobenzene was removed with steam. The residue was treated with chloroform and filtered. After evaporation of the chloroform, the remaining *o′*-nitro-*o*-diphenylaminodiphenyl was washed three times with ether. Yield 12.6 g (67% of theory). Mp 122–124° (from alcohol). The substance is moderately soluble in ether and acetone, readily soluble in benzene and chloroform.

Found, %: C 78.46; H 5.12
$C_{24}H_{18}N_2O_2$. Calculated, %: C 78.67; H 4.94

2. *o*-Amino-*o′*-diphenylaminodiphenyl. A solution of 3 g (0.008 mole) of *o′*-nitro-*o*-diphenylaminodiphenyl in 80 ml of 98% acetic acid was added to a mixture of 8 g (0.12 g-at.) of zinc dust, 6 ml of alcohol, and 6 ml of acetic acid. After stirring for 2 h at 20°, the reaction mixture was filtered, the acetic acid was removed from the filtrate in vacuo, and the residue was dissolved in ether. The ether solution was washed with soda, water, and dried over anhydrous K_2CO_3. After evaporation of the ether, 2.35 g (85% of theory) of *o*-amino-*o′*-diphenylaminodiphenyl remained. Mp 106–107° (from aqueous methanol).

Found, %: C 85.78; H 6.02; N 8.36
$C_{24}H_{20}N_2$. Calculated, %: C 85.70; H 5.93; N 8.33

3. Preparation of diphenyl-*o,o′*-diphenyleneammonium iodide. A solution of 6.3 g (0.02 mole) of *o*-amino-*o′*-diphenylaminodiphenyl in 70 ml of 98% acetic acid was diazotized with a saturated aqueous solution of 6 g (0.09 mole) of $NaNO_2$. After 20 min, 5 g of urea was added to the diazo solution, and it was cautiously heated on a wire gauze until a negative test with β-naphthol was obtained. The acetic acid was removed in vacuo at 35–40°; 60 ml of water was added to the residue, and from the resulting filtered solution of diphenyl-*o,o′*-diphenyleneammonium acetate the iodide was precipitated by addition of solid sodium iodide. Yield 3.95 g (43% of theory); melting point after reprecipitation with abs. ether from nitromethane, 273–275° (decomp.).

Found, %: C 64.36; H 4.02; I 28.17

$C_{24}H_{18}NI$. Calculated, %: C 64.44; H 4.05; I 28.37

4. Other salts of diphenyldiphenyleneammonium—see Table 1.

5. Decomposition of diphenyldiphenyleneammonium hydroxide. A finely ground mixture of 1 g (~0.002 mole) of diphenyldiphenyleneammonium iodide with freshly prepared Ag_2O paste, from 1 g (0.006 mole) of $AgNO_3$, was left for 12 h at 20°. The precipitate was centrifuged and washed with a small amount of water. The resulting aqueous solution of diphenyldiphenyleneammonium hydroxide, which had a strongly alkaline reaction, was boiled with a reflux condenser until neutral to litmus (8 h). After cooling, the reaction mixture was extracted with ether; the ether extract was treated with 10% NaOH and dried over $MgSO_4$. The alkaline extracts were acidified with 20% H_2SO_4. The resulting acidic solution was treated with bromine water and then extracted with ether. After evaporation of the ether, 0.66 g of tribromophenol remained, identified by thin-layer chromatography on Al_2O_3 (solvent—CH_3OH).

After removal of the ether from the ether extract treated with alkali, from the initial reaction mixture, 0.55 g of a mixture of N-phenylcarbazole and diphenyl ether remained (75% of theory). Part of this mixture (0.26 g) was recrystallized from alcohol with addition of activated charcoal; isolated 0.2 g of N-phenylcarbazole (56% of theory) with m.p. 85-86° (literature data: m.p. of N-phenylcarbazole 82-84° (10); 88° (11)). The other part of the mixture was chromatographed in a thin layer of Al_2O_3 with reference substances (solvent —1% solution of benzene in hexane). In this way only N-phenylcarbazole and diphenyl ether were detected.

Table 1

Salt anion	Decomp. temp., °C	C	H	N	F	J	Hg
J'	273-275	64.36 / 64.44	4.02 / 4.05			28.17 / 28.37	
BF_4'	236-237	70.75 / 70.78	4.40 / 4.46	3.47 / 3.44	18.30 / 18.66		
HgJ_4''	237-238	42.39 / 42.75	2.87 / 2.65				14.94 / 14.83
$C_6H_2(NO_2)_3O'$	234-235	65.52 / 65.70	3.77 / 3.66	10.18 / 10.21			
NO_3'	267-268	75.34 / 75.37	4.87 / 4.76				

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* Prepared according to the following scheme: *o*-nitroaniline → *o*-iodonitrobenzene (?) → *o,o′*-dinitrodiphenyl (?) → *o′*-nitro-*o*-aminodiphenyl (?).

* The numbers above the line are found; those below the line are calculated.

6. Reactions of diphenyldiphenyleneammonium iodide.

a) Reaction with $NaNO_2$. A mixture of 0.3 g (0.001 mole) of diphenyldiphenyleneammonium iodide, 0.5 g (0.07 mole) of $NaNO_2$, and 8 ml of water was boiled for 15 hr. On cooling, 0.23 g (80% of theory) of the starting iodide separated, m.p. 272-273° (after reprecipitation with absolute ether from nitromethane). No organic substances were found in the filtrate.

b) Reaction with sodium azide. 0.3 g (0.001 mole) of diphenyldiphenyleneammonium iodide was boiled for 24 hr in a solution of 2 g (0.03 mole) of sodium azide in 25 ml of water. 0.26 g (88% of theory) of the starting iodide was isolated, m.p. 271-273°.

c) Reaction with diethylamine. A mixture of 0.3 g (0.001 mole) of diphenyldiphenyleneammonium iodide, 11 ml (0.1 mole) of diethylamine, and 8 ml of water was boiled for 20 hr. After distilling off the diethylamine, 0.28 g (93% of theory) of the starting substance was isolated, m.p. 271-272°.

d) Reaction with 20% NaOH. 1.35 g (0.003 mole) of diphenyldiphenyleneammonium iodide was boiled with 20 ml of 20% NaOH solution for 12 hr. On cooling, 1.15 g (86% of theory) of the starting salt separated, m.p. 274-275°.

e) Reaction with 50% KOH. A mixture of 1 g (0.002 mole) of diphenyldiphenyleneammonium iodide and 10 ml of 50% KOH solution was boiled for 3 hr, then diluted with 15 ml of water and subjected to steam distillation. From the distillate, 0.18 g (40% of theory) of iodobenzene was isolated; chromatographically (in a thin layer on Al_2O_3 with reference substances, solvent hexane) an admixture of N-phenylcarbazole and diphenyl ether was detected in it. The residue from the steam distillation was extracted with ether. After evaporation of the ether, 0.5 g (93% of theory) of N-phenylcarbazole remained, m.p. 85-86° (from alcohol). The alkaline solution (after distillation of the iodobenzene and extraction of the N-phenylcarbazole) was acidified with 20% H_2SO_4. In the resulting acidic solution no phenol was detected (tests with bromine water and diazotized sulfanilic acid).

f) Heating in an ampoule. 1 g (~0.002 mole) of diphenyldiphenyleneammonium iodide in 20 ml of water was heated for 2 hr at 160–165° in a sealed-

ampule. When the ampule was opened, no excess pressure was detected. 0.95 g (95% of theoretical) of the starting salt was isolated, m.p. 271-272°.

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