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BROMINATION OF TRIPHENYLOXONIUM CATIONS

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It has been previously shown [1] that the triphenyloxonium cation, in contrast to all other aromatic onium cations, the key atom of which is meta-orienting in electrophilic substitution reactions, is nitrated almost exclusively in the para position. At the same time attempts were made to sulfonate this cation. However it was shown that under mild conditions it does not sulfonate, and under more rigorous conditions it is completely broken down.

In the present work we have described still another electrophilic substitution reaction of the triphenyloxonium cation — bromination. It was shown that on heating with Br_2 in the presence of Fe (sealed ampul, 100°C, 60 h) under conditions for bromination of the phenyl trimethylammonium salt [2] the triphenyloxonium borofluoride is not affected. We were able to carry out this bromination only in the presence of silver salts [3-5], of which the most effective appeared to be anhydrous AgBF₄ [6]. The reaction takes place readily at around 20°C and is accomplished best of all in excess Br_2 utilized at the same time as solvent inasmuch as the number of atoms of Br entering into the molecule of (I) is determined only by the quantity of Ag^+ ions introduced and reaches a maximum of six even when using a large excess of $AgBF_4$

$$[(C_6H_5)_3\overset{\dagger}{O}]BF_4^- \xrightarrow{Br_2}_{AgBF_4} [(BrC_6H_4)_3\overset{\dagger}{O}]BF_4^- \xrightarrow{Br_2}_{AgBF_4} [(Br_2C_6H_3)_3\overset{\dagger}{O}]BF_4^- \xrightarrow{Hr_2}_{AgBF_4} [(HII)]]$$

We proved the structure of the end product of bromination, the hexabromotriphenyloxonium borofluoride (III) by destroying the salt by refluxing it with 20% NaOH solution, as a result of which only 3,3',4,4'-tetrabromodiphenyl ether (V) and 3,4-dibromophenol were formed

(III)
$$\xrightarrow{20\% \text{ NaOH}}$$
 (3,4-Br₂C₆H₃)₂O + 3,4-Br₂C₆H₃OH
(IV)

They were subsequently identified by a TLC method. For identification of (IV) we arrived at a synthesis of (IV) by the scheme shown below for 2,2',4,4'-tetrabromodiphenyl ether [7] and not previously described for (IV)

$$(2-BrC_6H_4)_2O \xrightarrow{Br_2}_{AgBF_4} (2,4-Br_2C_6H_4)_2O$$
(1)

The identity of the latter with the ether obtained by decomposition of the hexabromotriphenyloxonium salt was established on the basis of analysis of the PMR spectra of all

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three tetrabromophenyl ether samples which we had available (see Experimental section) and also by mixed melting point tests.

To determine where the first Br atom enters in bromination of the triphenyloxonium cation it was necessary to obtain the pure tribromotriphenyloxonium salt. However for mole ratios of $AgBF_4/Ph_3O^+BF_4^-$ close to the theoretical almost always a difficultly separable mixture of salts with varying degrees of bromination is formed, and the separation of the pure tribromo derivative was accompanied by distinct difficulties. It is formed in a completely pure form with ratios of oxonium salt/AgBF_4 \approx 1:5 exactly under the conditions described in the Experimental section, and contains only a small admixture of salts with lesser bromine content, which can be eliminated by recrystallization or by two or three precipitations of salts from nitromethane or acetone.

Judging from the PMR spectrum, recrystallization of (II), as well as obtaining it from its iodide yields the pure para isomer.

To explain why the Br atom does not enter at least partly into the meta position relative to the oxonium center we compared the PMR spectrum (100 MHz, acetone) of the borofluoride of crude (II) before crystallization and (III) with the spectra (100 MHz, CF_3COOH) of the 3-bromo- and 3,4-dibromophenyltrimethylammonium iodides specially synthesized by us by quaternization of the corresponding aromatic amines as in [8].

In the aromatic part of the spectra of both ammonium salts a weak resolution of the multiplet of the H^2 atom was observed with centers at 8.44 ppm (monobromo salt) and 8.32 ppm (dibromo salt) and multiplets in the 8.32-7.90 region of H^{4-6} and 8.16-7.74 ppm (H^5 and H^6) with integral intensity ratios of 1:3 and 1:2 respectively.

In the spectrum of (III) the signal of the H^2 atom (an almost unresolved multiplet) is observed at 8.8 ppm and the multiplet for atoms H^5 and H^6 in the 8.33-8.03 ppm range with integral intensity ratio of 1:2. In the spectrum of (II) no signals in a weak field conforming to H^2 of the meta-substituted salt were observed.

Consequently in bromination of the triphenyloxonium cation the first bromine atom enters, just as in nitration [1] almost exclusively in the para position to the oxonium center and the second Br atom in position 3.

In the tris(4-bromophenyl)oxonium cation the Br atom is nevertheless more strongly ortho-para orienting in electrophilic substitution than the oxonium atom 0 and superimposing the electronic effect of both substituents results in the entrance of the second Br atom into the ring being essentially unhindered. For that reason it is difficult to stop the bromination of (I) (in contrast to nitration) at the stage of the tribromo derivative. It should be noted, for example, that an analogous picture is observed in the instance of pbromonitrobenzene which is brominated with formation of 3,4-dibromonitrobenzene under milder conditions than those for nitrobenzene itself [9].

EXPERIMENTAL

<u>Tris(4-bromophenyl)oxonium Borofluoride (II)</u>. To a solution of 0.5 g (1.5 mmoles) of (I) in 15 ml dry Br₂, with addition of 1.7 ml dry MeNO₂ was added in portions over a period of 30 min 1.5 g (7.7 mmoles) of anhydrous AgBF₄. The mixture was stirred 3 h at 20°C, dilute-ed with 100 ml CCl₄, the AgBr filtered off and then washed with CCl₄, water (10-ml portions) and 20 ml acetone. The acetone filtrate was evaporated to a volume of 1-2 ml and 0.5 g of (II) (59%) was precipitated from it by means of excess ether. Mp 182.5-185.5°C (after reprecipitation from MeNO₂, ether). Found: C 37.81; H 2.18%. C₁₈H₁₂Br₃F₄O. Calculated: C 37.87; H 2.10%. PMR spectrum (100 MHz, acetone, δ , ppm): 8.35-7.73 sym. m (4H, H_{arom}, J_{2,3} = 18, J_{2,6} = 9 Hz).

<u>Tris(4-bromophenyl)oxonium Iodide</u>. This was precipitated by addition of NaI to a solution of 0.25 g of (II) in a minimal volume of acetone and reprecipitated from MeNO₂ by ether. Yield 0.17 g (63%), mp 134-137°C. Found: C 36.26; H 2.44%. C₁₈H₁₂BrIO. Calculated: C 36.34; H 2.44%. PMR spectrum (100 MHz, DMSO, δ , ppm): 8.0-8.27 sym. m (4H, Harom, J_{2,3} = 20.8, J_{2,6} = 9.4 J_{2,5} = 3 Hz).

<u>Tris(3,4-dibromophenyl)oxonium Borofluoride (III)</u>. To a solution of 0.5 g (1.5 mmoles) of (I) in 15 ml dry Br_2 with addition of 1.4 ml $MeNO_2$, 4 g (20.5 mmoles) of AgBF₄ was added in portions over the course of 1 h at 20°C, the mixture stirred at 20°C for 3 h more, then the Br_2 evaporated in a stream of air, the residue repeatedly extracted with $MeNO_2$. The

nitromethane extract was filtered to remove AgBr, the filtrate evaporated to a volume of 1-1.5 ml, and 0.88 g (73%) of (IV) precipitated from it by ether. Mp 240-241°C. Found: C 26.66; H 1.31; Br 59.33%. $C_{18}H_{9}BBr_{6}F_{4}O$. Calculated: C 26.77; H 1.12; Br 59.37%. PMR spectrum (60 MHz, DMSO, δ , ppm) 8.8 poorly resolved m (1H, 2-H) 8.33-8.03 m (2H, 5-, 6-H).

Tris(3,4-dibromophenyl)oxonium Chloride. This was precipitated from acetone solution of 0.3 g of (IV) by addition of an alcoholic HCl solution, washed with acetone and ether. Yield 0.2 g (70%), mp 156-158°C. Found: C 28.34; H 1.44%. C18H9Br6ClO. Calculated: C 28.59; H 1.20%.

<u>Tris(3,4-dibromophenyl)oxonium Dichromate.</u> This was precipitated from an acetone solution of 0.1 g of (IV) by addition of $Na_2Cr_2O_7$, washed with water, acetone, ether and reprecipitated from dimethylformamide by ether. Yield 0.07 g (35%). The salt does not have a sharp melting point. It starts to darken at 135°C and does not change up to 300°C. Found: C 26.02; H 1.11%. $C_{36}H_{16}Br_{12}Cr_2O_9$. Calculated: C 26.08; H 1.09%.

 $\frac{\text{Tris}(3,4-\text{dibromophenyl}) \text{ oxonium Chloroplatinate.}}{\text{of 0.1 g of (IV) by addition of a solution of H_2PtCl_6, and washed with water, MeOH and ether. Yield 0.1 g (72%), mp 193-194°C (dec.) Found: C 24.05; H 1.33; Pt 10.90%. C_{36}H_{16}Br_{12}Cl_6O_2Pt. Calculated: C 23.79; H 1.00; Pt 11.16%.}$

<u>3,3',4,4'-Tetrabromophenyl Ether (IV).</u> a) <u>3,3'-Dibromodiphenylether (VI).</u> 3,3'-Diaminodiphenyl ether (12 g)* was dissolved in 60 ml conc. HBr and diazotized with 8.4 g NaNO₂. The transparent solution of the diazocompound was added in portions to a boiling solution of 34.5 g of Cu_2Br_2 in 100 ml of conc. HBr. After the usual work-up 6.71 g (34%) of (VI) was obtained with a bp 146-146.5° (2 mm): $n_D^{2°}$ 1.6322. Found: C 44.00; H 2.61; Br 48.14%. $C_{12}H_8Br_2O$. Calculated: C 43.94; H 2.47; Br 48.72%.

A mixture of 1.64 g of (VI) and 2.5 g dioxane dibromide was maintained at 100°C until the Br₂ color disappeared and the evolution of HBr ceased, then it was poured into 50 ml of cold water. The (IV) which separated was washed with water and ethanol and then dried. Yield 2 g (82%), mp 96.5-97.5°C (from ethanol). Found: C 29.95; H 1.41; Br 64.96%. $C_{12}H_6Br_4O$. Calculated: C 29.68; H 1.25; Br 65.79%. PMR spectrum (60 MHz, CCl₄, δ , ppm): 7.62 d (2H, 5-, 5'-H, J_{5,6} = 9 Hz), 7.32 d (2H, 2-, 2'-H, J_{2,6} = 2.6 Hz), 6.87 m (2H, 6-, 6'-H, J_{6,5} = 9, J_{6,2} = 2.6 Hz).

b) After 0.81 g of (III) was refluxed for 4 h with 15 ml of 20% NaOH, the (IV) which separated on cooling was extracted with ether. Yield 0.49 g ($^{0}100\%$), mp 90-93°C (from ethanol). PMR spectrum (60 MHz, CC14, δ , ppm): 7.54 d (2H, 5-, 5'-H, J_{5,6} = 9 Hz), 7.26 d (2H, 2-, 2'-H, J_{2,6} = 2.6 Hz), 6.80 m (2H, 6-, 6'-H, J_{6,5} = 9, J_{6,2} = 2.6 Hz).

Both (IV) samples have identical PMR spectra, and mixed melting point gave no temperature depression. The water solution remaining after extraction of (IV) was acidified and extracted with ether. By a TLC method by use of a control⁺ (Al₂O₃, 8:2 benzene—ethanol) 3,4-dibromophenol (R_f 0.74) was identified in the ether solution. The R_f of the control was 0.73.

2,2',4,4'-Tetrabromodiphenyl Ether (V). To a solution of 2.66 g 2,2'-dibromodiphenyl ether‡ in 4.5 ml dry Br₂ with 3 ml MeNO₂ and 3 ml CCl₄, 3.32 g of anhydrous AgBF₄ was added gradually over the course of 1 h. The mixture was stirred 3 h more at $\sim 20^{\circ}$, then Br₂ was removed in a stream of air, the residue treated with excess CCl₄ and the AgBr filtered off, the CCl₄ removed, the (V) remaining recrystallized three times from ethanol. Yield 3.4 g (86%), mp 83-84°C (see [7]). PMR spectrum (60 MHz, CCl₄, δ , ppm): 7.83 d (2H, 3-, 3'-H, J_{3,5} = 2.6 Hz, 7.42 m (2H, 5-, 5'-H, J_{5,3} = 2.6 Hz, J_{5,6} = 9 Hz), 6.72 d (2H, 6-, 6'-H, J_{6,5} = 9 Hz). A mixed melting point test of (V) and (IV) (from experiment b) showed a melting range of 57-74°C.

CONCLUSIONS

The triphenyloxonium cation is brominated only in the presence of anhydrous AgBF4 in which the first Br atom enters into each benzene ring almost exclusively in the para position

*Obtained according to the scheme: 3-nitrophenol →3,3'-dinitrophenyl ether [11] →3,3'-diaminodiphenyl ether [12]. †Synthesized according to the scheme: 3-bromoaniline →3,4-dibromoaniline [2] →3,4-dibromophenol [10]. ‡Obtained as in [13]. to the onium center, but the tris(4-bromopheny1)oxonium cation thus formed is readily brominated further under the same conditions with the formation of tris(3,4-dibromopheny1)oxonium borofluoride.

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REACTION OF 2-MERCAPTOPYRIMIDINES WITH SOME

 α, ω -DIHALOALKANES

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It is known that compounds whose structure is a function of the number of methylene groups (n) in α, ω -dihaloalkanes (DHA) and the conditions of the reaction are formed in the reaction of 2-mercapto-(I) and 4,6-dimethyl-2-mercaptopyrimidines (II) with DHA [1-3].

The reaction of the Na salts of (II), (IIIa), and 4,6-diamino-2-mercaptopyrimidine (IIIb) with various DHA in a DMF medium was investigated to determine the effect of the substituents in the pyrimidine ring, the n in the DHA, and the ratio of reagents on the result of alkylation of 2-mercaptopyridines (Table 1).



 $\begin{array}{l} \mathrm{R}^{1} = \mathrm{NH}_{2}, \mathrm{R}^{2} = \mathrm{Me} \ (\mathrm{IIIc}), \ n = 2, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVa}); \\ \mathrm{R}^{1} = \mathrm{NH}_{2}, \mathrm{R}^{2} = \mathrm{Me} \ (\mathrm{IIIc}), \ n = 2, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVa}); \\ n = 3, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVb}); \ n = 3, \ \mathrm{X} = \mathrm{Cl} \ (\mathrm{IVc}); \\ n = 4, \ \mathrm{X} = \mathrm{Cl} \ (\mathrm{IVd}); \ n = 4, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVe}); \\ n = 5, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVf}); \ n = 6, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVe}); \\ n = 7, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVh}); \ n = 8, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVg}); \\ n = 9, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{IVj}); \ \mathrm{R}^{1} = \mathrm{R}^{2} = \mathrm{Me}, \ n = 2, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{Va}); \\ \mathrm{R}^{1} = \mathrm{R}^{2} = \mathrm{Me}, \ n = 3, \ \mathrm{X} = \mathrm{Br} \ (\mathrm{Vb}); \ \mathrm{R}^{1} = \mathrm{R}^{2} = \mathrm{NH}_{2}, \ n = 2, \\ \mathrm{X} = \mathrm{Br} \ (\mathrm{Vc}); \ \mathrm{R}^{1} = \mathrm{R}^{2} = \mathrm{NH}_{2}, \ n = 3, \ \mathrm{X} = \mathrm{Cl} \ (\mathrm{Vd}); \end{array}$

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