SYNTHESIS OF 10H-DIBENZO[b,e]CHLORINIUM FLUOROBORATE AND DEUTERIUM EXCHANGE REACTIONS IN THE CH<sub>2</sub> UNIT OF 10H-DIBENZO[b,e]HALINIUM CATIONS

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The problem of the structure and reactivity of onium, including halonium, salts [1-3] is closely linked with the problem of the transmission of electronic influences in onium cations [4, 5], particularly cyclic cations. Thus, in 10-thiadibenzo[b,e]halinium (phenothiahalinium) salts containing a bridging S atom in the central six-membered ring in addition to a halonium atom a significant positive charge is localized on the latter increasing + + + markedly in the series I < Br < C1 [6]. The effect of the onium atom is displayed chemically in the S atom in these compounds being extremely inert towards the action of electrophiles, it is not oxidized, and is not alkylated even by such strong alkylating agents as triethyloxonium fluoroborate or MeI in the presence of AgBF<sub>4</sub> [7].

An assessment has been undertaken in the present work of the influence of the halonium atom on the other bridging group, the  $CH_2$  unit of 10H-dibenzo[b,e]halinium cations. For this purpose 10H-dibenzo[b,e]brominium fluoroborate (II) and the previously undescribed 10H-dibenzo[b,e]chlorinium fluoroborate (III) have been synthesized starting from 10H-dibenzo[b,e]iodinium fluoroborate (I) according to the scheme

Scheme 1



#### X = Br (II), Cl (III).

The first stage of the synthesis proceeds ambiguously, in contrast to the previously described thermolysis of 10H-dibenzo[b,e]iodinium halides leading in high yield to 2-halo-2'-iododiphenylmethane [8]. In addition to 2-iodo-2'-nitrodiphenylmethane (IV), which was the main product (yield < 50%), the formation was observed of a complex mixture of products of secondary radical conversions and a significant quantity of resin. 2-Iododiphenyl-methane (V), 1-iodofluorene (VI), and 1-iodofluorenone (VII) were identified in the mixture by GLC. Compounds (IV) (45%) and (VII) (~4%) were isolated in homogeneous form and also a mixture of (V) and (VI) (~5%) of composition 1:2 (GLC) by column chromatography on  $Al_2O_3$ .

The same reaction in a two-phase system of water-dichloroethane led to the formation of only (VII) (58%) and (VI) (0.1%). This result, unexpected at first glance, may be explained by the fact that the 10H-dibenzo[b,e]iodinium cation is transferred to the less polar phase exclusively in the form of the covalent hydroxide (aqueous phase has pH > 7), the homolytic decomposition of which (see below) also led to the observed products. It is possible that this secondary reaction was responsible for the formation of (V)-(VII) on interaction of (I) with NaNO<sub>2</sub> in aqueous DMSO.

The following three stages of the synthesis of (I) (see Scheme 1) occurred without complications in yields of ~90%. The secondary products of the first stage did not contain a

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. M. V. Lomonosov Moscow State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp.1347-1352, June, 1985. Original article submitted March 16, 1984. nitro group and were possibly released from them at the stage of diazotizing the amine. Consequently, when obtaining (III) compound (IV) was not isolated and all the intermediate stages were carried out with a mixture of products.

Cyclization of both diazonium salts in  $CF_3COOH$  according to [9] led to the formation of (II) and (III) in 30-35% yield.

Product (II) was also obtained by the oxidative cyclization of 2-bromodiphenylmethane according to [10] using XeF<sub>2</sub> as oxidizing agent, which was calculated to increase the yield of desired product. However, the yield of (II) was 11.5% overall.

To assess the influence of halonium atoms on the bridging group the comparative CH acidity of the  $CH_2$  unit of the 10H-dibenzo[b,e]halinium cations was studied. The latter might have proved to be significant in size if a quasiaromatic ylide structure with a planar central ring is brought about by removal of a proton.



But this is evidently impossible first of all from spatial considerations (large covalent radii of halogens, the nonplanar structure of the initial cations [11]); consequently, the acidity of the  $CH_2$  unit of 10H-dibenzo[b,e]halinium cations must be determined only by the electronic effects of the onium atoms. In fact, judging by PMR data the protons of this group are deshielded (4.26, 4.32, and 4.38 ppm in iodonium, bromonium, and chloronium cations, respectively) in comparison with the  $CH_2$  in diphenylmethane (3.92 ppm) almost the same as the  $CH_2$  protons in 4,4'-dinitrodiphenylmethane (4.22 ppm).

The determination of equilibrium CH acidity was excluded in our case since the strong bases used for this purpose in all the known methods [12] decompose halonium cations.

The single reaction permitting comparison of the influence of halonium atoms on the mobility of the  $CH_2$  bridge hydrogen proved to be the deuterium exchange reaction proceeding under conditions of alkaline catalysis at ~ 20°C approximately 20% and even under the same conditions was accompanied by partial decomposition of the salt. In this connection to carry out deuteration at a higher temperature to increase the degree of exchange is nonsense.

It was convenient to follow the course of the reaction by PMR spectra. These reactions do not go in acid and neutral media, and the PMR spectra of solutions of (I)-(III) in  $D_2O$  did not change with time. The aromatic portion of the spectra of (I)-(III) did not change in carbonate buffer solution in  $D_2O$  at pD 9.3, but the signal of the CH<sub>2</sub> group gradually changed in intensity and was not displaced and was not broadened. This indicates that the considered reaction, as for other cases of deuterium exchange catalyzed by bases [12], evidently occurred in two stages, the first of which determined the rate of the whole process.



The second stage occurred so rapidly that the formation of ylide (A) failed to be recorded on the PMR spectrum (the signal of the  $CH_2$  protons was not displaced and was not broadened).

After 1 h the protons of the  $CH_2$  group of (I) were exchanged on average by 4-5%, of (II) by 12-13%, and of (III) by 16-17%. Maximum exchange at 20°C was achieved after approximately 6 h and was 13-14% for (I), 15-16% for (II), and 27-28% for (III).\*

<sup>\*</sup> From the ratio of the integrated intensities of the PMR signals of the aromatic and  $CH_2$  protons (mean values of several measurements).

There was therefore a definite rule here for the influence of the onium atom on the bridging group similar to that detected by us previously in the example of 10-thiadibenzo-[b,e]halinium salts in [6]: The acidity of the CH<sub>2</sub> protons in (I)-(III) grew in parallel with the increase in electronegativity of the halogen atoms.

It was also shown that (I) was not methylated at the  $CH_2$  unit either by methyl iodide or by dimethyl sulfate in the presence of bases. The salt was either completely decomposed or was recovered in unchanged form as occurs on using weakly nucleophilic sterically hindered bases such as 1,2,2,6,6-pentamethylpiperidine or hexamethyldisilazylsodium. Decomposition occurred particularly readily under the action of weakly solvated hydroxyl anion and led to a complex mixture of products clearly of radical origin. Thus, from reaction of (I) with NaOH in MeCN, ~ 40% salt was recovered and (V)-(VII) were detected among the nonsaltlike products. On attempting methylation of (I) in the two-phase system Me<sub>2</sub>SO<sub>4</sub>/50% NaOH the salt was completely decomposed after 3 h at 20°C, and from the reaction mixture (V)-(VII) were also isolated in addition to a compound with mp 156-157°C which on the basis of its mass spectrum was assigned the structure of 6-iodo-2-(8-iodo-1-fluorenyl)diphenylmethane. The indicated products were evidently formed as a result of homolytic fission of the covalent form of 10H-dibenzo[b,e]iodinium hydroxide (VIII), which is a derivative of three-coordinate iodine.



In fact, we succeeded in establishing the formation of such forms in low-polarity nonsolvating solvents and showed that it was incomparably less stable than the ion. Thus, in the IR spectrum of a solution of (VIII) in CCl<sub>4</sub> also containing decomposition products a broad band was observed in the 2550-2650 cm<sup>-1</sup> region, which by analogy with [13] was assigned to the stretching vibration of an OH group covalently bonded to an I atom. Absorption above  $3000 \text{ cm}^{-1}$  was absent. On treating this solution with alcoholic HI the corresponding iodide (IX) was precipitated. Absorption in the 2500-2700 cm<sup>-1</sup> region and above  $3000 \text{ cm}^{-1}$  was not observed in the IR spectrum of the nonsaltlike products of decomposition of (VIII) isolated after separating (IX).

The ionic form of (VIII), which can exist in aqueous solution for a sufficiently extended time without decomposition, was isolated by us in crystalline form and had mp 94-98°C. It was converted quantitatively into (IX) by the action of HI. The usual OH band at 3100- $3600 \text{ cm}^{-1}$  was observed in its IR spectrum and absorption was absent from the 2500-2700 cm<sup>-1</sup> region.

#### EXPERIMENTAL

<u>1. Reaction of 10H-Dibenzo[b,e]iodinium Fluoroborate (I) with NaNO<sub>2</sub>.</u> a) A solution of (I)\* (10 g) and NaNO<sub>2</sub> (18.2 g) in a mixture of DMSO (130 ml) and water (90 ml) was boiled for 2 h until complete decomposition of the iodinium salt. The reaction mixture was cooled, extracted with ether, the ether solution washed from DMSO with water, and dried over MgSO<sub>4</sub>. After removal of ether the residue was chromatographed on  $Al_2O_3$  (activity II). A mixture (0.54 g) of 2-iododiphenylmethane (V) and 1-iodofluorene (VI) 1:2 (GLC) was eluted with petroleum ether, then 2-iodo-2'-nitrodiphenylmethane (IV) (4 g: 45%) of mp 45-47°C with a mixture of petroleum ether with acetone (12:1 by volume). Found: N 4.28%.  $C_{13}H_{10}NO_2I$ . Calculated: N 4.13%. 1-Iodofluorenone (VII) (280 mg: 4%) of mp 144-146°C (cf.[15]) was eluted with a mixture of petroleum ether with acetone (5:1 by volume).

b) A solution of (I) (0.5 g), NaNO<sub>2</sub> (1 g), and triethylbenzylammonium chloride (0.1 g) in a mixture of water (20 ml) and dichloroethane (20 ml) was boiled with vigorous stirring for 73 h, then 10H-dibenzo[b,e]iodinium iodide (IX) (37 mg: 7%) of mp 187-189°C (cf.[16]) was precipitated from the aqueous layer. The organic layer was evaporated to dryness and from the residue (VI) (40 mg: 0.1%) and (VII) (234 mg: 58%) of mp 144-145°C were isolated by preparative TLC on  $Al_2O_3$  (5/40  $\mu$ ) with a mixture of petroleum ether and acetone (10:1 by vol.).

<sup>\*</sup> Obtained according to [14].

<u>2. 2-Bromo-2'-nitrodiphenylmethane (X).</u> A mixture of (IV) (3.1 g),  $Cu_2Br_2$  (1.2 g), and DMF\* (12 ml) was boiled with stirring for 4 h then poured into water (60 ml) and extracted with ether. Compound (X) (2.32 g: 87%) of mp 50-54°C was obtained.

<u>3.</u> 2-Bromo-2'-aminodiphenylmethane (XI). A solution of (X) (2.32 g) in EtOH (6 ml) was added with stirring to a hot solution of  $SnCl_2 \cdot 2H_2O$  (4.5 g) in conc. HCl (15 ml) and the mixture boiled for 2.5 h. After the usual treatment (XI) (2 g: 97%) was obtained. The hydrochloride of (XI) had mp 186-191°C.

<u>4. 2-(2-Bromobenzyl)phenyldiazonium Fluoroborate (XII).</u> Compound (XI) (3.14 g) in conc. HCl (15 ml) was diazotized with a solution of NaNO<sub>2</sub> (1.38 g) in water (10 ml). Compound (XII) (4 g: 91%) of decomposition point 70-71°C was isolated by the addition of solid NaBF<sub>4</sub>.

5. 10H-Dibenzo[b,e]brominium Fluoroborate (II). a) A solution of (XII) (1 g) in  $CF_3COOH$  (15 ml) was boiled for 1 h until complete decomposition of the diazonium salt (test with  $\beta$ -naphthol), then evaporated in vacuum to a volume ~ 1 ml, (II) was precipitated with ether, and was reprecipitated from MeNO<sub>2</sub> with ether. The yield of (II) was 320 mg (36%), decomposition point 177-180°C; after dehydration in vacuum at 100°C the decomposition point was 194-195°C. Found: C 47.00; H 3.26%.  $C_{13}H_{10}BBrF_4$ . Calculated: C 46.90; H 3.03%. PMR spectrum (100 MHz in CF<sub>3</sub>COOH,  $\delta$ , ppm): 8.24-7.48 m (8H) and 4.32 s (2H).

b)  $XeF_2$  (0.97 g) was added with stirring to a solution of 2-bromodiphenylmethane [10] (1 g) in  $CH_2Cl_2$  (25 m1) at  $-70^{\circ}C$ ,  $Et_2O \cdot BF_3$  (3.6 m1) was then added slowly dropwise, stirring was continued for 1 h at  $-70^{\circ}C$ , 6 h at 20°C, and the mixture left overnight. The mixture was then diluted with ether and (II) was extracted many times with water. The aqueous extracts were evaporated to the beginning of crystallization. After cooling, the precipitated (II) was reprecipitated with ether from acetone. Yield of (II) was 150 mg (11.5%), decomposition point 174-176°C.

<u>6. 10H-Dibenzo[b,e]brominium Iodide</u>. This compound was obtained from (II) (0.16 g) in water (15 ml) by adding solid NaI in a yield of 170 mg (94%) and had decomposition point 128-130°C. Found: C 42.50: H 2.72%.  $C_{13}H_{10}BrI$ . Calculated: C 41.86; H 2.70%.

7. 2-(2-Chlorobenzy1)phenyldiazonium Fluoroborate (XIII). A solution of (I) (18.7 g) and NaNO<sub>2</sub> (34 g) in a mixture of DMSO (164 ml) and water (163 ml) was boiled until complete decomposition of the iodonium salt and the mixture treated as in experiment 1. After removing the ether the residue (15.2 g) was dissolved in DMF (60 ml),  $Cu_2Cl_2$  (10 g) added, the mixture boiled with stirring for 4 h, then poured into water (300 ml), and crude 2-chloro-2'-nitrodiphenylmethane (10 g) extracted with ether. This was dissolved without further purification in EtOH (25 ml), the solution added with stirring to a boiling solution of  $SnCl_2 \cdot 2H_2O$  (22.5 g) in conc. HCl (75 ml), and the mixture boiled for 2.5 h. After the usual treatment crude 2-chloro-2'-aminodiphenylmethane (8 g) was isolated, a solution of which in dilute (1:1) HCl (20 ml) was diazotized with a conc. solution of  $NaNO_2$  (2.8 g). The diazo solution was washed with ether from nonsaltlike products. Compound (XIII) (5.55 g) was isolated by adding solid NaBF<sub>4</sub> and had decomposition point 68-72°C. A further 0.6 g salt was extracted from the aqueous filtrate with a mixture of  $MeNO_2 - CHCl_3$  (3:1 by vol.) (it was precipitated with ether from the extracts after evaporation in vacuum), the overall yield was 6.15 g (39%) calculated on (I).

<u>8.</u> 10H-Dibenzo[b, e]chlorinium Fluoroborate (III). A solution of (XIII) (1 g) in  $CF_3COOH$  (25 ml) was boiled until complete decomposition of the salt (test with β-naphthol) then evaporated in vacuum to ~ 1 ml, (III) was precipitated with ether, and was purified by reprecipitation with ether from acetone (with addition of active charcoal), then from MeNO<sub>2</sub>, and dried in a Fischer pistol. The yield of (III) was 270 mg (30%), decomposition point 186-186.5°C. Found: C 53.96; H 3.39%.  $C_{13}H_{10}BCIF_4$ .Calculated: C 54.11; H 3.49%. PMR spectrum (100 MHz,  $CF_3COOH$ , δ, ppm): 8.22-7.52 m (8H), 4.38 s (2H).

<u>9. Deuterium Exchange Reaction on 10H-Dibenzo]b,e]halinium Fluoroborates.</u> Saturated solutions of (I)-(III) ( $2.9 \cdot 10^{-2}$ ,  $4.8 \cdot 10^{-2}$ , and  $5.4 \cdot 10^{-2}$  M, respectively) in carbonate buffer solution in D<sub>2</sub>O (for the preparation of which a weighed sample of NaOD·D<sub>2</sub>O was dissolved in D<sub>2</sub>O 99.8%, and pure dry CO<sub>2</sub> was passed into the solution until pD was 9.3†) were placed in a

<sup>\*</sup> According to the method of [17].

<sup>+</sup> The pD value at 25°C was obtained by adding 0.41 to that shown on a pH meter [18].

NMR ampul and the ratio of integrated signal intensities of the aromatic and  $CH_2$  protons measured for each of them 1, 6, and 18 h after the beginning of the reaction. The reaction mixture obtained from (II) was then acidified with  $D_2SO_4$  and the corresponding iodides of mp 133-156°C were precipitated by the addition of solid anhydrous NaI (see expt. 6). PMR spectrum (100 MHz,  $CF_3COOH$ ,  $\delta$ , ppm): 8.10-7.46 m and 4.40 s in a ratio 5:1 which corresponded to 20% deuterium exchange in the  $CH_2$  unit of (II).

<u>10. Reaction of 10H-Dibenzo[b,e]iodinium Fluoroborate with NaOH.</u> A 5% aqueous solution (0.61 ml) of NaOH was added at 0°C to a suspension of (I) (305 mg) in MeCN (30 ml) and the reaction mixture acquired an intense yellow color. After 20 min the solution was evaporated in vacuum at 20°C to 1.5-2.0 ml and (I) (125 mg: 41% of that taken) was precipitated with ether and had mp 206-208°C (cf. [16]). After removal of (I) a mixture of nonsaltlike products (184 mg) was isolated from the filtrate, among which (V)-(VII) were detected (TLC and GLC).

<u>11.</u> 10H-Dibenzo[b,e]iodinium Hydroxide (VIII). Compound (IX) (496 mg) was thoroughly ground in a mortar with freshly prepared AgOH (410 mg) and cooled EtOH (50 ml); the precipitate of AgI and AgOH was washed many times with cold EtOH on removal of which under vacuum at 20-25°C there remained a light-brown pastelike mixture of (VIII) with decomposition products. The latter were removed by many extractions of the mixture with  $CCl_4$ . The almost colorless solid of mp 94-98°C was pure (VIII). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3100-3600 (OH). From a solution of (VIII) (51 mg) in water (20 ml) compound (IX) (67.5 mg: 98%) of mp 188-189°C was precipitated by the addition of HI.

The yellow-colored solution in CCl<sub>4</sub> together with the decomposition products of (VIII) contained a small quantity of (VIII) in the covalent form. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2550-2650 OH covalently bound to the I atom [13], 1730 (CO, VII). A compound (52.1 mg:10% on IX taken) of mp 187°C was isolated by adding an alcoholic solution of HI to this solution. After evaporation of the filtrate and separation of (IX) a mixture (252.2 mg) of nonsaltlike products remained. These were identified as (V)-(VII) by GLC.

<u>12.</u> Attempts to Methylate 10H-Dibenzo[b,e]iodinium Fluoroborate at the CH<sub>2</sub> Unit. a) With dimethyl sulfate in the presence of 1,2,2,6,6-pentamethylpiperidine\* (PMP). PMP (1.08 g) was added to a solution of (I) (323.5 mg) in dimethyl sulfate (30 ml) at 0°C, the mixture was stirred for 3 days at 20°C and evaporated to dryness in vacuum. From a solution of the solid in water (15 ml) (IX) (313.1 mg: 90%) of mp 186°C was isolated by adding NaI. PMR spectrum (100 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 8.26-7.60 m (8 H) and 4.30 s (2 H).

b) With dimethyl sulfate in a two-phase system. A 50% aqueous solution (10 ml) of NaOH was added carefully to a solution of (I) (0.24 g) in dimethyl sulfate (10 ml), the mixture stirred vigorously for 3 h at 20°C (after this time I had completely decomposed), the alkaline layer was diluted into four volumes of water, extracted with  $CHCl_3$ , and the combined organic layer evaporated to dryness in vacuum. The residue was a resiny substance (180 mg) from which a mixture (28 mg) of (V) and (VI) (7:3 by GLC) was isolated by preparative TLC on silica gel (5/40  $\mu$ ) in petroleum ether, in addition to (VII) (46.2 mg) and 6-iodo-2-(8-iodo-1-fluorenyl)diphenylmethane (15.4 mg) of mp 156-157°C. Mass spectrum (m/z): 584 [C<sub>26</sub>H<sub>18</sub>I<sub>2</sub>]<sup>+</sup>, 457, 380, 367, 330, 291, 253.

c) With methyl iodide in the presence of hexamethyldisilazylsodium (HMDS-Na). A 1 N solution (3.2 ml) of HMDS-Na in abs. ether (the solution acquired a dark-red color) was added slowly with stirring at 0°C to a solution of (I) (1.23 g) in abs. DMF (15 ml) in a test tube protected from moisture. After 5 min MeI (2 ml) was added. The solution gradually became colored and a precipitate of NaI separated. The mixture was left overnight at 20°C, then evaporated in vacuum almost to dryness, and all the saltlike products were precipitated with ether. The isolated mixture of salts was treated with an excess of  $(Et_3O)^+BF_4^-$  in MeNO<sub>2</sub>; the filtered solution was evaporated in vacuum to ~ 1 ml and (I) (502 mg: 41% of that taken) of mp 204-207°C was precipitated.

## CONCLUSIONS

1. 10H-Dibenzo[b,e]chlorinium fluoroborate has been synthesized. Deuterium exchange reactions showed that the CH acidity of the methylene unit of 10H-dibenzo[b,e]halinium cat-

\* Obtained according to [19].

2. The existence of a covalent form of 10H-dibenzo[b,e]iodinium hydroxide was established and the products of its radical fission were investigated.

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# REACTIONS OF INTERNAL FLUOROOLEFINS WITH ETHYLENIMINE

AND PROPERTIES OF N-POLYFLUOROALKYL(ALKENYL)-

### SUBSTITUTED AZIRIDINES

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It is known that ethylenimine (EI) forms with terminal fluoroolefins addition products exclusively [1-6], while, on the contrary, with cyclic fluoroolefins  $(C_4-C_6)$ , it forms enamines only, which are the substitution products of the vinyl F atom [3, 4, 7, 8].

In the present work, we studied the reaction of EI with certain internal fluoroolefins: perfluoro-2-methyl-2-pentene (I) and perfluoro-4-methyl-2-pentene (II) (dimers of hexafluoropropylene), 3-hydroperfluoro-2-methyl-2-pentene (III), 2-chloroperfluoro-2-butene (IV), perfluoro-2-pentene (V), and perfluoro-1-methylcyclopentene (VI). It was found that the structure of the products depends on the structural features of the initial olefins. Thus, polyfluorotrialkyl-substituted olefins (I) and (III) form only adducts (VII) and (VIII) with EI.

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