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CONVERSIONS OF o-AMINOTRIPHENYLCARBINOL IN THE PRESENCE OF LEWIS ACIDS

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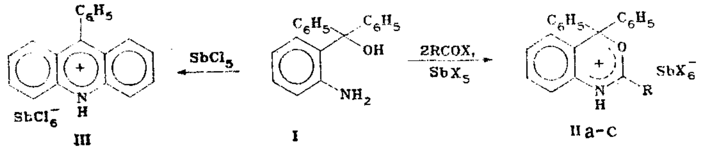
9-Phenylacridinium hexahaloantimonates were produced by the action of antimony pentahalides on o-aminotriphenylcarbinol. The presence of halides of carboxylic acids directs the reaction toward the formation of 4,4-diphenyl-1,2-dihydro-4H-3,1-benzoxazinium hexahaloantimonates.

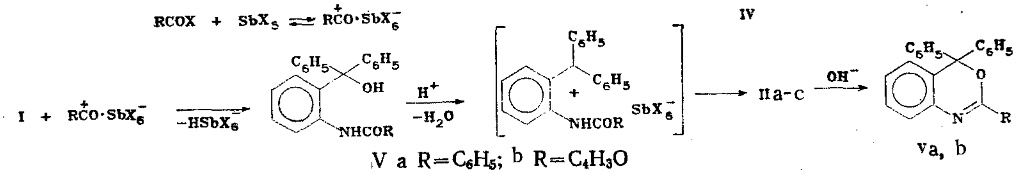
o-Aminotriphenylcarbinol (I) is converted in acylation to 4H-3,1-benzoxazine [1], while in thermal oxidation it forms 9-phenylacridine [2].

We were the first to investigate the heterocyclization of o-aminotriphenylcarbinol in the presence of Lewis acids. It was established that in the action of acid halides and antimony pentahalides on compound I in the cold in a 1:2:1 ratio, 4H-3,1-benzoxazinium hexachloro-(fluoro)antimonates IIa-c are readily formed. In the absence of acylating agents, 9-phenylacridinium hexahaloantimonates (III) are formed under these conditions.



II a $R=C_6H_5$, $X=F$; b $R=C_6H_5$, $X=Cl$; c $R=C_4H_3O$, $X=Cl$

In the presence of an excess of the acid halide, acylation of the amino group and binding of the water liberated during dehydration in acid medium occur first. An equimolar amount of the acid halide is insufficient for the production of the salts IIa-c, since evidently conditions are not created for the acylation of the NH_2 group. For example, at a 2:1 ratio of $SbCl_2$ and PhCOCl, crystals of 9-phenylacridinium III were isolated with a yield of 30%, while the unreacted initial carbinol I was detected in the filtrate by the method of thin-layer chromatography.



V a $R=C_6H_5$; b $R=C_4H_3O$

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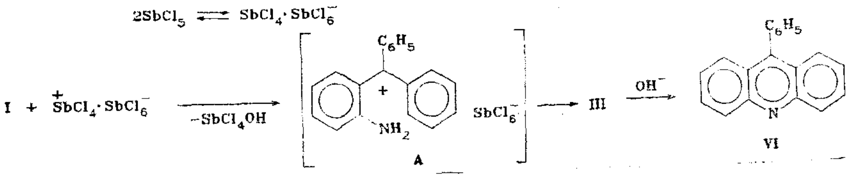
The production of salts IIa-c, occurs through the formation of the corresponding N-acyl derivative. This was confirmed on the example of synthesis of the salt IIb from o-(N-benzoyl)-aminotriphenylcarbinol IV under the action of $SbCl_5$.

The interaction of the carbinol I with antimony pentachloride leads to the production of the salt III along the pathway of formation of the cation A, analogous to that described for o-hydroxytriphenylcarbinol [3].



Thus, the action of $SbCl_5$ on the o-aminocarbinol I with the formation of o-aminotriphenylcarbonium cation A and then the acridinium salt III is the determining factor in comparison with the action of the acylating complex $\text{Ph}\overset{+}{\text{C}}\text{O}\bullet\text{SbCl}_6^-$, leading to benzoxazinium salts IIa-c.

The salts IIa-c and III are stable, colorless crystalline substances, with the exception of the salt III, which has a yellow color. Their structure was established by the method of IR spectroscopy and confirmed by the data of elementary analysis. The IR spectra of compounds IIa-c and III contain absorption bands of quaternized nitrogen in the region of 2735-2720 cm^{-1}, and in the spectra of compounds IIa-c of the $\overset{+}{\text{O}\cdots\text{C}\cdots\text{NH}}$ fragment at 2350, 1660-1650 cm^{-1}.

Another confirmation of the structure of the salts IIa-c and III is the production of the corresponding bases 2,4,4-triphenyl-4H-3,1-benzoxazine (Va), 4,4-diphenyl-2-furyl-4H-3,1-benzoxazine (Vb), and 9-phenylacridine (VI) when they are treated with a 5% KOH solution. The physicochemical constants of the compounds Va and VI correspond to those described in the literature [2, 4], and the structure of the base Vb was demonstrated by the methods of IR and PMR spectroscopy and the data of elementary analysis.

EXPERIMENTAL

The IR spectra were recorded on a Specord-71 IR instrument in liquid petrolatum, the PMR spectra on a Tesla BS-467 instrument (60 MHz) in $CDCl_3$, internal standard TMS. Thin-layer chromatography was carried out in the system benzene-ether (8:2) on Silufol UV-254 plates.

2,4,4-Triphenyl-1,2-dihydro-4H-3,1-benzoxazinium Hexachloroantimonate (IIb). A. To a mixture of 1.5 ml (0.01 mole) of benzoyl chloride in 0.65 ml (5 mmoles) $SbCl_5$ in 10 ml of chloroform, cooled to 0°C, we added with mixing 1.37 g (5 mmoles) o-aminotriphenylcarbinol. The mixture was left for 24 h at room temperature, after which it was precipitated with ether, the precipitate formed filtered off and washed with ether. Yield 2.95 g (80.6%), mp 223-225°C (chloroform, ether). IR spectrum: 1605, 2030 (C=C), 1660, 2350 ($\overset{+}{\text{O}\cdots\text{C}\cdots\text{NH}}$), 2735 cm^{-1} ($\overset{+}{\text{NH}}$). Found: C 44.5; H 2.7; Cl 30.4; N 2.2%. $C_{26}H_{20}Cl_6NOSb$. Calculated: C 44.8; H 2.9; Cl 30.6; N 2.0%.

B. To a suspension of 0.47 g (12 mmoles) o-(N-benzoyl)aminotriphenylcarbinol (IV) in 5 ml of chloroform we added dropwise 0.16 ml (12 mmoles) $SbCl_5$ in 5 ml of chloroform at 0°C. The dissolution of the precipitate and coloration of the solution blue-green were observed. After 5 min the solution was diluted with 30 ml of ether, the precipitate formed filtered off and washed with ether. Yield of compound IV 0.59 g (70%).

2,4,4-Triphenyl-1,2-dihydro-4H-3,1-benzoxazinium Hexafluoroantimonate (IIa). Produced analogously to IIb according to method A. Yield 83%, mp 161-162°C. IR spectrum: 1602, 3030 (C=C), 1650, 2315 ($\overset{+}{\text{O}\cdots\text{C}\cdots\text{NH}}$), 2720 cm^{-1} ($\overset{+}{\text{NH}}$). Found: C 52.4; H 3.4; N 2.4%. $C_{26}H_{20}F_6NOSb$. Calculated: C 52.3; H 3.3; N 2.3%.

4,4-Diphenyl-2-furyl-1,2-dihydro-4H-3,1-benzoxazinium Hexachloroantimonate (IIc). To a solution of 1.37 g (5 mmoles) of the carbinol I cooled to 0°C, in 10 ml of chloroform, 0.96 ml (0.01 mole) of pyromucic acid and 0.65 ml (5 mmoles) $SbCl_5$ in 5 ml of chloroform were added with mixing. The precipitate formed after addition of the acid chloride gradually disappeared, and the mixture was exposed at room temperature for 1 h. After this 40 ml of ether was added, and the precipitate formed was filtered off and washed with ether. Yield of the salt IIc, 1.82 g (57%), mp 200-202°C. IR spectrum: 1020, 1615, 3030, 3110 (C=C), 1650, 2350 $\overset{\cdots\cdots\cdots}{(O{-}\overset{+}{C}{-}NH)}$, 2730 cm^{-1} $(\overset{+}{N}H)$. Found: C 37.3; H 2.7; Cl 33.5; N 2.0%. $C_{24}H_{18}Cl_6NO_2Sb$. Calculated: C 37.6; H 2.8; Cl 33.3; N 2.2%.

9-Phenylacridinium Hexachloroantimonate (III). We mixed 1.37 g (5 mmoles) of the carbinol I and 1.3 ml (1 mmole) $SbCl_5$ in 10 ml of chloroform with cooling to 0°C and left the mixture for 24 h at room temperature. The salt III was precipitated with ether, filtered off, and washed with ether. Yield 1.77 g (60%), mp 222-224°C (chloroform, ether). IR spectrum: 1610, 3030 (C=C), 1660, 2550, 2735 cm^{-1} $(\overset{+}{N}H)$. Found: C 38.4; H 2.3; Cl 35.9; N 2.4%. $C_{19}H_{14}Cl_6NSb$. Calculated: C 38.6; H 2.4; Cl 36.1; N 2.3%.

4,4-Diphenyl-2-furyl-4H-3,1-benzoxazine (Vb). A mixture of 1 g (6 mmoles) of the salt IIc and 10 ml of a 5% solution of KOH was boiled for 1 h, cooled, and the organic portion extracted three times with 10 ml of chloroform, the extract removed, and dried with anhydrous Na_2SO_4. The solvent was distilled off, and the crystals obtained were recrystallized from benzene. Yield 0.32 g (75%), mp 224-226°C. R_f 0.71. IR spectrum: 1020, 1600, 3030, 3110 (C=C), 1630 cm^{-1} (C=N). PMR spectrum ($CDCl_3$): 6.45-7.53 ppm (m, 17H, aromatic and furan protons). Found: C 82.7; H 4.9; N 3.6%. $C_{24}H_{17}NO_2$. Calculated: C 82.1; H 4.8; N 3.9%. The bases Va and VI were produced analogously.

o-(N-Benzoyl)aminotriphenylcarbinol (IV). To a solution of 1.37 g (5 mmoles) of the carbinol I in 10 ml of chloroform, 1.15 ml (0.01 mole) benzoyl chloride was added with cooling to 0°C and mixing; the precipitated hydrochloride IV was filtered off and washed with ether, and then boiled in 10 ml of a 5% solution of KOH for 30 min. The precipitate was filtered off and washed with water. Yield 1.61 g (85%), mp 233-234°C; R_f 0.15. IR spectrum: 1610, 3030 (C=C), 1675 cm^{-1} (C=O). Found: C 82.4; H 5.5; N 3.7%. $C_{26}H_{21}NO_2$. Calculated: C 81.9; H 5.4; N 3.5%.

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