SYNTHESES BASED ON β-PHENYLETHYLAMINES

VI. SYNTHESIS AND MASS-SPECTROMETRIC PROPERTIES OF BIS-β-PHENYLETHYLBENZYLAMINES AND THE PRODUCTS OF THEIR METHYLATION

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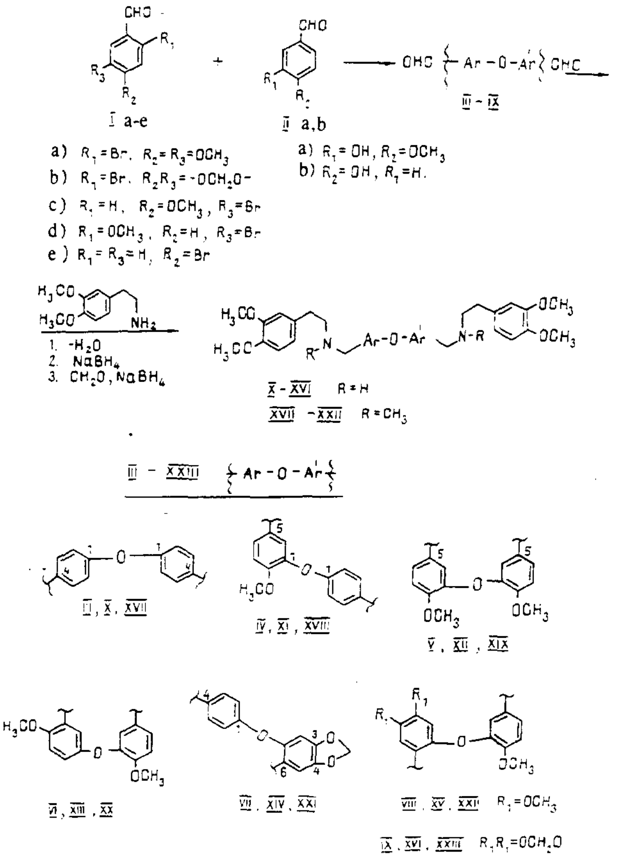
Fourteen previously undescribed bases of the bis-β-phenylethylbenzylamine series with a central diphenyl ether group differing by the relative positions of the oxygen bridge and the β-phenylethylbenzylamine substituent have been synthesized. The main directions of the fragmentationof these compounds under electron impact are competing single or successive processes of cleavage of the benzyl bonds, accompanied by the structure-dependent transfer of hydrogen atoms.

Interest in natural and synthetic derivatives of β-phenylethylamine is due to the broad spectrum of their biological activity [1] and the possibility of their use as intermediates for the synthesis of cyclic structures of the isoquinoline type [2]. Information obtained on the activity of compounds of the phenylalkylamine series [3] has induced us to expand the search in this direction and to obtain a series of dimeric phenylalkylamines with a central diphenyl ether group differing by the positions of the substituents and of the ether bridge in the diohenyl oxide part of the molecule.



Scheme 1

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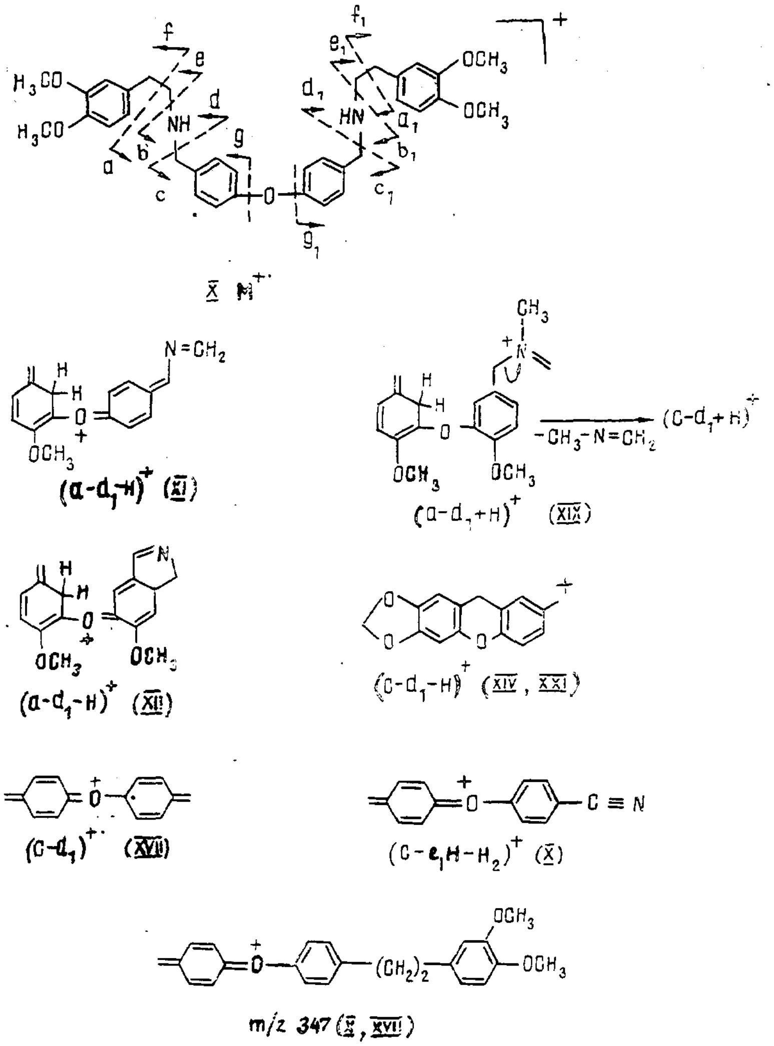
For this purpose, the bromo- and hydroxy-substituted benzaldehyees (I) and (II) were converted by mens of the Ullman reaction into the diformyldiphenyl ethers (II-IX) containing the oxygen bridge in the *para-para, para-meta, para-ortho, meta-meta* and *ortho-meta* positions with respect to the aldehyde groups. The condensation of the diphenyl ethers (III-IX) with homoveratrylamine, followed by reduction of the resulting imines gave the amines (X-XVI), the methylation of which formed the tertiary amines (XVII-XXIII) (scheme 1). The structures of the intermediates (III-IX) and of the products (X-XXIII) were shown with the aid of PMR and mass spectra (see the Experimental part).

The features of the fragmentation of bis-β-phenylethylbenzylamine derivatives of types (X-XXIII) under EI have not been studied previously and are of independent interest since their molecules combine the well-known properties of phenylethylamine derivatives and the little-studied characteristics of substituted diphenyl ethers with monotypical substituents in in various positions relative to the ether bridge and with additional OMe groups.

A study of the mass spectra of compounds (X-XIV) and (XVII-XXI) showed that their fragmentation took place in the manner of competition between the cleavages of the two pairs of benzyl bonds in which a considerable influence on the redistribution of the contributions of the various processes to the total ion current is exerted not only by the change in the nature and the mutual positions of the substituents of the diphenyl oxide moiety but also by the replacement of the NH groups of compounds (X-XIV) by $N-CH_3$ groups (compounds (XVII-XXI)). Particular interest is aroused by observations on the nature and features of the sequence of the breakdown of the two analogous β-phenylethybenzylamine groupings.



Scheme 2

TABLE 1. Mass Numbers (m/z), Letter Designations, Elementary Compositions, and Relative Intensities (%) of the Key Ions in the Spectra of Compounds (X-XIV) and (XVII-XXI)

X 556($M^{+\bullet}$, 0,2), 405[$a^+(a_1^+)^*$, $C_{25}H_{29}N_2O_3$, 24], 403 [(a—H_2)+, 5], 376(c+, $C_{24}H_{26}NO_3$, 43), 374 [(c—H_2)+, 18], 347 ($C_{23}H_{23}O_3$, 3), 237($C_{15}H_{13}N_2O$, 13), 224 [(a—$d_1)^{+\bullet}$[(a_1—d$)^{+\bullet *}$, 10], 208 [(c—e_1H—H_2)+, $C_{14}H_{10}NO$, 100], 196 [(c—$d_1)^{+\bullet}$, 22], 165 (e^+,5), 152 [$(f+H)^{+\bullet}$, $C_9H_{12}O_2$, 56], 151 (f^+, 26), 107 [(c—g_1+H$)^+$, 10]

XI 586 ($M^{+\bullet}$, 0,2), 435 (a^+, $C_{26}H_{31}N_2O_4$, 68), 433 [(a—$H_2)^+$, 26], 406 (c^+, $C_{25}H_{28}NO_4$, 17), 404 [(c—$H_2)^+$, 10] 254 [(a—d_1—H$)^+$, $C_{16}H_{16}NO_2$, 100] 243 ($C_{15}H_{15}O_3$, 16) ,238 [(c—e_1H—$H_2)^+$, 4], 227 [(c—d_1+H)+, $C_{15}H_{15}O_2$, 29], 226 [(c—d_1)+•, 12], 211 ($C_{14}H_{11}O_2$, 15),192(6), 181 (d+H)+•, 2], 165 (e+, 7), 152 [(f+H)+•, 20], 151 (f+, $C_9H_{11}O_2$, 21), 137 [(c—gl+H)+, 5]

XII 616 ($M^{+\bullet}$, 0.1), 465 (a^+, $C_{27}H_{33}N_2O_5$, 38), 463 [(a—$H_2)^+$, 10], 451 ($в^+$, 1), 436 (c^+, 4), 434 [(c—H_2)+, $C_{26}H_{28}NO_5$, 6], 284 [(a—d_1—H)+, $C_{17}H_{18}NO_3$, 88], 257 [(c—d_1+H)+, $C_{16}H_{17}O_3$, 9], 241 ($C_{15}H_{13}O_3$, 10), 166 ($C_9H_{12}NO_2$, 19), 165 (e^+, 4), 152 [$(f+H)^{+\bullet}$, $C_9H_{12}O_2$, 31], 151(f^+, 19), 137 [(c—g_1+H$)^+$, $C_8H_9O_2$, 100], 128(12)

XIII 616 ($M^{+\bullet}$, 0.2), 465 (a^+, $C_{27}H_{33}N_2O_5$, 63), 463 [(a—$H_2)^+$, 25], 449 [(в—H_2)+, 1], 436 (c^+, 8), 434 [(c—H_2)+, $C_{26}H_{28}NO_5$, 12], 284 [(a—d_1—H$)^+$, $C_{17}H_{18}NO_3$, 100], 257 [(c—d_1+H)+, $C_{16}H_{17}O_3$, 16], 243 (4), 241 ($C_{15}H_{13}O_3$, 7), 165 (e^+, 6), 164 [$(e—H)^{+\bullet}$, 3], 152 [$(f+H)^{+\bullet}$, 11], 151 (f^+, $C_9H_{11}O_2$, 17), 137 [(c_1—g+H)+, 9]

XIV 600($M^{+\bullet}$,0.4), 449 (a^+, $C_{26}H_{29}N_2O_5$, 54), 447 [(a-$H_2)^+$,26], 435 ($в^+$,3), 433 [(в-$H_2)^+$, 3], 420 (c^+, $C_{25}H_{26}NO_5$, 18), 418 [(c-$H_2)^+$, 18], 329 [(M-g_1-H$)^{+\bullet}$,4], 297 ($C_{17}H_{17}N_2O_3$, 3), 297 ($C_{18}H_{21}N_2O_2$; 12), 286 ($C_{16}H_{16}NO_4$; 16), 285 (15), 268 [a-d_1-H$)^+$, $C_{16}H_{14}NO_3$, 42), 257 ($C_{15}H_{13}O_4$, 54), 241 [(c-d_1+H$)^+$, $C_{15}H_{13}O_3$, 38], 240 [(c-$d_1)^{+\bullet}$, 8], 239 [(c-d_1-H$)^+$, $C_{15}H_{11}O_3$, 100], 227 (48), 197 (18), 194 ($C_{11}H_{16}NO_2$, 12), 165 (e^+, 42), 152 [$(f+H)^{+\bullet}$, 53], 151 (f^+, 65), 137 (23), 107 [(c_1-g+H$)^+$, 33]

XVII 584 ($M^{+\bullet}$, 0,3), 433 (a+, $C_{27}H_{33}N_2O_3$, 63), 431 [(a-$H_2)^+$, 2], 419 ($в^+$, $C_{26}H_{31}N_2O_3$, 2), 390 (c^+, $C_{25}H_{28}NO_3$, 73); 388 [(c-$H_2)^+$, 6], 347 ($C_{23}H_{23}O_3$, 63), 297 ($C_{19}H_{25}N_2O$, 6), 254 ($C_{17}H_{20}NO$, 23), 240 [(a-d_1+H$)^+$ 23], 239 [$(a-d)^{+\bullet}$, $C_{16}H_{17}NO$, 19], 196 [(c-$d_1)^{+\bullet}$, $C_{14}H_{12}O$, 100], 194 (d^+, 3), 165 (e^+, 4), 164 [$(e-H)^{+\bullet}$, 4], 152 [$(f+H)^{+\bullet}$, 15], 151 (f+, 19)

XVIII 614 ($M^{+\bullet}$, 0.4), 463 (a^+, $C_{28}H_{35}N_2O_4$, 79), 449 ($в^+$, 2), 420 (c^+, $C_{26}H_{30}NO_4$, 95), 418 [(c-$H_2)^+$, 6], 377 ($C_{24}H_{27}NO_3$, 9), 299 (3), 270 [(a-d_1+H$)^+$, $C_{17}H_{20}NO_2$, 9], 269 [(a-$d_1)^{+\bullet}$, 4], 256 ($C_{16}H_{18}NO_2$, 8), 254 ($C_{16}H_{16}NO_2$, 6), 253 ($C_{17}H_{17}O_2$, 7), 243 ($C_{15}H_{15}O_3$, 8), 241 ($C_{15}H_{13}O_3$, 13), 227 [(c-d_1+H$)^+$, $C_{15}H_{15}O_2$, 56],

226 [(c-$d_1)^{+\bullet}$, 55], 211 ($C_{14}H_{11}O_2$, 32), 194 (d^+, 21), 165 (e^+, 9), 164 [$(e-H)^{+\bullet}$, 6], 152 [$(f+H)^{+\bullet}$, 10], 151 (f^+, $C_9H_{11}O_2$, 100), 121 (8)

XIX 644 ($M^{+\bullet}$, 0.1), 495 [$(a+H_2)^+$, 5], 493 (a^+,$C_{29}H_{37}N_2O_5$, 82), 479 ($в^+$, 2), 478 [(в-H$)^{+\bullet}$, 2], 452 [$(c+H_2)^+$, 5], 450 (c^+, 86), 448 [(c-$H_2)^+$, 4], 316 (15), 300 (a-d_1+H$)^+$, 15], 286 [(c-e_1+H$)^+$, $C_{17}H_{20}NO_3$, 7], 284 [(c-e_1-H$)^+$, 7], 273 (53), 271 (15), 257 [(c-d_1+H$)^+$, $C_{15}H_{15}O_3$, 100], 256 [(c-$d_1)^{+\bullet}$, 18], 243 (16), 241 (40), 193 [$(d-H)^{+\bullet}$, 6], 192 [(d-$H_2)^+$, 6], 165 (e^+, 14), 164 [$(e-H)^{+\bullet}$, 13], 152 [$(f+H)^{+\bullet}$, 33], 151 (f^+, 40), 137 [(c-g_1+H$)^+$, 24], 128 (51)

TABLE 1. (Continued)

XX	644 ($M^{+\bullet}$, 0.2), 493 (a^+, $C_{29}H_{37}N_2O_5$, 36), 479 (в$^+$, 1), 450 (c^+, $C_{27}H_{32}NO_5$, 15), 448 [$(c-H_2)^+$, 3], 300 ($a-d_1+H$), 5], 286 [$(c-e_1+H)^+$, 2], 284 [$(c-e_1-H)^+$, 3], 257 $(c-d_1+H)^+$, $C_{16}H_{17}O_3$, 32], 243 (3), 241 (4), 224 ($C_{12}H_{18}NO_3$, 9], 194 (d^+, 7), 193 [$(d-H)^{+\bullet}$, $C_{11}H_{15}NO_2$, 6], 192 [$(d-H_2)^+$, 6], 180 ($C_{10}H_{14}NO_2$, 68), 178 (11), 167 ($C_9H_{11}O_3$, 12), 165 (e^+, 13), 164 [$(e-H)^{+\bullet}$, 13], 152 [$(f+H)^{+\bullet}$, 32], 151 (f^+ 50), 137 [$(c-g_1+H)^+$, $C_8H_9O_2$, 100], 128 (12)
XXI	628 ($M^{+\bullet}$, 0.2), 477 (a^+, $C_{28}H_{33}N_2O_5$, 29), 475 [$(a-H_2)^+$, 2], 463 (в$^+$, 4), 434 (c^+, $C_{26}H_{28}NO_5$, 33), 432 [$(c-H_2)^+$, 4], 343 [$(M-g_1-H)^{+\bullet}$, $C_{19}H_{21}NO_5$, 5], 314 ($C_{18}H_{20}NO_4$, 9), 284 [$(a-d_1+H)^+$, $C_{17}H_{18}NO_3$, 16], 271 ($C_{16}H_{15}O_4$, 23), 241 [$(c-d_1+H)^+$, $C_{15}H_{13}O_3$, 55], 240 [$(c-d_1)^{+\bullet}$, 12], 239 [$(c-d_1-H)^+$, $C_{15}H_{11}O_3$, 100], 193 [$(d-H)^{+\bullet}$, 11], 192 [$(d-H_2)^+$, 10], 165 (e^+, 19), 152 [$(f+H)^{+\bullet}$, 28], 151 (f^+, 29), 121 (18)

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*In other cases an alternative variant of the ion has been omitted from the table.

In the formula of compound (X), the dotted lines show the most characteristic cleavages, while the letters reflect the origins of the charged and the neutral fragments (scheme 2). Table 1 gives the mass numbers and relative intensities of the most important peaks in the spectra of compounds (X-XIV) and (XVII-XXI) and the elementary compositions of the key fragments denoted by letters. Tables 2 and 3 give the results obtained from metastable defocussing (MD) and linked scanning (B/E = const.) spectra.

In the spectra of all the compounds the peaks of the molecular ions were weak (0.1-0.4%). All the spectra contained the peaks of the ions $(M - H)^+$ and $(M - 2H)^{+\cdot}$ with intensities 2-3 times greater than that of the M^+ ion; in addition, the spectra of derivatives (X-XIV) contained the peaks of the $(M - H_2 - H)^+$ and $(M - 2H_2)^{+\cdot}$ ions. The dehydrogenation of the molecular ions took place through the ethylamine groupings and led to the formation of fragments with long conjugated chains. Process in which the $(M - H)^+$ and $(M - H_2)^{+\cdot}$ ions are formed by the ejection of protons from the diphenyl ether moieties of the molecules under consideration are not excluded. High selectivity of fragmentation was characteristic of the compounds investigated: usually about 80% of the ion current was due to 7-8 key fragments.

Processes leading to the more profound decomposition of the $M^{+\cdot}$ ions of compound (X-XIV) and (XVII-XXI) took place with the cleavage of one or two propylamino units. The first category of fragmentation reactions took place along the lines $a(a_1) \leftrightarrow f(f_1)$ and $c(c_1) \leftrightarrow d(d_1)$ and was typical for all the compounds (scheme 2). Since the substituted diphenyl ether fragments in the molecules of (XI-XIV) and (XVIII-XXI) are unsymmetrical, the splitting out of identical neutral parts of the dimethoxyphenylethylamino grouping from different ends of the molecule forms the isomeric ions a^+ and $a_1{}^+$, c^+ and $c_1{}^+$.

For all the compounds,the peaks of the $a^+(a_1{}^+)^*$ ions had heights of the same order (see Table 1) and in each case were one of the key diagnostic ions. The spectra of the N$-$H derivatives (X-XIV) contained the peaks of the $(a - H_2)^{+*}$ ions, the parents of which were the above-mentioned products of the dehydrogenation of the $M^{+\cdot}$ ions. In the spectra of the $N-CH_3$ derivatives, (XVII-XXI) the corresponding peaks were weak; i.e., the hydrogen atoms of the N$-$H groups participated in the dehydrogenation processes.

The peaks of the benzyl cations f^+ with mz 151 were of medium or high intensity. Except for (XVIII), the peaks of the dimethoxymethylenecyclohexadiene ions $(f + H)^{+\cdot}$ with m/z 152 had comparable heights.

Bond cleavages along the line c$\rightarrow$d led preferentially to charged fragments of the c^+ series with variable peak heights, greater for the $N-CH_3$ derivatives. They were also accompanied by the $(c - H_2)^+$ ions formed as the result of the preliminary dehydrogenation of the alternative phenylethylamine chain. These ions were, conversely, stronger for the NH derivatives. The

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*Here and below, the presence of isomeric ions, especially $(a_1 - H_2)^+$ is understood.

TABLE 2. Mass Numbers (m/z) and Relative Intensities (%) of the Parental Ions, Calculated from the MD Spectra of the Daughter Ions

Compound	Daughter ion	Parental ions
X	376	405 (100)
	347	376 (100)
	208	237 (100)
	196	405 (8), 376 (100), 237 (7), 224 (57)
	152	347 (100)
XI	435	586 (100)
	406	586 (2), 435 (100)
	254	433 (100), 406 (19)
	227	435 (10), 406 (100), 254 (49)
	211	435 (9), 406 (16), 254 (54), 226 (100)
XII	465	616 (100)
	436	616 (4), 465 (100)
	434	616 (3), 463 (100)
	284	463 (100)
	257	436 (42), 284 (100)
	241	284 (100), 256 (23)
	137	166 (100), 152 (32)
XIV	420	600 (2), 449 (100)
	297	449 (100)
	268	418 (100), 297 (8)
	257	329 (6), 285 (100)
	241	449 (10), 420 (58), 268 (100)
	239	433 (100), 418 (6), 268 (64)
	227	420 (80), 268 (11), 257 (100)
	194	449 (12), 420 (100)
XVII	390	433 (100)
	347	433 (1), 390 (100)
	254	390 (100), 297 (90)
	240	390 (100)
	239	433 (10), 390 (100)
	196	433 (7), 390 (13), 254 (21), 239 (100)
	151	347 (100)
XVIII	420	614 (1), 463 (100)
	377	463 (5), 420 (100)
	270	463 (100), 420 (15), 377 (77)
	256	449 (15), 420 (20), 377 (100), 299 (38)
	253	420 (3), 377 (100)
	243	286 (100)
	241	420 (100), 377 (83)
	227	420 (100), 270 (28)

TABLE 2. (Continued)

Compound	Daughter ion	Parental ions
	226	463 (36), 420 (30), 270 (100)
	211	253 (5), 241 (4), 226 (100)
	151	194 (100)
XIX	450	644 (1), 493 (100)
	286	450 (100)
	257	493 (10), 450 (100), 300 (52), 286 (15)
	243	286 (100)
	151	194 (100), 166 (20)
	137	180 (100), 168 (35), 152 (45)
XXI	284	477 (100), 434 (54)
	271	477 (80), 314 (100)
	241	434 (100), 284 (68)
	239	477 (5), 434 (100), 284 (10)

TABLE 3. Mass Numbers (m/z) and Relative Intensities (%) of the Daughter Ions, Calculated from the B/E = const. Spectra of the Parental Ions

Compound	Parental ion	Daughter ions
X	556	405 (86), 403 (100), 376 (30), 374 (80)
	405	376 (100)
	376	347 (100), 208 (24), 196 (10)
	237	208 (100)
XII	465	436 (100)
	463	434 (100), 284 (80)
	284	257 (39), 241 (100), 137 (9)
XIV	449	420 (100), 297 (10)
	447	268 (100)
	420	329 (11), 268 (18), 239 (100)
	297	268 (30), 165 (100)
	286	268 (28), 257 (100)
	257	239 (45), 227 (100)
XVII	584	433 (100), 390 (15)
	433	390 (100)
	390	347 (100)
XVIII	614	463 (100), 420 (15)
	463	420 (100)
	377	253 (100), 241 (50), 239 (25), 226 (11)
	270	227 (100)
	256	227 (100), 211 (24)
	241	226 (100), 211 (80)

TABLE 3. (Continued)

Compound	Parental ion	Daughter ions
XIX	493	450 (100), 300 (11)
	450	257 (100)
	286	257 (12), 243 (100)
	180	137 (100)
XX	644	493 (100), 450 (35), 448 (47)
	493	450 (100), 300 (25), 257 (18)
	450	257 (100)
	286	241 (100)
	180	151 (23), 137 (100)

parents ions of the c^+ $[(c - H_2)^+]$ ions were not only the $M^{+\cdot}$ $[M - H_2)^{+\cdot}]$ ions but, as follows from the MD and B/E spectra, the a^+ $[(a - H_2)^+]$ ions, eliminating a $CH_2{=}NH$ molecule (X-XIV) or a $CH_2{=}NCH_3$ molecule (XVII-XXI) (see Tables 2 and 3).

In the case of the N–H derivatives, the fragments of the d^+ type were unstable. In the spectra of the compounds with $N-CH_3$ groups the d^+ ions were recorded in the form of peaks of medium intensity, and they acted as some of the precursors of the f^+ ions (see Table 2).

Cleavages on the line $b \leftrightarrow e$ are not characteristic for the compounds under consideration. Weak peaks of the b^+ ions were present in the spectra of (XII), (XIV), (XVII), (XVIII), (XX), and (XXI). The peaks of the e^+ ions with m/z 165 were weak in the spectra of (X-XIV), but in the N-CH_3 derivatives their intensities were greater.

The most stable cations in the spectra of (X-XIV) and (XVII-XXI) arose as the result of processes involving the cleavage of two bonds in the main chain of the molecule. In many cases, the origin of these ions was specific and could be explained by the particular relative positions of the substituents in the diphenyl ether moiety of the molecule, but it also depended on the nature of the nitrogen atom. A relatively more common feature of he spectra of the NH derivatives was the formation of the $(a - d_1 - H)^+$ ions, the peaks of these ions being the maximum peaks (XI, XIII) or very strong (XII) in the spectra of compounds in the molecule of which at least one of the phenylethylaminobenzyl substituents occupied the *meta*-position in relation to the ether bridge. This permits the conclusion that the ions under consideration included a methylenecyclohexadiene fragment, the formation of which is preferential in the case of the *m*- derivatives [4]. The precursors of the $(a - d_1 - H)^+$ ions were the $(a - H_2)^+$ ions (see Tables 2 and 3). The structures of the corresponding ions should differ for compounds (XII and XII) and for compound (XI) (see scheme 2). There is also the medium-intensity peak of an ion with an analogous nature in the spectrum of compound (XIV).

The presence of $N-CH_3$ groups in compounds (XVII-XXI) did not prevent the appearance of of a methylenecyclohexadiene fragment but suppressed the dehydrogenation of the chain, and, therefore, in these spectra the peaks of ions $(a + H - d_1)^+$ of low or medium intensity appeared (see scheme 2). Analysis of the MD spectra of the ions $(a + H - d_1)^+$ and $(a - d_1 - H)^+$ showed that their precursors were not only the a^+ ions but also the c^+ ions. It follows from this that these daughter ions could have been formed as the result of alternative processes — $(c - f_1 - H)^+$ and $(c - f_1 + H)^+$, leading to fragments of the same composition.

The most characteristic two-stage process in the fragmentation of the $N-CH_3$ derivatives was the formation of the nitrogen-free fragments $(c - d_1)^{+\cdot}$ or $(c - d_1 + H)^+$. Judging from the MD spectra, they were formed not only in two stages — $M^{+\cdot} \rightarrow c^+ \rightarrow (c\text{-}d_1 + H)^+$ — but also in three stages in the following sequence: $M^{+\cdot} \rightarrow a^+ \rightarrow (a\text{-}d_1 + H)^+ \rightarrow (c\text{-}d_1 + H)^+$. The latter process probably prevailed over the other pathways for the formation of the $(c - d_1 + H)^+$, since their precursors $(a - d_1 + H)^+$ were not common in the spectra of (XVII-XXI). At the same time, for compounds with different types of substitution of the diphenyl ether moiety there were individual features of the formation of ions of the type under consideration. Thus, the di-*para*-substituted compound (XVII) gave the resonance-stabilized odd-electron fragment $(c - d_1)^{+\cdot}$ with m/z 196 and the peak of 100% intensity (see scheme 2).

Bases (XIX) and (XX), in which the side chain and the ether bridge are in the *meta*- relationship, formed predominantly the the even-electron fragments $c - d_1 + H)^+$, including methylenecyclohexadiene and benzyl fragments. These ions arose, in particular, through the splitting out of a $CH_3-N=CH_2$ molecule from the $(a - d_1 + H)+$ ions (see scheme 2). It must be mentioned that compound (XVIII), in which these substituents are present in the *meta-* and *para-* positions to one another give the peaks of $(c - d_1)^{+\cdot}$ and $(c - d_1 + H)^+$ ions of equal intensity.

In this respect, a special position is occupied by base (XXI), in the spectrum of which, in addition to the aovementioned ions there was the 100% peak of the $(c - d_1 - H)^+$ ion with m/z 239. We explain this fact by the existence of *ortho-* substitution, which makes possible the formation of the tricyclic system of xanthene by the splitting out of a hydrogen atom from the *ortho-* position of the second phenyl nucleus (scheme 2). Incidentally, this is the only case where N–H and $N-CH_3$ derivatives (XIV and (XXI) form abundant fragments of the same structure. We may mention that there were also dibenzyl ether fragments of the type under consideration in the spectra of all the N–H derivatives and, although the intensities of their peaks (apart from (XIV) were less than for the $N-CH_3$ derivatives, their dependence on the mutual positions of the phenylethylbenzylamine chain and the ether bridge was the same as for compounds (XVII-XXI).

Thus, we have studied the general properties of bases (X-XIV) and (XVII-XXI). We shall now pass to the characteristics of individual features of the spectra of the compounds.

In the mass spectrum of base (X) the maximum peak was that of an ion with m/z 208 ($C_{14}H_{10}NO$, Table 1). The precursors of this ion were ions with m/z 376 (c^+) and m/z 237 (Tables 2 and 3). In the first case, in the c^+ ion bond cleavage took place along the line $b_1 \leftrightarrow e_1$ with the migration of three hydrogen atoms to the fragment split out, and in the second case a $CH_2=NH$ molcule is split out from the ion with m/z 237 ($C_{15}H_{13}N_2O$). The preferential nature of the formation of the $(c - e_1H - H_2)^+$ ion in the case of base (X) is explained by two factors: the possibility of the dehydrogenation of the $-CH_2-NH-CH_2-$ chain, and the *para-* position of the phenylethylbenzylamine substituents with respect to the ether bridge (scheme 2).

An unusual direction of fragmentation was observed in the spectra of compounds (X) and (XVII), which contained the peaks of ions with m/z 347 ($C_{23}H_{23}O_3$; (X) — 3%, (XVII) — 63%) (Table 1). In the corresponding MD spectra the maximum peak was that of the transition $c^+ \rightarrow 347^+$. This process took place through through the elimination of part of the linear chain in the form of $CH_2=NH$ (X) and $CH_2=N-CH_3$ (XVII), its contribution in the second case being greater, in agreement with Hammond's postulate [5]. The quinoid structure of the ions formed explains why the process under consideration was not realized for the other compounds. We may emphasize that the struture given for the m/z 347 ion is not the only one. In particular, it does not explain the transition of this even-electron fragment into an odd-electron one with m/z 152 (Table 2), which is feasible only if the ionization potential of the neutral fragment is higher than that of the ion $[H_3C-C_6H_4(OCH_3)_2]^+$ [6]. This condition was realized through a multistage mechanism, which we do not give.

The spectra of compounds (XII) and (XIII) each contained the peak of an ion with m/z 241 ($C_{15}H_{13}O_3$) in the MD spectrum of which the maximum peak was that of the transition $284^+ \rightarrow 241^+$ The formation of this daughter ion from the $(a - d_1 - H)^+$ ions shows the possibility of the splitting out of a C_2H_5N particle by cleavage of a bond adjacent to a six-membered ring.

Among the fragmentary ions from compounds (XIV) and (XXI) there were $(M - g_1 - H)^{+\cdot}$ ions of medium intensity (Table 1) the formation of which took place with migration of the benzyl H atom to a carbon atom of the ether bond being cleaved [7]. In the case of (XIV), the precursors of these ions were the c^+ ions, and in the case of (XXI) the a^+ ions. The further breakdown of the $(M - g_1 - H)^{+\cdot}$ ions, leading to the formation of fairly widespread fragments can be traced from the spectra of metastable ions:

$$\text{XIV } (M\text{-}g_1\text{-}H)^{+\bullet} \xrightarrow[-CH_3-CO\ (CHO)]{} 286^+\ (285^+) \xrightarrow[-CH_2=NH\ (CH_2=N)]{} 257^+ \xrightarrow[-CH_2O]{} 227^+. \quad \text{XXI } (M\text{-}g_1\text{-}H)^{+\bullet} \xrightarrow[-CHO]{} 314^+ \xrightarrow[-CH_2=N-CH_3]{} 271^+.$$

The spectrum of compound (XVII) contained the peak of an ion with m/z 254 ($C_{17}H_{20}ON$) formed either from c^+ ions (m/z 390) with the ejection of a 136 a.m.u. ($C_8H_8O_2$) fragment or from m/z 297 ions with the elimination of a C_2H_5N particle (Tables 1-3).

In the spectrum of base (XVIII) attention is attracted by, in addition to those already mentioned, the peaks of ions with m/z 377, 256, 254, 253, and 241. The m/z 377 ions arose through the successive elimination of $CH_3 + CO$ from the c^+ ions (m/z 420) and were parental in relation to the ions with m/z 253 and 241; however, the mechanism of the appearance of the latter is indeterminate. The ions with m/z 256 and 254 were formed by a combination of processes of cleavage along the lines $a \leftrightarrow f$ and $c_1 \leftrightarrow d_1$.

Thus, on analyzing the spectra of compounds (X-XIV) and (XVII)-(XXI) we find the existence of a whole series of competing fragmentation reactions. In a number of cases it is impossible to take into account all the structural factors affecting the contribution of a particular process of breakdown. Thus, we have scarcely considered the influence of the oxygen-containing substituents of the diphenyl oxide fragment (MeO— and $-OCH_2O-$). Nevertheless, in a number of cases the presence of these groups caused the appearance of intense peaks in the spectra. In the spectra of bases (XII) and (XX) the 100% peaks were those of ions with m/z 137 having the composition $C_8H_9O_2$ $(c - g_1 + H)^+$. There is no doubt that an important role in the increase in their contribution was played by the possibility of migration of the hydrogen of the *ortho*-methoxy group to the bridge oxygen atom. However, it is not in all cases that the presence of such a structural element leads to the appearance of a high-intensity m/z 137 ion or an analogue of it.

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EXPERIMENTAL

MKh 1310 mass spectrometer, direct insertion of the sample, chamber temperature 150-170°C, temperature of the heater bulb 100-140°C, ionizing voltage 70 V, collector current 60 μA. For the conditions of recording the MD spectra, see [8] and for the B/E = const. spectra, see [9].

6-Nitroveratraldehyde was obtained by the method of [9], yield 84%, mp 129-131°C (from ethanol).

p-Bromobenzaldehyde was synthesized by the method of [10] from *para*-bromoaniline, yield 40%, mp 57-58°C (from ethanol).

6-Bromoveratraldehyde (Ia). With stirring, 0.3 ml (0.006 mole) of bromine in 2 ml of acetic acid was added to a solution of 1 g (0.006 mole) of veratraldehyde in 15 ml of acetic acid. The mixture was stirred for a further 20 h at room temperature, and was then poured into 100 ml of water with ice, and the resulting mixture was left for 12 h. The precipitate of 6-bromoveratraldehyde that had deposited (1.3 g, 67%) was filtered off, mp 142-144°C (from benzene).

The following compounds were obtained analogously: 6-bromopiperonal, mp 125-127°C (from benzene), yield 90%; 3-bromo-4-methoxybenzaldehyde, yield 60%, mp 45-47°C (from alcohol); and 5-bromo-2-methoxybenzaldehyde, mp 105-107°C (from ethanol), yield 58%.

Synthesis of Diformyldiphenyl Ethers. A mixture of a bromobenzaldehyde (I, 0.043 mole), a hydroxybenzaldehyde (II, 0.045 mole), 5.16 g of CuO, and 10.35 g of K_2CO_3 in 80 ml of absolute pyridine was heated at 145-150°C in a current of nitrogen with vigorous stirring for 24 h. After the end of the reaction, the inorganic substances were filtered off, the pyridine was distilled off under vacuum, and the residue was dissolved in ethyl acetate. The solvent was distilled off and the mixture was purified on a column of AlO_2 [sic] (20:1), with elution by benzene, benzene—ether (1:1), and ether. The diformyldiphenyl ethers formed are given below.

5,6'-Diformyl-2-methoxy-3',4'-methylenedioxydiphenyl ether (IX) was obtained from 8.66 g of 6-bromopiperonal and 6.81 g of isovanillin; yield 7.02 g (50%), mp 120-122°C (from ethanol). Found: M^+ 300.0623. $C_{16}H_{12}O_6$. Calculated: M^+ 300.0634. Mass spectrum, m/z (I_{rel}., %): 300 M^+ (19), 164 (100), 152 (29), 151 (36), 149 (12), 136 (13), 135 (17). PMR spectrum (δ, ppm): 3.85 (s, OCH_3), 5.49 (s, OCH_2O), 6.22 (s, H^2), 7.01 (d, H^3), 8.5 Hz, 7.18 (s, H^5), 7.35 (d, H^6, J 2 Hz), 7.57 (dd, H^4, J 8.5 Hz, J 2 Hz), 9.68 (s, CHO), 10.27 (s, CHO).

5,6'-Diformyl-2,3',4'-trimethoxydiphenyl ether (VII) was obtained from 4.06 g of 6-bromoveratraldehyde and 3.36 g of isovanillin. Yield 3.11 g (59%), mp 90-92°C (from ethanol). Composition $C_{17}H_{16}O_3$. Mass spectrum, m/z (I_{rel}, %): 316 ($M^{+\cdot}$ 70), 285 (13), 181 (16), 180 (100), 165 (23), 152 (15), 151 (13), 137 (12), 119 (9). IR soectrum (ν, cm^{-1}): 2900, 1700, 1600, 1300. PMR spectrum (δ, ppm): 3.65 s, 3.77 s, 3.85 (s, 9H, OCH_3), 6.25 (s, H^2), 6.95 (d, H^3, J 8.5 Hz), 7.10 (s, H^5), 7.22 (d, H^6, J 2 Hz), 7.50 (dd, H^4, J 8.5 Hz, J 2 Hz), 9.67 (s, CHO), 10.17 (s, CHO).

5,6'-Diformyl-2,2'-dimethoxydiphenyl ether (V) was obtained analogously from 6.01 g of 3-bromo-4-methoxybenzaldehyde and 4.50 g of isovanillin. Yield 1.99 g (25%), mp 110-112°C (from ethanol). Composition $C_{16}H_{14}O_5$. Mass spectrum, m/z (I_{rel}, %): 286 (M^+, 2), 152 $(M-134)^+$, 100, 151 (96), 137 (20), 123 (18), 109 (16), 81 (16).

5,5′-Diformyl-2,4′-dimethoxydiphenyl Ether (VI). The synthesis was effected from 7.01 g of 5-bromo-2-methoxybenzaldehyde and 6.02 g of isovanillin. Yield 2.89 g (31%), mp 94-96°C (from ethanol). Composition $C_{16}H_{14}O_5$. Mass spectrum, m/z (I_{rel}, %): 286 (M^+, 100), 271 (9), 257 (3), 226 (4), 151 (5), 149 (6), 135 (3), 119 (5).

4′,5-Diformyl-2-methoxydiphenyl ether (IV) was obtained from 10.02 g of *para*-bromobenzaldehyde and 8.16 g of isovanillin. Yield 8.85 g (64%), mp 70-72°C (from ethanol). Composition $C_{15}H_{12}O_4$. Mass spectrum, m/z (I_{rel}, %): 256 (100), 255 (74), 240 (6), 239 (7), 184 (5), 183 (5), 128 (8), 127 (16), 119 (8), 91 (5), 77 (10). PMR spectrum (δ, ppm): 3.80 s OCH_3, 6.97 (dd, H^2, H^6, J 8.5 Hz, J 2 Hz), 7.08 (d, H^3, J 8.5 Hz), 7.50 (d, H^6, J 2 Hz), 7.65 (dd, H^4, J 8.5 Hz, J 2 Hz), 7.75 (dd, H^5, H^3, J 8.5 Hz, J 2 Hz), 9.76 (s, CHO), 980 (s, CHO).

4′,6-Diformyl-3,4-methylenedioxydiphenyl ether (VII) was obtained from 17.32 g of 6-bromopiperonal and 12.45 g of *para*-hydroxybenzaldehyde. Yield 2.03 g (10%), mp 130-132°C (from ethanol). Composition $C_{15}H_{10}O_5$. Mass spectrum, m/z (I_{rel}, %): 270 ($M^{+\cdot}$ 100), 269 (27), 241 (19), 238 (9), 209 (9), 183 (12), 165 (45), 164 (64), 136 (15), 105 (11), 77 (12). PMR spectrum (δ, ppm): 6.00 (s, 2H, OCH_2O), 6.43 (s, H^2), 7.00 (dd, H^2, H^6, J 8.5 Hz), 7.25 (s, H^5), 7.80 (dd, H^3, H^5, J 8.5 Hz, J 2 Hz), 9.81 (s, CHO), 9.90 (s, CHO).

4,4′-Diformyldiphenyl Ether (III). The synthesis was carried out by the method described above, taking 6.51 g of *para*-bromobenzaldehyde and 4.52 g of *para*-hydroxybenzaldehyde. Yield 1.91 g (24%), mp 55-57°C (from ethanol). Composition $C_{14}H_{10}O_3$. Mass spectrum, m/z (I_{rel}, %): 226 (M^+ 100), 225 (99), 197 (4), 169 (5), 168 (7), 141 (14), 139 (5), 115 (10), 112 (8), 77 (6).

General Procdure for Obtaining the Amines (X-XVI). A mixture of homoveratrylamine (0.0108 mole or 0.0216 mole), benzene (50 ml), and a diformyldiphenyl ether (0.0108 mole) was boiled under reflux with the azeotropic distillation of water, using a Dean-Stark trap, for 2 h. The solvent was distilled off, and the residue was dissolved in 50 ml of methanol. The imine was reduced with 5 g of $NaBH_4$ at 0±5°C. The methanol was distilled off, the residue was diluted with water, the amine was exhaustively extracted with ether, and the ethereal solution was washed with water and was dried with sodium sulfate. The residue after the solvent had been distilled off gave the amine.

The hydrochloride of the amine was obtained by mixing an acetone solution of the base with concentrated hydrochloric acid to give a weak acid reaction (pH 5). The salt that precipitated was separated off and was recrystallized from a suitable solvent.

5″,6′-Bis(3,4-dimethoxyphenethylaminomethyl)-2″-methoxy-3′,4′-methylenedioxydiphenyl ether (XVI) was obtained from 5 g (0.0017 mole) of 5,6′-diformyl-2-methoxy-3′,4′-methylenedioxydiphenyl ether and 6.03 g (0.33 mole) of homoveratrylamine). Yield 9.8 g (93.3%). Melting point of the hydrochloride of the amine 125-127°C (from acetone–methanol (4:1)). Composition $C_{36}H_{42}O_8N_2$. PMR spectrum (δ, ppm): 3.67 (s, 9H, OCH_3), 3.70 (s, 6H, OCH_3), 2.70 (t, 8H, CH_2), 3.40 s, 345 (s, 4H, $-CH_2$), 5.80 (s, OCH_2O), 6.20-7.12 (aromatic protons).

Mass spectrum (m/z, %): 630 [$M^{+\cdot}$, $C_{36}H_{42}N_2O_8$, 0.6], 479 [a^+, 95], 477 [$(a\text{-}2H)^+$, 18], 450 [c^+, 67], 448 [$(c\text{-}2H)^+$, 16], 298 [$(a\text{-}d_1\text{-}H)^+$, 25], 271 [$(c\text{-}d_1+H)$, 76], 269 [$(c\text{-}0d_1H)^+$, 100], 137 [$(c_1\text{-}d\text{-}H)^+$, 25].

5″,6′-Bis(3,4-dimethoxyphenethylaminomethyl)-2″,3′,4′-trimethoxydiphenyl ether (XV)_was obtained from 4,51 g (0.0142 mole) of 5,6′-diformyl-2,3′,4′-trimethoxydiphenyl ether (IX) and 5.158 g (0.0285 mole) of homoveratrylamine. Yield 7.83 g (85%), mp of the hydrochloride 110-112°C (from acetone–ethanol (4:1)). Composition $C_{37}H_{46}O_8N_2$. PMR spectrum (δ, ppm): 2.70 (t, 8H, CH_2), 3.65 s, 3.68 (s, 4H, $-CH_2$), 3.69 (s, 6H, OCH_3).

Mass spectrum (m/z, %): 646 [$M^{+\cdot}$, $C_{37}H_{46}N_2O_8$, 0.8], 495 [a^+, 79], 493 [$(a\text{-}2H)^+$, 19], 466 [c^+, 70], 464 [$(c\text{-}2H)^+$, 21], 314 [$(a\text{-}d_1\text{-}H)^+$, 10], 287 [$(c\text{-}d_1+H)^+$, 38], 285 [$(c\text{-}d_1\text{-}H)^+$, 100], 3.75 (c, 15H, OCH_3), 6.25-7.25 (aromatic protons).

5′,5″-Bis(3,4-dimethoxyphenethylaminomethyl)-2′,2″-dimethoxydiphenyl ether (XII) was synthesized from 1.51 g (0.0052 mole of 5,5′-diformyldiformyl-2,2′-dimethoxydiphenyl ether and 1.89 g (0.0105 mole) of homoveratrylamine. Yield 2.91 g (90%), mp of the hydrochloride 248-250°C (from acetone–ethano (3:1)). Composition $C_{36}H_{44}O_7N_2$. PMR spectrum (δ, ppm): 2.75 (t, *h, CH_2), 3.30 s, 3.35 (s, 4H, $-CH_2$), 3.63 (s, 6H, OCH_3), 3.67 (s, 12H, OCH_3), 6.50-7.20 (12 H, aromatic protons).

5′,5″-Bis(3,4-dimethoxyphenylaminomethyl)-2″,4′-dimethoxydiphenyl ether (XIII) was obtained from 1.52 g (0.0052 mole) of 5,5′-diformyl-2,4′-dimethoxydiphenyl ether and 1.88 g (0.0104 mole) of homoveratrylamine. Yield 84 g (87%) [sic], mp of the hydrochloride 210-212°C (from acetone). Composition $C_{36}H_{44}O_7N_2$. PMR spectrum (δ, ppm): 3.12 (t, 8H, CH_2), 3.77, 4.10 (s, 4H, $-CH_2$), 3.70 (s, 18H, OCH_3), 6.67-7.28 (12 H, aromatic protons).

4′,4″-Bis(3,4-dimethoxyphenethylaminomethyl)diphenyl ether (X) was obtained from 1.88 g (0.0083 mole) of 4,4′-diformyldiphyl ether and 3.004 g (0.0166 mole) of homoveratrylamine. Yield 3.60 g (78%), mp of the hydrochloride 250-

252°C (from acetone–methanol (4:1). Composition $C_{34}H_{40}O_5N_2$. PMR spectrum (δ, ppm): 2.70-2.78 (8H, CH_2), 3.40 s, 3.42 (s, 4H, $-CH_2$), 3.63 s, 3.75 (s, 12H, OCH_3), 6.65-7.25 (14 H, aromatic protons).

4″,6′-Bis(3,4-dimethoxyphenethylaminomethyl)-3′,4′-methylenedioxydiphenyl ether (XIV) was obtained in a way similar to that described above from 1.23 g (0.0045 mole) of 4′,6-diformyl-3,4-methylenedioxydiphenyl ether and 1.64 g (0.0091 mole) of homoveratrylamine. Yield 2.28 g (84%), mp of the hydrochloride 168-170°C (from acetone). Composition $C_{35}H_{40}O_7N_2$. PMR spectrum (δ, ppm): 2.70-2.80 (8H, CH_2), 3.44 s, 3.47 (s, 4H, $-CH_2$), 3.75 (s, 12H, OCH_3), 5.82 (s, OCH_2O), 6.30-7.25 (12 H, aromatic protons).

4″,5′-Bis(3,4-dimethoxyphenethylaminomethyl)-2′-methoxydiphenyl ether (XI) was synthesized under analogous conditions from 3.08 g (0.012 mole) of 4′,5-diformyl-2-methoxydiphenyl ether and 4.35 g (0.024 mole) of homoveratrylamine. Yield 5.78 g (82%), mp of the hydrochloride 222-224°C (from acetone–methanol (1:3)). Composition $C_{32}H_{38}O_5N_2$. PMR spectrum (δ, ppm): 2.70-2.75 (8H, CH_2), 3.60 s, 3.62 (s, 4H, $-CH_2$), 3.72 (s, OCH_3), 3.75 (s, 12H, OCH_3), 6.65-7.25 (13 H, aromatic protons).

Preparation of the Amines (XVII-XXII). A mixture of 0.0012 mole of an amine (X-XVI), 100 ml of methanol, and 10 ml of 30% formalin was boiled under reflux for 1 h. Then the reaction mixture was cooled to 0-5°C, and 3 g of $NaHB_4$ was added in portions over 1 h. The solvent was distilled off in vacuum, and the residue was mixed with water and extracted with ether. The ethereal solution was washed with water and dried with sodium sulfate. The residue after the solvent had been distilled off gave the tertiary amine, which was purified via the hydrochloride. The hydrochlorides were obtained by a method similar to that described above.

5″,6′-Bis(N-methyl-3,4-dimethoxyphenethylaminomethyl)-2″-methoxy-3′,4′-methylenedioxydiphenylether(XXIII)was obtained from 2.5 g (0.004 mole) of 5″,6′-bis(3,4-dimethoxyphenethylamine)-2″-methoxy-3′,4′-methylenedioxydiphenylether. Yield 2.55 g (97%), mp of the hydrochloride 120-122°C (from acetone–methanol (3:1)). Composition $C_{38}H_{46}O_8N_2$. PMR spectrum (δ, ppm): 2.12 s, 2.20 (s, 6H, $N-CH_3$), 2.50-2.70 (8H, CH_2), 3.30 s, 3.40 (s, 4H, $-CH_2$), 3.72 s, 3.75 (s, 15H, OCH_3), 5.80 (s, OCH_2O), 6.50-7.20.

Mass spectrum (m/z, %): 658 [$M^{+\cdot}$, $C_{38}H_{46}N_2O_8$, 0.2], 507 [a^+, 16], 464 [c^+, $C_{27}H_{30}NO_6$, 29], 314 [$(a\text{-}d_1+H)^+$, 14], 271 [$(c\text{-}d_1+H)^+$, 100], 269 [$(c\text{-}d_1\text{-}H)^+$, 16], 165 [$e^+$, 9], 164 (12), 152 (26), 151 (f^+, 27).

5″,6′-Bis(N-methyl-3,4-dimethoxyphenethylaminomethyl)-2″,3′,4′-trimethoxydiphenyl ether (XXII) was synthesized from 2 g (0.003 mole) of 5″,6′-bis(3,4-dimethoxyphenethylaminomethyl)-2″,3′,4′-trimethoxydiphenyl ether. Yield 1.46 g (70%), mp of the hydrochloride 118-120°C. Composition $C_{37}H_{50}O_8N_2$. PMR spectrum (δ, ppm): 2.22 (s, 3H, $N-CH_3$), 2.24 (s, $N-CH_3$), 2.70-2.75 (8H, CH_2), 3.65 s, 3.68 (s, 4H, $-CH_2$), 3.75 (s, 21H, OCH_3), 6.20-7.25 (11H, aromatic protons).

Mass spectrum (m/z, %): 674 [$M^{+\cdot}$, $C_{39}H_{50}N_2O_8$, 0.3], 523 [a^+, $C_{30}H_{39}N_2O_6$, 20], 480 [c^+, 40], 287 [$(c\text{-}d_1+H)^+$, $C_{17}H_{19}O_4$, 100], 285 [$(c\text{-}d_1+H)^+$, 16], 165 [e^+, 21], 151 (f^+, 43).

5′,5″-Bis(N-methyl-3,4-dimethoxyphenethylaminomethyl)-2′,2″-dimethoxydiphenyl ether (XIX) was obtained analogously from 2.22 g (0.0036 mole) of 5′,5″-bis(3,4-dimethoxyphenethylaminomethyl)-2′,2″-dimethoxydiphenyl ether. Yield 1.91 g (82%), mp of the hydrochloride 105-107°C (from acetone–ethanol (3:1)). Composition $C_{38}H_{48}O_7N_2$. PMR spectrum (δ, ppm): 2.21 (s, $N-CH_3$), 2.23 (s, $N-CH_3$), 2.75-2.77 (8H, CH_2), 3.64 s, 3.67 (s, 4H, $-CH_2$), 3.70 s, 3.73 (s, 18H, OCH_3), 6.45-7.25 (12 H, aromatic protons).

3′,5″-Bis(N-methyl-3,4-dimethoxyphenethylaminomethyl-2″,4′-dimethoxydiphenyl ether (XX) was obtained from 0.27 g (0.0004 mole) of 3′,5″-bis(3,4-dimethoxyphenethylaminomethyl)-2″,4′-dimethoxydiphenyl ether. Yield 1.86g (80%), mp of the hydrochloride 195-197°C (from acetone–ethanol (3:1)). Composition $C_{38}H_{48}O_7N_2$. PMR spectrum (δ, ppm): 2.20 (s, $N-CH_3$), 2.23 (s, $N-CH_3$), 2.50-2.60 (8H, CH_2), 3.30 s, 3.33 (s, 4H, $-CH_2$), 3.75 s, 3.73 (s, 18H, OCH_3), 6.60-7.20 (11 H, aromatic protons).

4″,6′-Bis(N-methyl-3,4-dimethoxyphenethylaminomethyl)-3′,4′-methylenedioxydiphenyl Ether (XXI). This was obtained under analogous conditions from 0.71 g (0.0012 mole) of 4″,6′-bis(N-methyl-3,4-dimethoxyphenethylaminomethyl)-3′,4′-methylenedioxydiphenyl ether. Yield 0.63 g (85%), mp of the hydrochloride 116-118°C (from acetone–methanol (3:1)). Composition $C_{37}H_{44}O_7N_2$, PMR spectrum (δ, ppm): 2.20 (s, 6H, $N-CH_3$), 2.55-2.60 (8H, CH_2), 3.45 (s, 4H, $-CH_2$), 3.75 (s, 12H, OCH_3), 5.82 (s, OCH_2O), 6.30-7.25 (12 H, aromatic protons).

4′,4″-Bis(N-methyl-3,4-dimethoxyphenethylaminomethyl)diphenyl ether (XVII) was obtained from 1.91 g (0.0034 mole) of 4′,4″-bis(3,4-dimethoxyphenethylaminomethyl)diphenyl ether. Yield 1.8 g (90%), mp 120-122°C (from acetone–ethanol (3:1)). Composition $C_{36}H_{40}O_5N_2$. PMR spectrum (δ, ppm): 2.21 (s, 6H, $N-CH_3$), 2.50-2.75 (8H, CH_2), 3.45 (s, 4H, $-CH_2$), 3.75 (s, 12H, OCH_3), 6.55-7.25 (14 H, aromatic protons).

4″,5′-Bis(N-methyl-3,4-dimethoxyphenethylaminomethyl)-2′-methoxydiphenyl ether (XVIII) was obtained from 2.1 g (0.0035 mole) of 4″,5″-bis(3,4-dimethoxyphenethylaminomethyl)-2′-methoxydiphenyl ether. Yield 1.65 g (75%)), mp of the hydrochloride 117-119°C (from actone−methanol (4:1). Composition $C_{37}H_{46}O_6N_2$. PMR spectrum (δ, ppm): 2.30 (s, N−CH_3), 2.40 (s, N−CH_3), 2.60-2.75 (8H, CH_2), 3.65 (s, 4H, −CH_2), 3.75 s, 3.77 (s, 15H, OCH_3), 6.60-7.25 (13 H, aromatic protons).

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