Vinyl ethers and sulfides containing antioxidant functional groups*

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Methods for the synthesis of compounds combining in the molecule fragments of known antioxidants with reactive vinyloxy and vinylthio groups have been developed. Transesterification of methyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propionate with 2-(vinyloxy)- or 2-(vinylthio)-ethanol furnished the high yields of 2-(vinyloxy)- and 2-(vinylthio)ethyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propionates. The reaction of 2-[(vinyloxy)ethoxymethyl]- and 2-[(vinylthio)-ethoxymethyl]oxiranes with 2,2,6,6-tetramethylpiperidin-4-ol and 4-aminodiphenylamine proceeds with the oxirane ring opening and leads to the corresponding vinyloxy and vinylthio derivatives of 2,2,6,6-tetramethylpiperidin-4-ol and mono- and bisvinyloxy and -vinylthio derivatives of 4-aminodiphenylamine at the primary amino group.

Key words: vinyl ethers and sulfides, antioxidants.

Most organic materials such as lubricants, rubbers, polymers, biomaterials undergo oxidative destruction in the presence of molecular oxygen, which is a complex radical chain process.[1,2] To inhibit autooxidation of organic substrates antioxidants should be added. The most well known antioxidants are sterically hindered phenols, thiophenols, as well as aromatic and sterically hindered heterocyclic amines, mainly derivatives of diphenylamine, naphthylphenylamine, and piperidine.[1,2] In the last years, both a systematic search for new antioxidants[3—5] and a structural modification of existing antioxidants in order to increase their efficiency are under way.[6—14] In this case, an introduction of unsaturated groups into the structure of antioxidants significantly increases a possibility of their further transformations, providing preparation of new monomeric or polymeric antioxidants.[11—14] The latter are considered as potential nonmigrating stabilizers of plastics possessing important technical advantages, in particular, they are nonvolatile, difficult to wash away, and sometimes better compatible with the polymer.[11]

The data published earlier[15] have demonstrated that antioxidants containing a vinyloxy group are very promising. For example, it was shown that vinyl ethers of polyalkylpiperidin-4-ols, as well as their polymers, are well compatible with polypropylene and exhibit excellent light-stabilizing properties over a long period of time. To the best of our knowledge, this is the only class of antioxidants modified by introduction of a vinyloxy group. In the work mentioned,[15] the vinyl ethers of polyalkylpiperidin-4-ol were obtained in 60—80% yield by the vinylation of the corresponding alcohols with acetylene under pressure in the presence of potassium or sodium hydroxyde or by transvinylation with excess of vinyl ether or ester in the presence of mercury salts. Later, it was shown[16] that the use of superbasic system KOH—DMSO allowed one to significantly reduce the temperature of vinylation of polymethyl-substituted piperidin-4-ols (from 170—180 to 90 °C).

Unlike piperidinols, other commonly used stabilizers of polymers contain no functional groups capable of vinylation with acetylene. In the present work, we suggested a new approach to the synthesis of antioxidants with vinyloxy and vinylthio groups based on the reaction of stabilizers with functional fragments of available vinyl ethers and sulfides, with reactive vinyloxy and vinylthio groups in the molecule being unaffected.

The transesterification of methyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propionate (**1**) with 2-(vinyloxy)- (**2a**) or 2-(vinylthio)ethanol (**2b**) in the presence of base catalysts (10—40 mol.%) leads to the formation of 2-(vinyloxy)ethyl or 2-(vinylthio)ethyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propionates (**3a,b**, Scheme 1). The alkoxides obtained by the reaction of alcohols **2a,b** with metallic sodium have proved the best catalysts of the process.

* Dedicated to Academician O. N. Chupakhin on the occasion of his 75th birthday.

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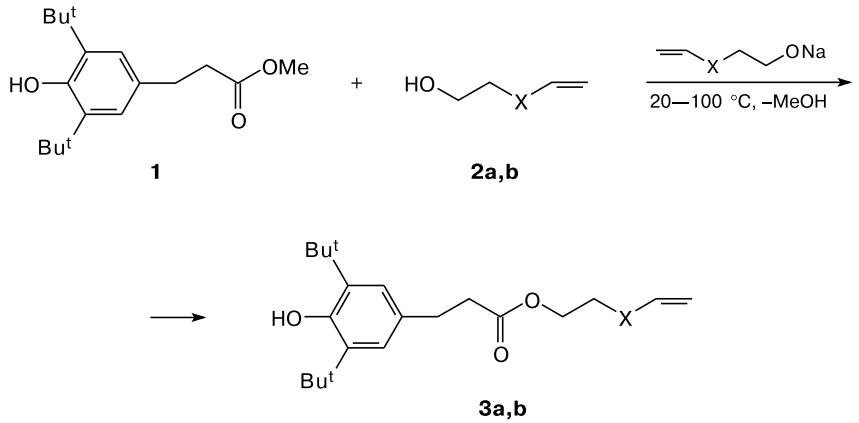
Scheme 1



X = O (**a**), S (**b**)

The reaction is reversible, which is typical of transesterification.[17] In the case of 2-(vinyloxy)ethanol (**2a**), the equilibrium is shifted to the right due to the low solubility of forming propionate **3a** in this alcohol taken in excess, the product precipitated from the reaction mixture as a colorless needle-like crystals. When 30—40 mol.% of the catalyst with respect to the starting compound **1** is used, the reaction is completed after 1 h at room temperature, but can be carried out further by addition of a fresh portion of propionate **1**, which results in higher conversion of vinyloxyethanol **2a**, with the yield of ester **3a** being 78%.

Transesterification of propionate **1** with 2-(vinylthio)-ethanol (**2b**) proceeds otherwise: the product **3b** formed is a viscous liquid, in which a part of unreacted starting compound **1** dissolves. Since both esters have close properties, their separation failed. To drive the equilibrium to the right, it is not enough to only use a large (up to 10-fold) excess of vinylthioethanol **2b** and the methanol formed cannot be distilled off even at 145 °C, whereas transesterification at temperatures above 100 °C is accompanied by considerable resinification.

These difficulties can be avoided by running the process in low vacuum (~20 Torr). In this case, methanol is being distilled off at 80—100 °C during the entire synthesis (in a mixture with (vinylthio)ethanol **2b** taken in excess), the equilibrium is driven to the right, and pure vinyl sulfide **3b** can be obtained in up to 91% yield.

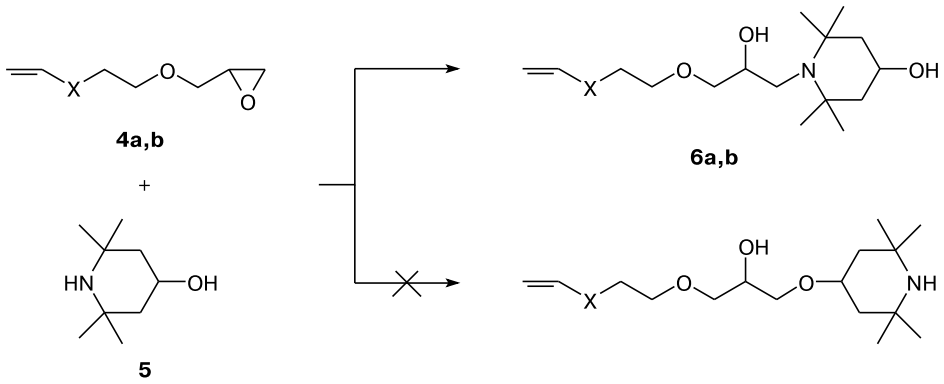
The reaction of 2-[(vinyloxy)ethoxymethyl]- and 2-[(vinylthio)ethoxymethyl]oxiranes (**4a,b**) with 2,2,6,6-tetramethylpiperidin-4-ol or 4-aminodiphenylamine, common antioxidants belonging to the classes of heterocyclic and aromatic amines, became a basis for the method of introduction of vinyloxy or vinylthio groups into the structure of these amine antioxidants. Earlier,[18,19] it has been shown that oxirane **4a** easily reacts with aliphatic amines to exclusively form addition products at the terminal carbon atom of the oxirane ring (the Krasuskii rule).

The reaction between 2-[(vinyloxy)ethoxymethyl]-(**4a**) or 2-[(vinylthio)ethoxymethyl]oxirane (**4b**) and sterically hindered amine, *viz.*, 2,2,6,6-tetramethylpiperidin-4-ol (**5**), smoothly proceeds upon heating (90—150 °C) and leads chemo- and regioselectively to the formation of 1-{2-hydroxy-3-[2-(vinyloxy)ethoxy]propyl}-2,2,6,6-tetramethylpiperidin-4-ol (**6a**) or 1-{2-hydroxy-3-[2-(vinylthio)ethoxy]propyl}-2,2,6,6-tetramethylpiperidin-4-ol (**6b**) (Scheme 2). The process was carried out in a sealed system with equimolar ratio of reagents in the absence of a solvent and a catalyst. The reaction course was monitored by IR and ^{1}H NMR spectroscopy from the disappearance of characteristic absorption band (ν ~3000 cm^{-1}) and signals for the oxirane ring (δ 3.14, 2.77, 2.60) and retention of major frequencies (ν/cm^{-1}: 1620 (H_2C=CHO), 1580 (H_2C=CHS)) and signals for the vinyloxy (δ 6.49, 4.18, 4.01) or vinylthio groups (δ 6.35, 5.12), respectively.

Despite the hydroxy group in the molecule of piperidinol **5** unlike the amine group is sterically unhindered, there is no formation of alternative products of the oxirane ring opening of compounds **4a,b** with participation of the hydroxy group of alcohol **5** even if potassium or sodium hydroxyde is used as a catalyst. This is inferred from analysis of the ^{1}H and ^{13}C NMR spectra, in which there are present the signals for the NCH_2 group (in the region δ 2.7, 2.5, and 44.4—44.8) and absent additional signals for the OCH_2 group (δ ~3.3—3.8 and ~60—75). The fact that oxiranes **4a,b** do not react with cyclohexanol under indicated conditions serves as an indirect evidence that the hydroxy group is inert in this process.

Adducts **6a,b** are viscous undistillable liquids. They need no purification, since, according to the IR and NMR spectra, the process occurs with 100% conversion of reagents. Heating *in vacuo* does not lead to isolation of the starting or other volatile compounds.

Scheme 2



X = O (**a**), S (**b**)

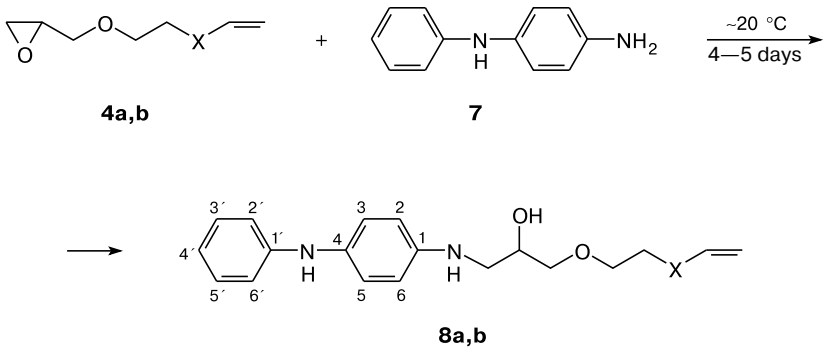
The reaction of oxiranes **4a,b** with 4-aminodiphenylamine (**7**), containing amino groups different in character, leads to the formation of addition products exclusively involving the primary amino group (Scheme 3). The evidence comes from the IR spectra of dilute solutions of the reaction mixtures in CCl_4. As the reaction progresses, the absorption bands for the primary amino group at 3390 and 3470 cm^{-1} gradually decrease, whereas the absorption band for the secondary amino group at 3425 cm^{-1} remains. In addition, earlier[20] it has been shown that diphenylamine, the structural analog of amine **7**, does not react with oxirane **4a**.

It is known that alkyloxiranes react with aromatic amines significantly slower than with aliphatic.[21] In addition, the reactions of monoalkyloxiranes with aliphatic amines lead only to the addition products of the amines to the terminal carbon atom,[18,21] whereas their reactions with aromatic amines can give both regioisomers, though the addition product to the less substituted carbon atom of the oxirane ring is still predominant.[22,23] In addition, depending on the ratio of reagents amine **7** can give with oxiranes **4a,b** both the mono- and the diadducts or their mixtures. The synthesis of monoadducts of oxiranes **4a,b** with amine **7**, in which the content of the starting antioxidant fragments is higher than in diadducts, corresponds better to the goal of the present work.

Monitoring of the reaction course can be performed by IR spectroscopy from the disappearance of the absorption bands for the primary amino group, however more precisely the reaction course can be controlled using ^{1}H NMR spectra, in which the signals for the oxirane ring (δ 2.77 and 2.60), having no overlap with the signals for the forming products, gradually disappear.

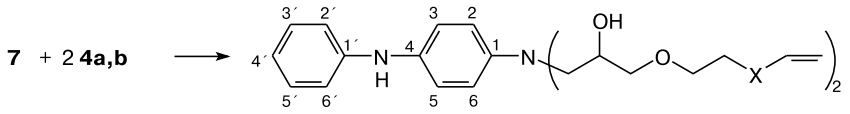
According to the literature data,[21] the reaction of oxiranes **4a,b** with aminodiphenylamine **7** (Scheme 3) is slower than the earlier studied reactions of oxirane **4a** with aliphatic amines.[18,19] For instance, at room temperature and equimolar ratio of reagents (**7** and **4a** or **4b**), the signals for the oxirane ring completely disappear after 4—5 days, whereas at the ratio **4a,b** : **7** = 2 : 1, after 12—14 days. At 50 °C, the reaction time decrease to 13—14 h (equimolar ratio of reagents) and 18—20 h

Scheme 3



X = O (**a**), S (**b**)

Scheme 4



9a,b

X = O (**a**), S (**b**)

(**4a,b** : **7** = 2 : 1), at 100 °C, to 3 and 5 h, respectively, however, at temperatures 100 °C and above, there is observed an increase in viscosity of the products, that can be due to the partial polymerization at the epoxide group.

Analysis of the ^{1}H and ^{13}C NMR spectra of the products of this transformation shows that along with monoadducts **8a,b**, a significant amount of the corresponding diadducts **9a,b** is formed not only at the equimolar ratio of reagents, but also if a 2-fold excess of amine **7** is used, whereas no formation of regioisomeric addition products of the amine at the internal carbon atom is observed. This is also confirmed by analysis of the IR spectra of dilute solutions of products obtained in CCl_4. They contain only the absorption band for the secondary hydroxy group at 3580 cm^{-1}, whereas the absorption band for the primary OH group (ν ~3630 cm^{-1}) is absent.

Since diadducts **9a,b** are formed, a part of the starting 4-aminodiphenylamine remains unconsumed. According to the NMR spectroscopic data, the reaction of oxiranes **4a,b** with amine **7** with an equimolar ratio of reagents leads to a mixture of monoadduct **8**, diadduct **9**, and unreacted compound **7** in the ratio ~3 : 1 : 1.

When a 2-fold amount of oxirane **4a,b** is used in the reaction with amine **7**, diadducts **9a,b** are formed (Scheme 4) as a mixture of two diastereomers in the ratio 1 : 1, that can be clearly seen from the double set of signals in the ^{1}H and especially ^{13}C NMR spectra.

Products **8a,b** and **9a,b** are very viscous liquids black in color, liquefying on heating. From the practical point of view, there is no need to isolate individual monoadducts **8a,b** from the forming reaction mixtures. Most likely, the whole mixtures, as well as polymers on their basis, will behave as antioxidants.

In conclusion, compounds combining fragments of known antioxidants and reactive vinyloxy and vinylthio groups have been synthesized. The products obtained are promising for the use both as independent antioxidants and for the synthesis of new compounds with antioxidant properties on their basis, including high-molecular-mass nonmigrating stabilizers for industrial polymers.

Experimental

IR spectra were recorded on a Bruker JFS-25 spectrometer neat and in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 and 100.62 MHz, respectively) at ~20 °C in $CDCl_3$ with HMDS as an internal standard. Assignment of signals in the ^{1}H and ^{13}C NMR spectra was performed using two-dimensional homonuclear (COSY) and heteronuclear (HMBS, HSQC) correlation techniques. Commercial methyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propionate (**1**), 4-aminodiphenylamine (**7**) (Uniroyal Chemical Co.), 2,2,6,6-tetramethylpiperidin-4-ol (**5**), 2-(vinyloxy)ethanol (**2a**) (Aldrich Chemical Co.) were used in this work. 2-(Vinylthio)-ethanol (**2b**) was obtained by vinylation of 2-hydroxyethanethiol with acetylene according to procedure described earlier.[24] 2-[(Vinyloxy)ethoxymethyl]oxirane (**4a**) was synthesized from 2-(vinyloxy)ethanol (**2a**) and epichlorohydrin as described in monograph.[18]

2-(Vinyloxy)ethyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]-propionate (3a). A catalyst prepared from metallic sodium (0.3 g, 13 mmol) and 2-(vinyloxy)ethanol (**2a**) (5.6 g, 63 mmol) was added to a solution of methyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propionate (**1**) (10.0 g, 34 mmol) in 2-(vinyloxy)ethanol (**2a**) (22.0 g, 250 mmol). After 1 h, a white precipitate formed was filtered off, propionate **1** (5.0 g, 17 mmol) was added to the mother liquor, and the homogeneous reaction mixture formed was stirred for another 3 h at ~20 °C, a precipitate formed was again filtered off, the last portion of propionate **1** (5.0 g, 17 mmol) was added, and the mixture was left for 24 h. A precipitate obtained was combined with two previous, dissolved in diethyl ether, the ethereal solution was repeatedly washed with cold water, dried with K_2CO_3. After the solvent was evaporated, the product was obtained (18.6 g, 78%), m.p. 86 °C (light petroleum—ethanol, 3 : 1), colorless crystals, well soluble in diethyl ether, acetone, chloroform, moderately in alcohols and hydrocarbons. Found (%): C, 72.54; H, 9.38. $C_{21}H_{32}O_4$. Calculated (%): C, 72.38; H, 9.26. IR (KBr), ν/cm^{-1}: 3431 (OH); 3080, 3005 (=CH, $=CH_2$); 1713 (C=O); 1622 (C=C). ^{1}H NMR, δ: 1.47 (s, 18 H, Me); 2.67 (t, 2 H, $ArC\underline{H}_2$, J = 7.8 Hz); 2.92 (t, 2 H, $ArCH_2C\underline{H}_2$, J = 7.8 Hz); 3.92 (t, 2 H, CH_2O, J = 4.7 Hz); 4.07 (dd, 1 H, $=CH_{cis}$, J = 6.8 Hz, J = 2.1 Hz); 4.22 (dd, 1 H, $=CH_{trans}$, J = 14.4 Hz, J = 2.1 Hz); 4.35 (t, 2 H, $OCOCH_2$, J = 4.7 Hz); 5.08 (s, 1 H, $ArO\underline{H}$); 6.51 (dd, 1 H, OCH=, J = 14.4 Hz, J = 6.8 Hz); 7.01 (s, 2 H, H(2), H(6) arom.). ^{13}C NMR, δ: 30.2 (Me); 31.0 ($\underline{C}Me_3$); 34.2 ($ArCH_2\underline{C}H_2$); 36.3 ($Ar\underline{C}H_2$); 62.5 ($OCO\underline{C}H_2$); 65.7 (CH_2O); 87.0 ($=CH_2$); 124.7 (C(2), C(6) arom.); 130.9 (C(1) arom.); 135.9 (C(3), C(5) arom.); 151.3 (OCH=); 152.1 (C(4) arom.); 173.0 (C=O).

2-(Vinylthio)ethyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]-propionate (3b). A mixture of methyl 3-[3,5-di(*tert*-butyl)-4-hydroxyphenyl]propionate (**1**) (1.75 g, 6 mmol), 2-(vinylthio)-ethanol (**2b**) (3.06 g, 29 mmol), and hydroquinone (0.3 g) was placed into a three-neck flask equipped with thermometer, dropping funnel, and an adapter with condenser for distillation of volatile compounds. The system was connected to a vacuum pump (20 Torr), heated with stirring to 91 °C, followed by a slow

(over entire synthesis) dropwise addition of a catalyst (prepared from metallic sodium (0.014 g, 0.6 mmol) and 2-(vinylthio)-ethanol (**2b**) (1.73 g, 17 mmol)) to the solution formed with simultaneous evaporation of liberated methanol (in a mixture with 2-(vinyloxy)ethanol). The process was stopped after 5 h, a residual (2.88 g) viscous dark liquid was dissolved in diethyl ether and the solution was passed through a short column with Al_2O_3 to remove the resin-like products. The ethereal solution was washed 4 times with small amounts of water and dried with K_2CO_3. Diethyl ether and the residue of unreacted 2-(vinylthio)ethanol (**2b**) were evaporated (the latter, *in vacuo* (5 Torr)). The residue contained propionate **3b** (2.0 g, 91%) as a moderately viscous yellowish liquid, n_D^{20} 1.4771. Found (%): C, 69.11; H, 8.70; S, 8.65. $C_{21}H_{32}O_3S$. Calculated (%): C, 69.19; H, 8.85; S, 8.79. IR (neat), ν/cm^{-1}: 3637 (OH); 3089, 3005 (=CH, $=CH_2$); 1736 (C=O); 1586 (C=C). ^{1}H NMR, δ: 1.48 (s, 18 H, Me); 2.67 (t, 2 H, ArC$\underline{H}_2$, J = 7.8 Hz); 2.93 (t, 2 H, $ArCH_2C\underline{H}_2$, J = 7.8 Hz); 2.96 (t, 2 H, CH_2S, J = 6.8 Hz); 4.31 (t, 2 H, $C\underline{H}_2CH_2S$, J = 6.8 Hz); 5.13 (s, 1 H, ArO$\underline{H}$); 5.26 (d, 1 H, $=CH_{trans}$, J = 16.6 Hz); 5.29 (d, 1 H, $=CH_{cis}$, J = 10.0 Hz); 6.37 (dd, 1 H, SCH=, J = 16.6 Hz, J = 10.0 Hz); 7.04 (s, 2 H, H(2), H(6) arom.). ^{13}C NMR, δ: 29.9 (CH_2S); 30.2 (Me); 30.8 ($\underline{C}Me_3$); 34.2 (Ar$\underline{C}H_2$); 36.2 ($ArCH_2\underline{C}H_2$); 62.6 ($OCO\underline{C}H_2$); 111.9 (CH_2=); 124.7 (C(2), C(6) arom.); 130.9 (C(1) arom.); 131.2 (SCH=); 135.9 (C(3), C(5) arom.); 152.1 (C(4) arom.); 172.8 (C=O).

2-[(Vinylthio)ethoxymethyl]oxirane (4b). Epichlorohydrin (37.0 g, 400 mmol) was added to a mixture of 2-(vinylthio)-ethanol (**2b**) (10.4 g, 100 mmol) and NaOH (6.0 g, 150 mmol) over 20 min, followed by stirring for 6 h at 45—50 °C. A precipitate formed was filtered off, washed with diethyl ether, the ethereal solution obtained was combined with the filtrate. Diethyl ether and excess epichlorohydrin were evaporated, the residue was distilled *in vacuo* to obtain compound **4b** (10.2 g, 64%), b.p. 80—82 °C (4 Torr), n_D^{20} 1.5025, which corresponds to the literature data.[25] Found (%): C, 52.88; H, 7.79; S, 19.65. $C_7H_{12}O_2S$. Calculated (%): C, 52.47; H, 7.55; S, 20.01. IR (neat), ν/cm^{-1}: 3054 (=CH); 2999 (CH oxirane); 1585 (C=C); 1254, 907 (oxirane ring). ^{1}H NMR, δ: 2.61 (dd, 1 H, CHC$\underline{H}_2$, J = 2.7 Hz, J = 5.0 Hz); 2.79 (dd, 1 H, CHC$\underline{H}_2$, J = 4.2 Hz, J = 5.0 Hz); 2.90 (t, 2 H, SCH_2, J = 6.7 Hz); 3.14 (m, 1 H, CH); 3.40 (dd, 1 H, OC$\underline{H}_2$CH, J = 5.8 Hz, J = 11.6 Hz); 3.70 (m, 2 H, CH_2O); 3.78 (dd, 1 H, OC$\underline{H}_2$CH, J = 2.8 Hz, J = 11.6 Hz); 5.15 (d, 1 H, $=CH_{trans}$, J = 16.7 Hz); 5.19 (d, 1 H, $=CH_{cis}$, J = 10.1 Hz); 6.35 (dd, 1 H, =CHS, J = 16.7 Hz, J = 10.1 Hz). ^{13}C NMR, δ: 30.99 (SCH_2); 44.05 ($CH\underline{C}H_2$); 50.65 (CH); 70.0 (CH_2O); 71.56 (CH_2O); 111.26 (CH_2=); 131.93 (=CHS).

1-{2-Hydroxy-3-[2-(vinyloxy)ethoxy]propyl}-2,2,6,6-tetramethylpiperidin-4-ol (6a). A mixture of alcohol **5** (1.57 g, 10 mmol) and oxirane **4a** (1.44 g, 10 mmol) in a tightly capped vessel or tube was heated for 4.5 h at 135 °C with magnetic stirring. The reaction reached completion if the reaction mixture became homogeneous after cooling; otherwise, the reaction mixture grew turbid due to the precipitation of the starting compound **5**. The product **6a** was obtained as a viscous yellowish liquid in quantitative yield, n_D^{20} 1.4930. Found (%): C, 64.00; H, 10.71; N, 4.60. $C_{16}H_{31}NO_4$. Calculated (%): C, 63.75; H, 10.37; N, 4.65. IR (neat), ν/cm^{-1}: 3402 (OH); 3117, 3072, 3031 ($=CH_2$, =CH); 1636, 1619 (C=C). ^{1}H NMR, δ: 1.05, 1.10 (both s, 12 H, Me); 1.38 (t, 2 H, CH_2 ring, J = 11.6 Hz); 1.88 (ddd, 2 H, CH_2 ring, J = 3.7 Hz, J = 11.6 Hz, J = 11.6 Hz); 2.54 (dd, 1 H, NCH_2, J = 9.1 Hz, J = 15.0 Hz); 2.66 (dd, 1 H, NCH_2, J = 6.1 Hz, J = 15.0 Hz); 3.49 (d, 2 H, $CH(OH)C\underline{H}_2O$, J = 4.5 Hz); 3.62 (m, 1 H, C$\underline{H}$OH); 3.74, 3.84 (both m, 4 H, OCH_2CH_2O); 3.99 (dd, 2 H, $=CH_{cis}$, C$\underline{H}$OH ring, J = 6.8 Hz, J = 1.8 Hz); 4.17 (dd, 1 H, $=CH_{trans}$, J = 14.4 Hz, J = 1.8 Hz); 4.22 (br.s, 1 H, OH); 6.47 (dd, 1 H, =CHO, J = 14.4 Hz, J = 6.8 Hz). ^{13}C NMR, δ: 22.33, 23.50, 33.40, 34.46 (Me); 44.81 (NCH_2); 49.97 (CH_2 ring); 56.42, 56.77 ($N\underline{C}Me_2$); 63.31 (CHOH ring); 66.90 (CHOH); 67.41 ($O\underline{C}H_2CH_2O$); 70.02 ($OCH_2\underline{C}H_2O$); 74.83 ($CH(OH)\underline{C}H_2O$); 86.78 ($=CH_2$); 151.83 (=CHO).

1-{2-Hydroxy-3-[2-(vinylthio)ethoxy]propyl}-2,2,6,6-tetramethylpiperidin-4-ol (6b) was obtained similarly to compound **6a** by heating a mixture of alcohol **5** (1.57 g, 10 mmol) and oxirane **4b** (1.60 g, 10 mmol) for 4.5 h at 135 °C in a sealed tube. The yield of product **6b** was quantitative, viscous yellowish liquid, n_D^{20} 1.5280. Found (%): C, 59.86; H, 9.94; N, 4.43; S, 9.63. $C_{16}H_{31}NO_3S$. Calculated (%): C, 60.53; H, 9.84; N, 4.41; S, 10.10. IR (neat), ν/cm^{-1}: 3406 (OH); 3093 (=CH); 1584 (C=C). ^{1}H NMR, δ: 1.06, 1.11 (both s, 12 H, Me); 1.38 (t, 2 H, CH_2 ring, J = 11.4 Hz); 1.87 (ddd, 2 H, CH_2 ring, J = 3.7 Hz, J = 11.4 Hz, J = 11.4 Hz); 2.55 (dd, 1 H, NCH_2, J = 9.2 Hz, J = 15.0 Hz); 2.66 (dd, 1 H, NCH_2, J = 6.1 Hz, J = 15.0 Hz); 2.90 (t, 2 H, CH_2S, J = 6.8 Hz); 3.45 (d, 2 H, $CH(OH)C\underline{H}_2O$, J = 4.8 Hz); 3.61 (m, 1 H, C$\underline{H}$OH); 3.69 (t, 2 H, $OC\underline{H}_2CH_2S$, J = 6.8 Hz); 3.99 (m, 1 H, C$\underline{H}$OH ring); 4.12 (br.s, 1 H, OH); 5.15 (d, 1 H, $=CH_{cis}$, J = 10.2 Hz); 5.18 (d, 1 H, $=CH_{trans}$, J = 16.6 Hz); 6.35 (dd, 1 H, =CHS, J = 16.6 Hz, J = 10.2 Hz). ^{13}C NMR, δ: 21.95, 23.13 (Me); 30.68 (CH_2S); 33.04, 34.15 (Me); 44.45 (NCH_2); 49.53 (CH_2 ring); 56.01, 56.37 ($N\underline{C}Me_2$); 62.63 (CHOH ring); 66.40 (CHOH); 69.87 ($O\underline{C}H_2CH_2S$); 74.07 ($CH(OH)\underline{C}H_2O$); 110.81 ($=CH_2$); 131.83 (SCH=).

Reaction of 2-[(vinyloxy)ethoxymethyl]- and 2-[(vinylthio)-ethoxymethyl]oxiranes (4a,b) with 4-aminodiphenylamine (7). ***A*. Monoadducts.** An equimolar mixture of oxirane **4a,b** and 4-aminodiphenylamine (**7**) was thoroughly stirred until complete dissolution of amine **7** in oxirane **4a,b** and kept for 5 days at ~20 °C until complete disappearance of signals at δ 2.60 (dd) and 2.78 (t) (corresponding to the CH_2 group of the oxirane ring) in the ^{1}H NMR spectrum of the reaction mixture to obtain dark very viscous products, which liquefied upon heating, soluble in acetone, chloroform, benzene, and insoluble in water and hexane. According to the ^{1}H and ^{13}C NMR spectra, the products obtained are mixtures of the starting amine **7** (~20%), monoadduct **8a,b** (~60%), and diadduct **9a,b** (~20%), the latter, as two diastereomers. Column chromatography of the reaction mixture (alumina, eluent, CH_2Cl_2—hexane, 1 : 1) resulted in the separation of the mixture of monoadduct **8a** and the starting amine **7** from diadduct **9a**, which remained on the column.

1-(4-Anilinoanilino)-3-[2-(vinyloxy)ethoxy]propan-2-ol (8a). IR (neat), ν/cm^{-1}: 3386 (NH); 3540 sh (OH); 3114, 3015 (=CH, $=CH_2$); 1636, 1618 (C=C). ^{1}H NMR, δ: 2.63 (br.s, 1 H, OH); 3.14 (dd, 1 H, NCH_2, J = 6.8 Hz, J = 12.7 Hz); 3.28 (dd, 1 H, NCH_2, J = 4.3 Hz, J = 12.7 Hz); 3.57 (dd, 1 H, $CH(OH)C\underline{H}_2O$, J = 6.6 Hz, J = 9.8 Hz); 3.64 (dd, 1 H, $CH(OH)C\underline{H}_2O$, J = 3.6 Hz, J = 9.8 Hz); 3.75, 3.85 (both m, 4 H, OCH_2CH_2O); 4.04 (dd, 2 H, $=CH_{cis}$, C$\underline{H}$OH, J = 6.8 Hz, J = 2.0 Hz); 4.22 (dd, 1 H, $=CH_{trans}$, J = 14.3 Hz, J = 2.0 Hz); 5.38 (br.s, 2 H, NH); 6.49 (dd, 1 H, =CHO, J = 14.3 Hz, J = 6.8 Hz); 6.62 (d,

2 H, H(2), H(6) arom., J = 8.7 Hz); 6.77 (t, 1 H, H(4′) arom., J = 7.2 Hz); 6.83 (d, 2 H, H(2′), H(6′) arom., J = 7.8 Hz); 6.99 (d, 2 H, H(3), H(5) arom., J = 8.7 Hz); 7.17 (m, 2 H, H(3′), H(5′) arom.). ^{13}C NMR, δ: 47.13 (NCH_2); 67.20 ($OCH_2\underline{C}H_2O$); 68.91 (CHOH); 69.81 ($O\underline{C}H_2CH_2O$); 73.65 ($CH(OH)\underline{C}H_2O$); 86.98 (CH_2=); 114.12 (C(2), C(6) arom.); 114.84 (C(2′), C(6′) arom.); 118.72 (C(4′) arom.); 123.46 (C(3), C(5) arom.); 129.13 (C(3′), C(5′) arom.); 133.20 (HN—C(1) arom.); 144.32 (HN—C(4) arom.); 146.00 (HN—C(1′) arom.); 151.56 (=CHO).

1-(4-Anilinoanilino)-3-[2-(vinylthio)ethoxy]propan-2-ol (8b). IR (neat), ν/cm^{-1}: 3385 (NH); 3540 sh (OH); 3086, 3020 (=CH, =CH_2); 1585 (C=C). ^{1}H NMR, δ: 2.91 (t, 2 H, SCH_2, J = 6.3 Hz); 3.14 (dd, 1 H, NCH_2, J = 6.9 Hz, J = 12.7 Hz); 3.27 (dd, 1 H, NCH_2, J = 4.3 Hz, J = 12.7 Hz); 3.52 (dd, 1 H, $CH(OH)C\underline{H}_2O$, J = 6.6 Hz, J = 9.6 Hz); 3.59 (dd, 1 H, $CH(OH)C\underline{H}_2O$, J = 3.7 Hz, J = 9.6 Hz); 3.70 (m, 2 H, $OC\underline{H}_2CH_2S$); 4.00 (m, 1 H, $C\underline{H}OH$); 5.17 (d, 1 H, $=CH_{trans}$, J = 16.8 Hz); 5.20 (d, 1 H, $=CH_{cis}$, J = 10.1 Hz); 5.38 (br.s, 2 H, NH); 6.35 (dd, 1 H, =CHS, J = 16.8 Hz, J = 10.1 Hz); 6.62 (d, 2 H, H(2), H(6) arom., J = 8.7 Hz); 6.76 (t, 1 H, H(4′) arom., J = 7.2 Hz); 6.82 (d, 2 H, H(2′), H(6′) arom., J = 8.0 Hz); 6.99 (d, 2 H, H(3), H(5) arom., J = 8.7 Hz); 7.16 (t, 2 H, H(3′), H(5′) arom., J = 7.2 Hz). ^{13}C NMR, δ: 31.37 (CH_2S); 47.26 (NCH_2); 69.02 (CHOH); 70.13 ($O\underline{C}H_2CH_2S$); 73.33 ($CH(OH)\underline{C}H_2O$); 111.57 (CH_2=); 114.23 (C(2), C(6) arom.); 114.97 (C(2′), C(6′) arom.); 118.89 (C(4′) arom.); 123.58 (C(3), C(5) arom.); 129.24 (C(3′), C(5′) arom.); 132.15 (SCH=); 133.18 (HN—C(1) arom.); 144.40 (HN—C(4) arom.); 146.07 (HN—C(1′) arom.).

***B*. Diadducts** were obtained from oxiranes **4a,b** and 4-aminodiphenylamine (**7**) at molar ratio **4a,b** : **7** = 2 : 1 under conditions described above for the reaction at equimolar ratio of reagents. In this case, the entire disappearance of the signals for the oxirane rings in compounds **4a,b** (δ 2.60 (dd) and 2.78 (t)) in the ^{1}H NMR spectrum of the reaction mixture, indicating the completion of the reaction, at ~20 °C was observed after 11—13 days, at 47—50 °C, after 18—20 h, at 100 °C, after 5 h. The diadducts **9a,b** were obtained as dark, very viscous liquids, liquefying on heating. The double character of the most of signals in the ^{1}H and ^{13}C NMR spectra of diadducts **9a,b** indicates formation of two diastereomers.

10-(4-Anilinophenyl)-3,6,14,17-tetraoxa-10-aza-1,18-nonadecadiene-8,12-diol (9a). Found (%): C, 66.19; H, 8.09; N, 5.69. $C_{26}H_{36}N_2O_6$. Calculated (%): C, 66.08; H, 7.68; N, 5.93. IR (neat), ν/cm^{-1}: 3385 (NH); 3520 sh (OH); 3115, 3015 (=CH, =CH_2); 1636, 1619 (C=C). ^{1}H NMR, δ: 3.16 (dd, 1 H, NCH_2, J = 8.8 Hz, J = 14.9 Hz); 3.36 (dd, 1 H, NCH_2, J = 7.8 Hz, J = 14.9 Hz); 3.44 (dd, 1 H, NCH_2, J = 3.9 Hz, J = 14.9 Hz); 3.50 (dd, 2 H, $CH(OH)C\underline{H}_2O$, J = 6.1 Hz, J = 9.8 Hz); 3.57, 3.60 (both dd, 2 H, $CH(OH)C\underline{H}_2O$, J = 4.3 Hz, J = 9.8 Hz); 3.75, 3.85 (both m, 11 H, $OC\underline{H}_2C\underline{H}_2O$, $C\underline{H}(OH)$, NCH_2); 4.02 (dd, 2 H, $=CH_{cis}$, J = 6.7 Hz, J = 1.8 Hz); 4.07 (br.s, 1 H, OH); 4.19 (dd, 3 H, $=CH_{trans}$, OH, J = 14.3 Hz, J = 1.8 Hz); 5.41 (br.s, 1 H, NH); 6.48 (dd, 2 H, =CHO, J = 14.3 Hz, J = 6.7 Hz); 6.68 (d, 1 H, H(2), H(6) arom., J = 8.7 Hz); 6.81 (m, 2 H, H(2), H(6), H(4′) arom.); 6.85, 6.87 (both d, 2 H, H(2′), H(6′) arom., J = 6.11 Hz); 7.02, 7.03 (both d, 2 H, H(3), H(5) arom., J = 8.5 Hz); 7.17 (t, 2 H, H(3′), H(5′) arom., J = 7.1 Hz). ^{13}C NMR, δ: 55.78, 57.65 (NCH_2); 67.35, 67.38 ($OCH_2\underline{C}H_2O$); 68.40, 68.85 (CHOH); 69.97, 70.03 ($O\underline{C}H_2CH_2O$); 73.24, 73.33 ($CH(OH)\underline{C}H_2O$); 86.98 (CH_2=); 113.95, 115.10 (C(2), C(6) arom.); 115.29, 115.42 (C(2′), C(6′) arom.); 119.01, 119.14 (C(4′) arom.); 122.71, 123.22 (C(3), C(5) arom.); 129.28 (C(3′), C(5′) arom.); 132.75, 133.37 (HN—C(1) arom.); 144.21, 144.88 (HN—C(4) arom.); 145.65, 145.88 (HN—C(1′) arom.); 151.67 (=CHO).

10-(Anilinophenyl)-6,14-dioxa-3,17-dithia-10-aza-1,18-nonadecadiene-8,12-diol (9b). Found (%): C, 61.54; H, 7.05; N, 5.41; S, 12.68. $C_{26}H_{36}N_2O_4S_2$. Calculated (%): C, 61.87; H, 7.19; N, 5.55; S, 12.71. IR (neat), ν/cm^{-1}: 3378 (NH); 3530 sh (OH); 3091, 3030 (=CH, =CH_2); 1585 (C=C). ^{1}H NMR, δ: 2.90, 2.91 (both t, 4 H, SCH_2, J = 6.4 Hz); 3.17 (dd, 1 H, NCH_2, J = 9.0 Hz, J = 15.0 Hz); 3.36 (dd, 1 H, NCH_2, J = 7.9 Hz, J = 15.0 Hz); 3.44 (dd, 1 H, NCH_2, J = 4.3 Hz, J = 15.0 Hz); 3.47 (dd, 2 H, $CH(OH)C\underline{H}_2O$, J = 5.9 Hz, J = 9.5 Hz); 3.54, 5.56 (both dd, 2 H, $CH(OH)C\underline{H}_2O$, J = 4.4 Hz, J = 9.5 Hz); 3.70 (m, 7 H, $OC\underline{H}_2CH_2S$, $C\underline{H}OH$, NCH_2); 4.06, 4.15 (both br.s, 2 H, OH); 5.16 (d, 2 H, $=CH_{trans}$, J = 16.5 Hz); 5.19 (d, 2 H, $=CH_{cis}$, J = 10.1 Hz); 5.42 (br.s, 1 H, NH); 6.35 (dd, 2 H, =CHS, J = 16.5 Hz, J = 10.1 Hz); 6.68 (d, 1 H, H(2), H(6) arom., J = 8.8 Hz); 6.80 (m, 2 H, H(2), H(6), H(4′) arom.); 6.85, 6.86 (both d, 2 H, H(2′), H(6′) arom., J = 7.0 Hz); 7.02, 7.04 (both d, 2 H, H(3), H(5) arom., J = 8.4 Hz); 7.18 (t, 2 H, H(3′), H(5′) arom., J = 7.0 Hz). ^{13}C NMR, δ: 31.27 (CH_2S); 55.78, 57.65 (NCH_2); 68.33, 68.80 (CHOH); 70.19, 70.26 ($O\underline{C}H_2CH_2S$); 72.84, 72.93 ($CH(OH)\underline{C}H_2O$); 111.45 (CH_2=); 113.91, 114.96 (C(2), C(6) arom.); 115.11, 115.33 (C(2′), C(6′) arom.); 119.02, 119.16 (C(4′) arom.); 122.59, 123.14 (C(3), C(5) arom.); 129.26 (C(3′), C(5′) arom.); 132.16 (SCH=); 132.77, 133.47 (HN—C(1) arom.); 144.12, 144.77 (HN—C(4) arom.); 145.56, 145.80 (HN—C(1′) arom.).

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