Electron transfer in the peroxytrifluoroacetic acid-assisted sulfoxidation and oxidative destruction of benzhydryl sulfides

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The reactions of benzhydryl sulfides Ph_2CHSCH_2R (R = H, $CONH_2$, COOH, CN) with peroxytrifluoroacetic acid in CF_3COOH were studied experimentally and by the quantum chemical density functional theory (DFT) method and exhibited an unusual dependence on the substituent R. When R ≠ H, a complicated oxidative destruction of the substrates occurs to form 2,4,6-tribenzhydrylphenol as one of the products, while in the case of R = H, the starting benzhydryl sulfide is smoothly sulfoxidated. This fact is due to the common electron transfer from the substrate to reagent at the initial step and the difference in subsequent transformations of the species formed.

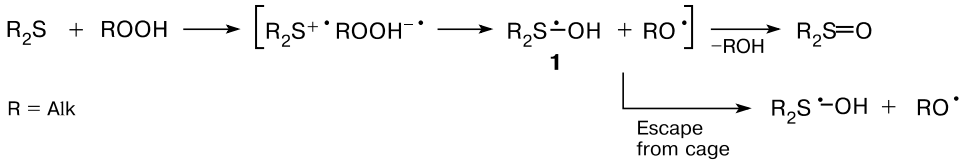
Key words: sulfoxidation, peroxytrifluoroacetic acid, benzhydryl sulfides, debenzhydrylation, electron transfer, radical cations, density functional theory, fragmentation, deprotonation, oxidative destruction, concerted mechanism, hydroxylation, protolysis.

Some organic reactions earlier considered to be purely heterolytic, for example, arene nitration (see reviews[1—5]), proceed in fact or can proceed *via* the single-electron transfer (SET) mechanism with the intermediate formation of highly reactive and, as a rule, very short-living radical ions. When the energy of a complex of reactants is lower than the energy of a complex of the electron transfer (ET) products, the ET is considered as the transition of the reaction system from the ground to electron-excited state. In an opposite case, it is considered that in the course of ET the initial electron-excited state of the complex of the reactants is transformed into the ground state of the complex of ET products.[6—8]

For sulfide sulfoxidation with hydroperoxides, which was initially assumed to proceed *via* the S_N2-similar mechanism,[9,10] the SET mechanism involving a series of paramagnetic intermediates, including the sulfide radical cation and sulfuranyl radical **1** (Scheme 1), was proposed[11] for alkyl hydroperoxides as an example.

However, at present, only sulfoxidation with some nonperoxide agents, resulting in the transformation of the sulfide radical cation into sulfoxide by the interaction with the product of the single-electron reduction of the reactant and/or with the medium, first of all, with water molecules (see, *e.g.*, Refs 12—18), is classified as SET-sulfoxidation. Sulfoxidation with hydroperoxide reagents, whose some representatives are fairly weak electron acceptors,[19]

Scheme 1



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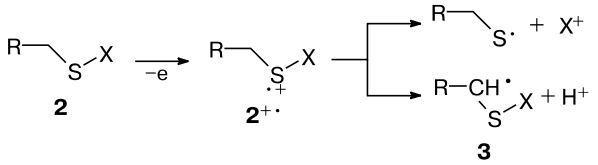
is presently continued to be considered as a non-radical reaction, but it is interpreted as the concerted double atom transfer with the migrations of atoms of the hydroperoxide OH group. In particular, during this transfer the hydrogen atom migrates to the alternative proton-acceptor center of the reactant.[20,21] The second peroxide oxygen atom served as a proton-acceptor center in hydrogen peroxide and in alkyl hydroperoxides and, hence, the very energy-consuming intrareactant 1,2-proton transfer occurs, which can be rather efficiently catalyzed by proton-donor molecules.[22,23]

It is considered (see, *e.g.*, Refs 24 and 25) that sulfoxidation with acyl hydroperoxides (carboxylic peroxyacids) proceeds similarly. In this case, the only distinction is the absence of proton-donor catalysis[24,25] and the presence of a more convenient proton-acceptor center, namely, the sp^2-oxygen atom of the CO group, which does not require the formation of sterically strained reaction sites for functioning.

An important feature of carboxylic peroxyacids is their much higher (compared to non-acid hydroperoxides) tendency to add one electron (see comparative data on the reduction potentials and electron affinities[19,26—28]). This feature should be especially pronounced for peroxytrifluoroacetic acid (PTFA) with the lowest-lying antibonding MO $\sigma^*_{(O-O)}$ (see Ref. 29) and exhibiting the extreme oxidative ability incomparable with non-acid hydroperoxides.[30,31] So, PTFA readily (without preliminary homolysis) oxidizes thiophenes and dibenzothiophene to sulfoxides or even to sulfones (in spite of the dearomatization of the heterocycle),[32,33] whereas some alkanes and cycloalkanes are oxidized to alcohols.[34,35] These properties of peroxy acids and relatively low ionization potentials and standard redox potentials of sulfides[36,37] should, evidently, favor sulfoxidation *via* an alternative single-electron mechanism.

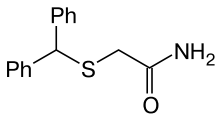
Sulfides containing this or another group X readily leaving in the form of carbocation, for instance, benzhydryl or *tert*-butyl group, are interesting for studying the sulfoxidation mechanism. These sulfides, such as **2** (Scheme 2) are sharply destabilized on transforming into the radical cation state because of the very strong weakening of the S—X bond and, therefore, their radical cations easily dissociate to the carbocation X^+ and thiyl free radical.[13,18,38] Hyperlability of the radical cations is also confirmed by the thermodynamic cycle method, according to which the energy of the Ph_2CH—S in the benzhydryl phenyl sulfide radical cation (X = Ph_2CH) is negative (−2.2 kcal mol^{-1}). The dissociation rate constant of this radical cation is $2 \cdot 10^5$ s^{-1} under usual conditions.[39] In addition, sulfide radical cations, especially those containing the electron-withdrawing group in the α-position, are characterized by the $C_{(\alpha)}$—H fragmentation caused by the $C_{(\alpha)}$—H acid bond dissociation (which can be more acidic than the O—H bond in CF_3COOH) and the formation of highly reactive electroneutral radicals, for example, of the **3** type (see Scheme 2).[40—42]

Scheme 2



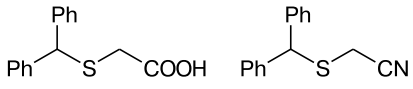
Therefore, it is not surprising that the sulfoxidation of sulfides **2** and similar compounds by non-peroxide reagents is often accompanied by the formation of larger or smaller amounts of the C—S or C—H fragmentation products (see, *e.g.*, Refs 13 and 38), which is not characteristic of other sulfides and indicates the SET mechanism.

As far as we know, fragmentation at the C—S bond is not described in literature for similar reactions involving hydroperoxides. In particular, it was not observed for benzhydrylsulfanylacetamide (**2a**), *viz.*, key precursor of the drug-bestseller Modafinil **4a** (see Scheme 3), which although belongs to sulfides of type **2**, but is smoothly sulfoxidized with hydrogen peroxide in acetic and formic acids.[23] The direct oxidant is H_2O_2 in the form of cyclic hydrogen-bonded associates with carboxylic acids,[23] since almost no more reactive carboxylic peroxyacids are formed in this case.



2a

As it was revealed by our further studies of the Modafinil chemistry, benzhydryl sulfide **2a** and its nearest structural analogs, *viz.*, 2-benzhydrylthioacetic acid (**2b**) and 2-benzhydrylthioacetonitrile (**2c**)*, behave in quite a different manner: they interact with solutions of H_2O_2 in trifluoroacetic acid in which the reaction proceeds *via* the complicated and unusual (for R_2S—hydroperoxide systems) oxidative destruction. We explain such a sharp qualitative change in the reactivity of formally one-type oxidation systems H_2O_2—RCOOH on going from R = H, Me to $R = CF_3$ considered in this work by the ability of stronger trifluoroacetic acid to efficiently acylate hydrogen peroxide to PTFA,[43] which interacts with sulfides **2a—c** in a special manner, different from that typical of H_2O_2.



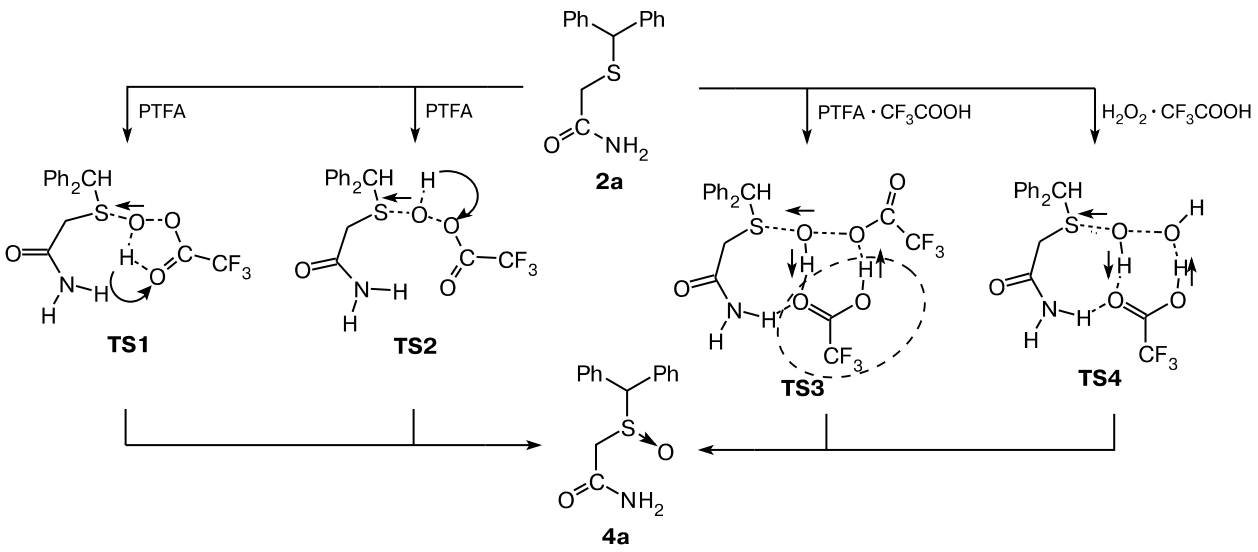
2b **2c**

Results and Discussion

We found that the oxidation of functionalized benzhydryl sulfides **2a—c** with solutions of PTFA in trifluoroacetic acid, prepared by the dissolution of 33% hydrogen

* Compounds **2a—c** were synthesized by the desulfobenzhydrylation of the corresponding functionalized Bunte salts.[23]

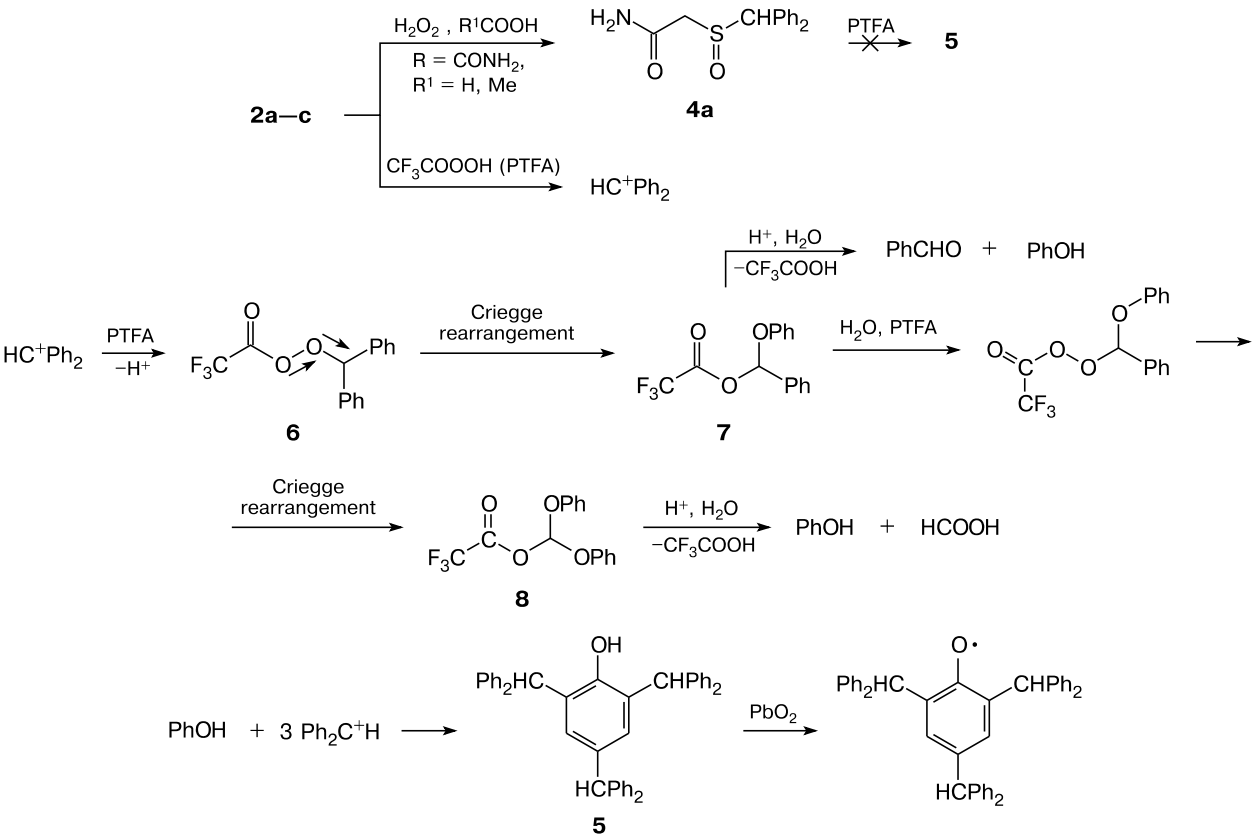
Scheme 3



* The directions of migration of O and H atoms in the course of the reaction are indicated by arrows.

peroxide in this acid, occurs very easily already under standard conditions. At the equimolar ratio of the reactants, the reaction affords complex viscous mixtures containing almost no sulfoxides that are not characteristic of the earlier studied sulfides. These mixtures contain sterically hindered 2,4,6-tribenzhydrylphenol (**5**) (Scheme 4), the product of oxidative destruction of the substrates, isolated in yields of 34, 15, and 40%, respectively.[44]

Scheme 4



The structure of phenol **5** was confirmed by the X-ray diffraction analysis data, according to which a molecule of this compound contains three propeller-shaped diphenylmethane fragments with the common central benzene ring and has an approximate symmetry of C_s (*m*) with the mirror-reflection plane passing through the O(1), C(1), C(4), and C(20) atoms (Fig. 1). The proton of the hydroxy group of this molecule forms no intermolecular hydrogen bonds because of shielding by the phenyl substituents; however, the internuclear distances OH...C(8) and OH...C(9) (2.55 and 3.04 Å, respectively) indicate that this proton forms a weak intramolecular hydrogen bond with the π-system of the adjacent benzene ring OH...π(C(8)=C(9)) (see Fig. 1). The ^{1}H NMR spectrum of compound **5** exhibits a substantially high deshielding of the α-protons of the *o*-benzhydryl groups compared to the *p*-benzhydryl group because of the influence of the nearby OH group. The oxidation of phenol **5** with lead dioxide in toluene affords not very stable free phenoxyl radical (see Scheme 4), whose ESR spectrum contains 15 lines (incompletely resolved doublet of triplet of triplets with hyperfine coupling constants of 8.9, 4.2, and 1.7 G attributed to the α-protons of the *p*- and *o*-benzhydryl groups and *m*-protons of the phenoxyl fragment, respectively; $g = 2.00427$.[45]

Phenol **5** is formed, most likely, by the complicated interaction of sulfides **2a—c** with PTFA, involving transbenzhydrylation and dephenylation along with other stages. In principle, the unusual reactivity exhibited by sulfides **2a—c** could be explained by steric hindrance of their concerted sulfoxidation by the bulky benzhydryl group. To check this possibility, we performed the quantum chemical study of the reactions of compound **2a** with non-associated PTFA and with cyclic hydrogen-bonded 1 : 1 associates of PTFA and H_2O_2 with CF_3COOH, because similar associates have the sulfoxidation ability and are usually responsible for the proton-donor catalysis observed in sulfoxidation.

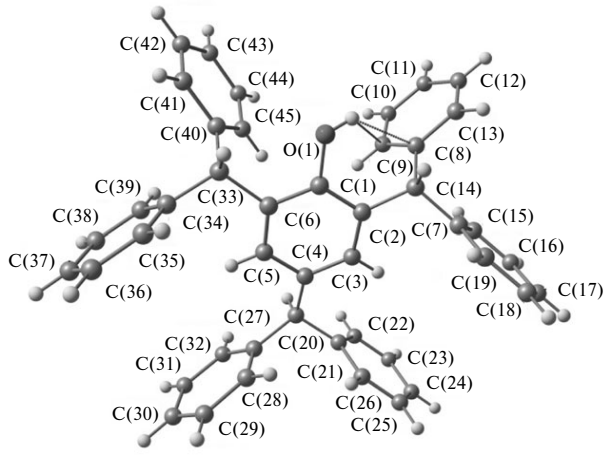


Fig. 1. Molecular structure of 2,4,6-tribenzhydrylphenol (**5**). The intramolecular hydrogen bond of the O—H...π type is shown by dashed line.

Table 1. Energy and some other characteristics of the reactants, products, transition states, and intermediates of sulfoxidation according to the RB3LYP/6-31G** and UB3LYP/6-31G** quantum chemical calculations

Structure	$\Delta^{\neq}G^{\circ}$ (BDE) /kcal mol^{-1}	μ_{calc}/D	$-\nu_i$/cm^{-1}
2a	—	2.8	—
2a$^{+\cdot}$	(11.7)	—	—
2c	—	5.4	—
2c$^{+\cdot}$	(8.9)	—	—
2d	—	1.6	—
2d$^{+\cdot}$	(11.6)	—	—
H_2O_2	—	1.8	—
CF_3COOH	—	2.1	—
CF_3COOOH	—	0.3	—
TS1	13.4	4.1	258
TS2	18.0	8.7	261
TS3	15.1	1.9	224
TS4	18.1	3.1	534
TS5	24.4	5.8	586
Ph_2CH^+	—	—	—
$^{\cdot}S...CH_2CONH_2$	—	2.3	—
$^{\cdot}S...CH_2CN$	—	3.3	—
$^{\cdot}S...Me$	—	1.8	—
3c	(25.8)	3.3	—
12c	(−7.1)	—	—

Note. $\Delta^{\neq}G^{\circ}$ is the free activation energy of the reaction calculated relatively to the initial reactants and corresponding to the presented TS; BDE is the calculated dissociation energy of the Ph_2HC—S bond in the corresponding structure (in parentheses); μ_{calc} is the calculated dipole moment of the structure; ν_i is the frequency of the imaginary vibrational mode of the TS.

The transition states (TS) of sulfoxidation **TS1—TS4** were found by the DFT* study of the indicated reactions (see Scheme 3, Fig. 2, Table 1).

Of four reaction channels corresponding to **TS1—TS4**, two channels with **TS1** and **TS2** are attributed to the sulfoxidation of **2a** with non-associated PTFA. In one case (**TS1**), the oxygen atom of the CO group serves as a proton-acceptor center; in the second case (**TS2**), this is the second oxygen atom of the peroxide fragment. The other two reaction channels (trimolecular **TS3** and **TS4**) correspond to the sulfoxidation by cyclic monosolvates of the reactants, PTFA·CF_3COOH (in this case, the CO group of PTFA is the proton acceptor) and H_2O_2·CF_3COOH (Fig. 2). According to the data obtained by the intrinsic reaction coordinate (IRC) method, the CF_3COOH molecule acts as a switcher of the proton transfer to the relay-race

* All quantum chemical calculations, if not specially indicated, were performed using the B3LYP functional (UB3LYP for paramagnetic species) and 6-31G** basis set.

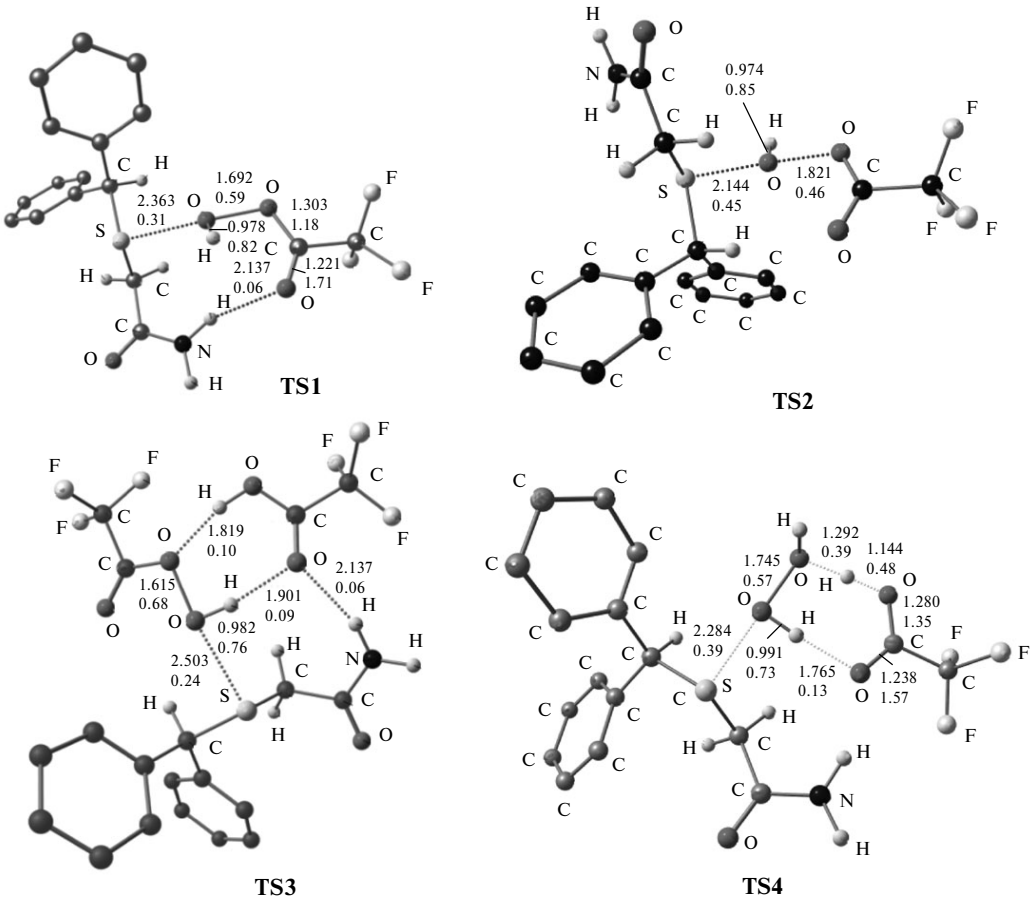


Fig. 2. Transition states of the sulfoxidation of benzhydryl sulfide **2a** with PTFA (**TS1**, **TS2**), PTFA·CF_3COOH (**TS3**), and H_2O_2·CF_3COOH (**TS4**) (here and in Fig. 3, hydrogen atoms of the phenyl groups are omitted).

mode in trimolecular sulfoxidation. For this purpose, the molecule is included into the composition of seven-membred intermolecular hydrogen cycles that play the role of reaction sites of the proton transfer. The wave functions of **TS1**—**TS4** are stable on going from RB3LYP to UB3LYP.

The values $\Delta^{\neq}G^{\circ}_{calc}$ and $\Delta^{\neq}H^{\circ}_{calc}$ that characterize the easiness of different variants of the gas-phase concerted sulfoxidation of compound **2a** (see Scheme 3) are low, being 13.4, 0.9 (**TS1**), 18.0, 6.2 (**TS2**), 15.1, –9.1 (**TS3**), and 18.1, –2.4 (**TS4**) kcal mol^{-1}.*

The data presented indicate that the concerted sulfoxidation of benzhydryl sulfides **2a**—**c** in the considered reaction system should occur with a high rate involving predominantly non-associated PTFA (**TS1**) and, to a lower extent, associate PTFA·CF_3COOH (**TS3**). On the whole, the reaction occurs without a substantial steric influence of the benzhydryl group and is mainly limited by the entropy factor, especially in the case of trimolecular sulfoxidation. For the sulfoxidation of sulfide **2a** with PTFA itself (**TS1**) and its associate with CF_3COOH (**TS3**), the activation entropy is $\Delta^{\neq}S^{\circ}_{calc}$ = –42.0 and –80.9 cal mol^{-1} K^{-1}, respectively. Thus, for carboxylic peroxy acids, the entropy unfavorable factor of the trimolecular TS overbalances the positive effect of a decrease in the activation enthalpy caused by the facilitation of the proton transfer (for the **2a**—PTFA system it achieves –10.0 kcal mol^{-1}). Note that these results explain well the experimental data on the incapability of proton-donor molecules of catalyzing sulfoxidation with peroxycarboxylic acids.[24,25] Since two comparatively close in energy topomeric **TS1** and **TS2** exist for free PTFA, the so-called "paradigm of reactivity of peroxycarboxylic acids," characteristic of the Prilezhaev epoxidation of alkenes[46,47] that appears as a competition in the reaction of two proton-acceptor centers is also inherent of sulfoxidation.

On the whole, the data considered suggest that the steric factor exerts no effect on the specific reactivity of benzyhydryl sulfides **2a**—**c** towards PTFA.

* The negative values of $\Delta H^{\neq\circ}_{calc}$ for the reactions proceeding *via* **TS3** and **TS4** are the result of somewhat formalized calculation in which the enthalpies of three initial molecules were used instead of the enthalpies of the substrate and corresponding bimolecular associate.

General scheme of the oxidative destruction of sulfides 2a—c. As it was found for compound **4a**, sulfoxides, unlike sulfides, do not form phenol **5** upon the treatment with PTFA in trifluoroacetic acid. This indicates that the oxidative destruction of the substrates in systems **2a**—**c**—PTFA is the fastest transformation that is not related to sulfoxidation.

The initial stage is evidently the debenzhydrylation of sulfides with the detachment of the benzhydrylium carbocation. The latter reacts with PTFA undergoing indirect dephenylation to give initially benzhydryl peroxytrifluoroacetate **6**. Then, ester **6** undergoes Criegge rearrangment[48,49] resulting in acylated hemiacetal **7**, which is possibly capable of a similar rearrangement to orthoester **8**. The cleavage of acid-labile compounds **7** and **8** leads to the detachment of phenyl groups to form unsubstituted phenol and phenol **5** (see Scheme 4).

According to Scheme 4, phenol **5** can also be obtained from benzhydrol by the treatment with PTFA in CF_3COOH, during which the Ph_2CH^+ cation is also generated first and then the stages of oxidative dephenylation and benzhydrylation occur. The mechanism of this transformation resembles the oxidation of triphenylmethanol to diphenyl carbonate by the action of PTFA in CF_3COOH.[50]

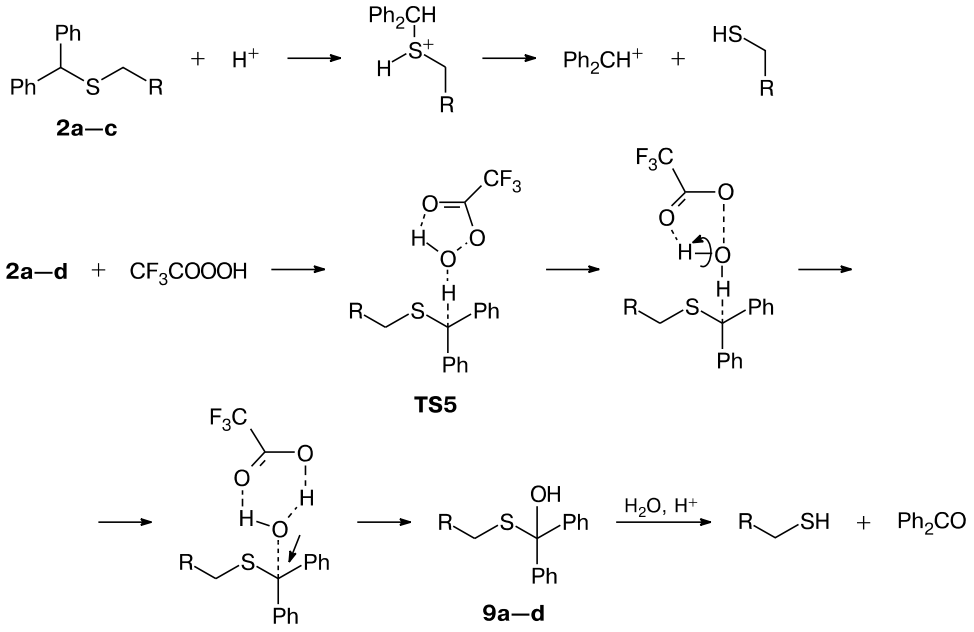
Debenzhydrylation stage. Debenzhydrylation is the most complicated stage of oxidative destruction of sulfides **2a**—**c** in **2**—H_2O_2—PTFA—CF_3COOH systems, because, particularly, it can proceed not only *via* the SET mechanism but also by the protolysis of the substrate or its hydroxylation under the action of PTFA to hydroxy derivatives **9a**—**c** and their further acid-catalyzed cleavage (Scheme 5). The latter reaction route should not result in the generation of the benzhydrylium cation but can make a certain contribution to the overall debenzhydrylation process.

It is difficult to evaluate the easiness of the initiating ET from **2a**—**c** to PTFA, in particular, because of its dissociative character, which does not allow one to use the Marcus equations[51] frequently used for the solution of problems of this type. However, it can be shown that the non-radical debenzhydrylation is too inefficient to provide the fast oxidative destruction of benzhydryl sulfides **2a**—**c** under the action of PTFA. For example, under mild conditions of oxidative destruction, almost no proto-*S*-debenzhydrylation of benzhydryl sulfides with trifluoroacetic acid (see Scheme 5 and Refs 52—54) occurs, as it was established for compound **2a** as an example.

Debenzhydrylation through α-hydroxylation cannot either be fast enough, which follows from the quantum chemical data obtained for the model structure (simplest benzhydryl sulfide) of compound **2d**. They show that this compound can be hydroxylated, in principle, with PTFA similar to hydroxylation of alkanes with peroxy acids,[55—57] namely, by the concerted replacement of the hydrogen atom with the very unusual electrophilic attack of the reactant at this atom (see Scheme 5).

As can be seen from the structure of transition state **TS5** of the hydroxylation of **2d** (Fig. 3), the oxygen atom of the cationoid-polarized[35,57] OH group of PTFA participates in the electrophilic frontal attack. Unlike similar

Scheme 5



R = $C(O)NH_2$ (**a**), COOH (**b**), CN (**c**), H (**d**)

TS of alkanes,[57,58] **TS5** is characterized by the stability of the wave function (on going from RB3LYP to UB3LYP), indicating the non-biradicaloid character of hydroxylation. Taking into account this fact, it is reasonable to classify the hydroxylation considered as the electrophilic substitution of the hydrogen atom at the sp^3-hybridized carbon atom with some extension of the existing classification of transformations of this type[59] (Scheme 6).

Scheme 6

$$Ph_2CHSMe\ (\mathbf{2d}) + CF_3COOOH \longrightarrow \mathbf{TS5} \longrightarrow Ph_2C(OH)SMe\ (\mathbf{9d}) + CF_3COOH$$

Such an exotic variant of substitution is possible for carboxylic peroxy acids only due to a substantial negative charge[29] on the electrophilic oxygen atom, providing the interaction with the positively charged attacked hydrogen atom, and due to a special mechanism of the removal of the substituted hydrogen atom (deteriorating the reaction) from the path of motion of the OH group of the reactant. For sulfides **2** this mechanism is the same as that for alkanes[56] and includes the formation (at the final stage of the reaction, *i.e.*, after passing the TS) the "transient" (virtual) water molecule[56] in the composition of the nonequilibrium ion pair $Ph_2C^{\delta+}SMe...HOH...^{\delta-}OOC—CF_3$ (see Fig. 3). In this pair, the H_2O molecule turns by approximately 180° around the bond formed with the participation of the substituted hydrogen atom of the substrate. As a result, this atom "deteriorating" the further transformation at first is completely shifted from the plane of the reaction site and then returns into this plane, getting already behind the OH group. The latter can recombine with the benzhydryl group of the substrate to form hydroxy derivative **9d** (see Scheme 6). Such a complicated mechanism of hydroxylation of sulfides **2** substantially impedes this reaction, for which $\Delta^{\neq}G^{\circ}_{calc} = 24.4$ kcal mol^{-1}, which is much higher than a similar value for the concerted sulfoxidation of **2a** with PTFA (see data presented above).

Thus, it can be concluded that the initiating stage of the debenzhydrylation of benzhydryl sulfides with both PTFA and non-peroxide sulfoxidating agents is ET resulting in radical cations **2a**—**c**$^{+\cdot}$, which are more easily undergo debenzhydrylation than transformation into sulfoxides.

The SET mechanism is also favored by the fact that in acetonitrile (acetonitrile is an efficient trap of carbocations) the benzhydryl sulfides considered interact with nitrosonium perchlorate ($NO^+ClO_4^-$), which is a strong electron acceptor, to form *N*-benzhydrylacetamide (**10**), *viz.*, the addition product of the Ph_2CH^+ cation to MeCN *via* the Ritter reaction (the yields of compound **10** from sulfides **2a** and **2c** are 46 and 37%, respectively) (Scheme 7). Another important argument for this course of the process can be the direct proof of the capability of PTFA of abstracting one electron from sulfide molecules. This proof was obtained using phenoxathiin (**11**) as an example. The treatment of compound **11** with a PTFA solution in CF_3COOH affords intensely colored blue solutions containing radical cation of **11**$^{+\cdot}$, which is kinetically fairly stable and is not prone to fragmentation. The color of the solution is probably due to radical cation **11** (see Scheme 7), whose ESR spectrum (Fig. 4) consists of 31 equidistant lines, which reflects the interaction of an unpaired electron with four pairs of protons of the phenoxathiin system with the HFS constants that are approximately multiple to the lowest constant ($a^{H(3,6)} \approx 2.4$, $a^{H(2,7)} \approx 1.2$, $a^{H(1,8)} \approx$ ≈ 0.6, and $a^{H(4,5)} \approx 0.3$ G (*cf.* Ref. 60)).

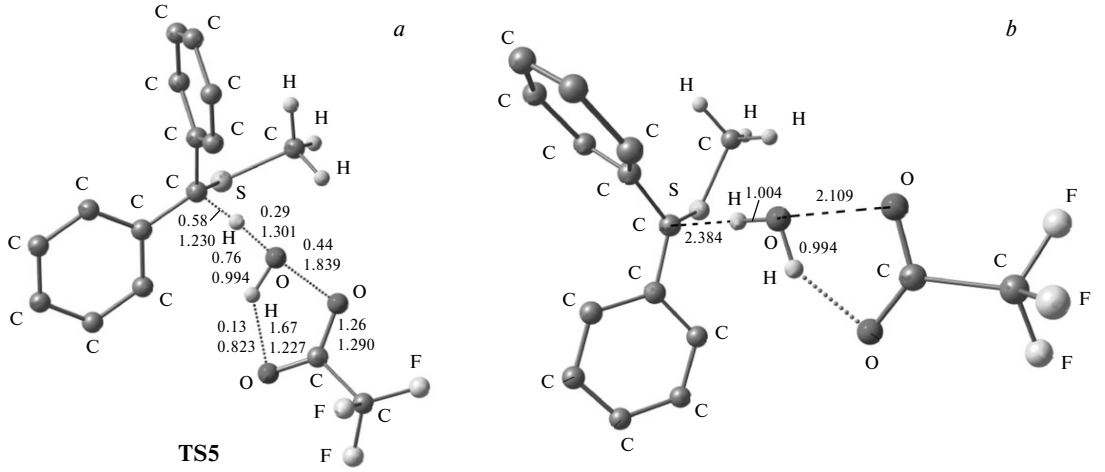
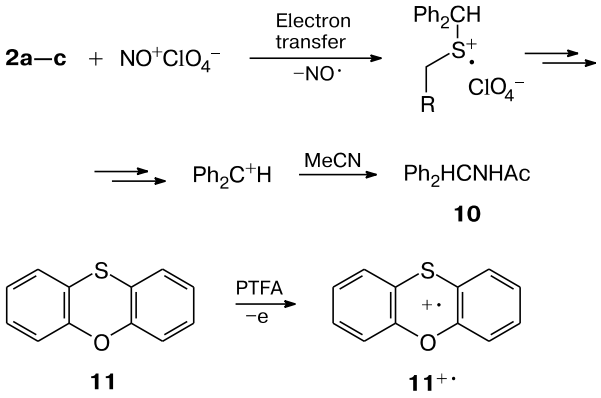


Fig. 3. Transition state **TS5** (*a*) and the nonequilibrium ion-molecular complex $Ph_2C^{\delta+}SMe...HOH...^{\delta-}OOCCF_3$ containing the nonequilibrium water molecule, which was formed from **TS5** by the hydroxylation of sulfide **2d** (*b*).

Scheme 7



The electron transfer from sulfides **2a**—**c** to PTFA can be accompanied by three types of secondary processes involving the radical cations: (1) detachment of the benzhydryl carbocation from these radical species; (2) their α-deprotonation (for instance, by the action of the PTFA radical anion), resulting in the products of C—H fragmentations; and (3) recombination with the hydroxyl radical (with the formation of O-protonated sulfoxides) (Scheme 8). In our opinion, similar transformations can occur in some extent in the primary cage of solvent. In this case, the deprotonation is favored by the electron-withdrawing groups in the radical cations, whereas sulfoxidation is favored by an extreme reactivity of the hydroxyl radical. This results in the situation when its recombination with radical cations becomes energetically very favorable. According to the quantum chemical calculation for radical cation $\mathbf{2d}^{+\cdot}$, a decrease in the energy of the reaction system in the course of recombination with ·OH with a correction to the vibrational energy is about 58 kcal mol^{-1}.

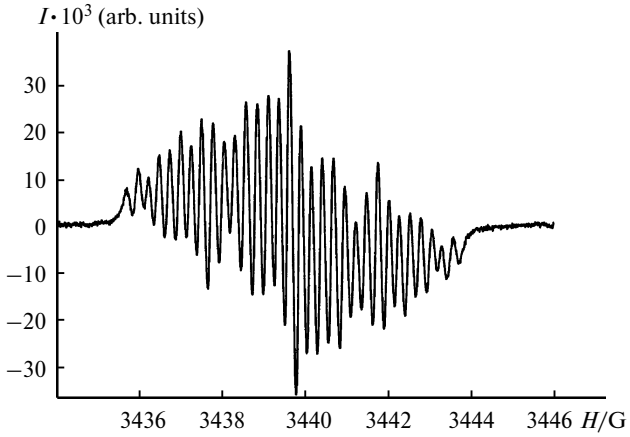
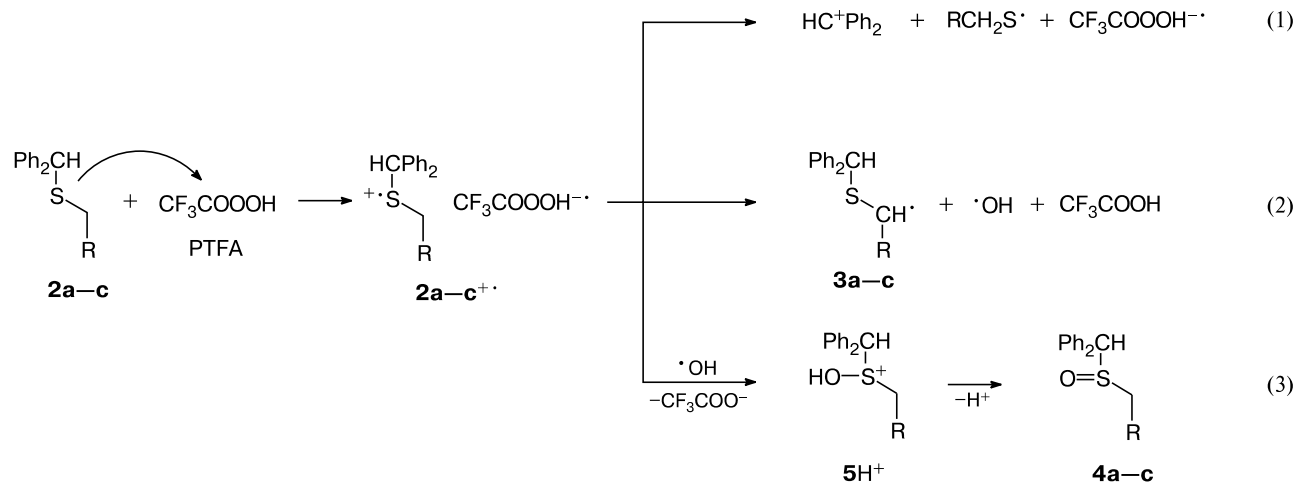


Fig. 4. ESR spectrum of radical cation $\mathbf{11}^{+\cdot}$ formed by the reaction of phenoxathiin (**11**) with PTFA obtained by the dissolution of hydrogen peroxide in CF_3COOH (ambient temperature).

Let us consider further how the fragmentation of benzhydryl sulfide radical cations proceeds and results in their debenzhydrylation under the oxidative destruction conditions. According to the UB3LYP/6-31G** calculations, the Ph_2HC—S bond in radical cations $\mathbf{2}^{+\cdot}$ is strongly weakened and its energy depends slightly on the presence or type of the functional group, being 11.7 ($\mathbf{2a}^{+\cdot}$), 8.9 ($\mathbf{2c}^{+\cdot}$), and 11.6 kcal mol^{-1} ($\mathbf{2d}^{+\cdot}$) (12.0 kcal mol^{-1} for the 6-31++G** basis set). With allowance for this, one could assume that radical cations $\mathbf{2a}$—$\mathbf{c}^{+\cdot}$ lose the benzhydryl fragment due to the direct dissociation of the C—S bond. However, another, earlier unconsidered fragmentation route with the S—X bond cleavage exists for the radical cations of sulfides containing the readily leaving X group, particularly, benzhydryl group, at the sulfur atom (Scheme 9). In this reaction route, the α-proton is first abstracted from

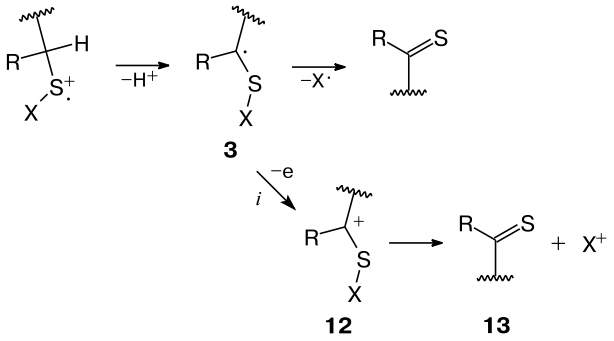
Scheme 8



R = $C(O)NH_2$ (**a**), COOH (**b**), CN (**c**)

the radical cation. Electroneutral radical **3** that formed is subjected to single-electron oxidation to carbocation **12** with a significantly destabilized C—X bond, which cleaves at the final stage to form carbocation X^+ and thiocarbonyl compound **13**. Evidently, the electron-withdrawing group, which substantially enhances the CH-acidity of the radical cation, in the second substituent at the sulfur atom plays an important role in this fragmentation mechanism.

Scheme 9



i. Main reaction route; X is readily leaving group containing carbocation center, *e.g.*, $CHPh_2$, R is electron-withdrawing group.

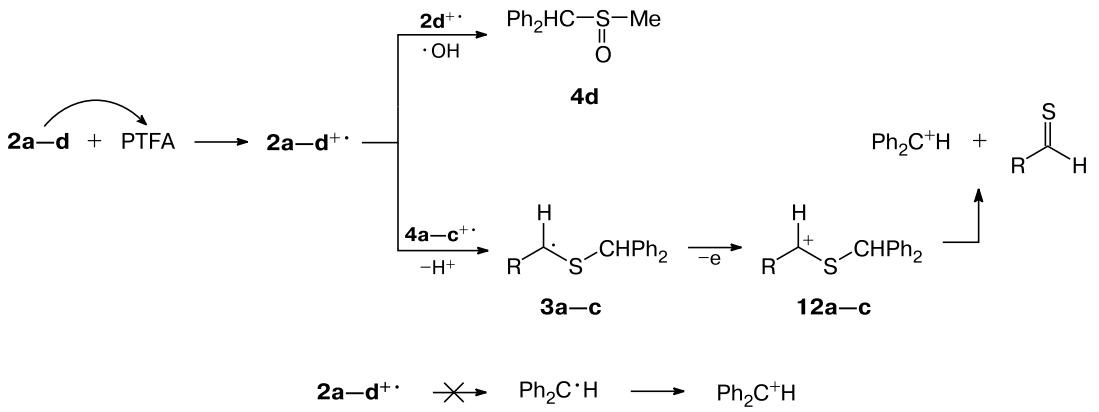
The quantum chemical calculation for cyano-containing radical $\mathbf{2c}^{+\cdot}$ shows that the transition from radical cations $\mathbf{2a—c}^{+\cdot}$ to the corresponding electroneutral radicals **3a—c** is accompanied by the strengthening of the $Ph_2HC—S$ bond (by approximately 17 kcal mol^{-1} for $\mathbf{2c}^{+\cdot}$). However, the further single-electron oxidation of radicals **3** to the corresponding carbocations **12** exerts an opposite effect. For cyano-containing radical **3c**, the effect is about 32 kcal mol^{-1} and, as a result, the $Ph_2CH—S$ bond in the corresponding carbocation turns out to be absolutely destabilized (BDE_{calc} = –7.1 kcal mol^{-1}) and much weaker than that in the initial radical cation. Nevertheless, carbocation **12c** is a minimum on the potential energy surface of the system. It follows from this that there is kinetic barrier in the way of the spontaneous cleavage of the S—X bond in cations **12** (Scheme 10).

It is most likely that the indirect C—S fragmentation of radical cations $\mathbf{2a—c}^{+\cdot}$ is the main route for their debenzhydrylation under the conditions of oxidative destruction of sulfides **2a—c**. This is indicated by the at first glance unexpected fact that benzhydryl sulfide **2d** containing no functional groups only sulfoxidates to sulfoxide **4d** in reaction with PTFA (79% yield) and forms no phenol **5**. So sharply different behavior of benzhydryl sulfide **2d** can be explained by the relatively low CH acidity of the corresponding radical cation $\mathbf{2d}^{+\cdot}$. As a result, the deprotonation of radical cation $\mathbf{2d}^{+\cdot}$ is slower than its transformation into sulfoxide **4d** (see Scheme 10).

A similar, although not so pronounced influence of the sulfide structure on the result of the reaction is observed for SET-sulfoxidation by some sulfoxidizing agents, for example, cytochrome P-450. This enzyme oxidizes thioanisole to a mixture of sulfoxide and sulfone due to the low CH-acidity of the primarily formed radical cation.[61] At the same time, cyanomethyl phenyl and phenacyl phenyl sulfides, whose radical cations are much stronger CH acids, under similar conditions form considerable amounts of the deprotonation products of the radical cations, namely, diphenyl sulfide and functionalized aldehydes RCHO (R = = CN, PhCO). Note that carbocations similar to cations **12** and bearing no readily leaving groups with carbocationic centers at the sulfur atom are intermediates of the anodic α-methoxylation and α-acetoxylation of sulfides.[62,63]

To conclude, the data presented indicate an important role of ET and free radical intermediates, in particular, radical cations of sulfides, in the sulfoxidation reactions involving PTFA.

Scheme 10



R = $C(O)NH_2$ (**a**), COOH (**b**), CN (**c**)

Experimental

^{1}H and ^{13}C NMR (in $CDCl_3$) and ESR spectra were obtained on Varian XL-300 and Bruker EMX 10/12 spectrometers, respectively. Quantum chemical calculations were performed using the Firefly program[64] partially based on algorithms of the Gamess program.[65] The energy characteristics are given with a correction to the vibrational energy using a scaling factor of 0.961.[66]

2-Benzhydrylsulfanylacetamide (**2a**) was synthesized using a known procedure.[23] Sodium carboxymethyl thiosulfate, sodium carbamoylmethyl thiosulfate, and sodium cyanomethyl thiosulfate were synthesized from the corresponding halogen derivatives and sodium thiosulfate using described procedures.[67,68]

X-ray diffraction analysis of compound 5. The crystals of compound **5** ($C_{45}H_{36}O$, M = 592.74) are monoclinic, space group $P2_1/c$, at T = 153 K: a = 24.7306(18) Å, b = 5.8559(4) Å, c = 23.1693(17) Å, β = 106.203(2)°, V = 3222.1(4) Å^3, Z = 4, d_{calc} = 1.222 g cm^{-3}, $F(000)$ = 1256, μ = 0.071 mm^{-1}. Unit cell parameters and intensities of 29 160 reflections (7021 independent reflections, R_{int} = 0.054) were measured on a Bruker SMART 1K CCD automated three-circle diffractometer (λ(Mo$K\alpha$) radiation, graphite monochromator, φ and ω scan modes). The structure was determined by a direct method and refined by the full-matrix least-squares method for F^2 in the anisotropic approximation for non-hydrogen atoms. The hydrogen atom of the hydroxy group was objectively localized by the Fourier syntheses and included into refinement with fixed positional and thermal (U_{iso}(H) = 1.5U_{eq}(O)) parameters. The positions of other hydrogen atoms were calculated geometrically and included into refinement with fixed positional (riding model) and thermal (U_{iso}(H) = 1.2U_{eq}(C)) parameters. The final values of R factors are R_1 = 0.045 for 4550 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.123 for all independent reflections, goodness-of-fit being 1.001. All calculations were performed using the SHELXTL program package.[67] The tables of atomic coordinates, bond lengths, bond and torsion angles, and anisotropic temperature parameters for compound **5** were deposited with the Cambridge Crystallographic Data Centre (CCDC 935910).

2-Benzhydrylsulfanylacetic acid (2b). Water (5 mL) and 98% HCOOH (20 mL) were added to a mixure of benzhydrol (3.68 g, 20 mmol) and sodium carboxymethyl thiosulfate (3.88 g, 20 mmol). The solution was heated to 70 °C and kept at this temperature until benzhydrol was completely dissolved. Then the reaction mixture was cooled, water (~50 mL) was added, and the solution was neutralized with aqueous ammonia. The precipitate was filtered off and dried. The yield was 5.12 g (93%); m.p. 126—128 °C (Pr^{i}OH)[69]. ^{1}H NMR, δ: 3.09 (s, 2 H, CH_2), 5.41 (s, 1 H, CH); 7.20—7.36 (m, 6 H, H_p, H_m of Ph groups); 7.40—7.46 (m, 4 H, H_o, Ph). Found (%): C, 69.58; H, 5.57; S, 11.95. $C_{15}H_{14}O_2S$. Calculated (%): C, 69.74; H, 5.46; S, 12.41.

2-Benzhydrylsulfanylacetonitrile (2c). Water (2.5 mL) and 98% HCOOH (10 mL) were added to a mixture of benzhydrol (1.84 g, 10 mmol) and sodium cyanomethyl thiosulfate (1.75 g, 10 mmol). The solution was heated to boiling and stirred. Then water (20 mL) was added, the solution was cooled, and the precipitate was filtered off, washed with water, and dried at ambient temperature. The yield was 2.24 g (94%); m.p. 78—79 °C (Pr^{i}OH) (*cf.* Ref. 70: 77—78 °C). ^{1}H NMR, δ: 3.08 (s, 2 H, CH_2); 5.43 (s, 1 H, CH); 7.24—7.48 (m, 10 H, 2 Ph). Found (%): C, 75.28; H, 5.43; N 5.66; S, 13.22. $C_{15}H_{13}NS$. Calculated (%): C, 75.28; H, 5.47; N, 5.85; S,13.40.

Benzhydryl methyl sulfide (2d). Iodomethane (1.24 mL, 2 mmol) and ethanol (6 mL) were added to a solution of sodium thiosulfate (5.96 g, 2 mmol) in water (5 mL). The reaction mixture was refluxed for 2 h, and EtOH was distilled off under reduced pressure. Benzhydrol 3.68 g, 2 mmol) in 20 mL of 98% HCOOH was added to the obtained solution of methyl thiosulfate, and the mixture was refluxed until a transparent solution was formed. The reaction mixture was cooled, and water (50 ml) was added. The organics was extracted with ethyl acetate, and the solvent was distilled off to obtained product **2d** as a colorless oil in a yield of 3.16 g (74%). The product was purified by chromatography on a column packed with Al_2O_3 (toluene as an eluent). ^{1}H NMR, δ: 1.97 (s, 3 H, Me); 5.04 (s, 1 H, CH); 7.15—7.46 (m, 10 H, 2 Ph) (almost the same chemical shifts are presented[71] for compound **2d**). Found (%): C, 78.26; H, 6.71; S, 14.89. $C_{14}H_{14}S$. Calculated (%): C, 78.46; H, 6.58; S, 14.96.

2,4,6-Tribenzhydrylphenol (5). ***A.*** A solution of PTFA (1.6 mL) in trifluoroacetic acid, prepared from 0.54 mL of 33% H_2O_2 (6 mmol of the reagent), was added for 10 min at ~10 °C with vigorous stirring to a solution of amide **2a** (1.62 g, 6.3 mmol) in trifluoroacetic acid (5 mL). Then water (40 mL) was added, and the solution was alkalized with aqueous ammonia. The viscous product that formed was separated, dried, and triturated with Pr^{i}OH (5 mL), and the precipitate formed was filtered off. The yield was 0.32 g (34%); m.p. 166—168 °C (MeCN) (*cf.* Ref. 45: 168 °C). ^{1}H NMR, δ: 4.49 (s, 1 H, OH); 5.23 (s, 1 H, 4-C<u>H</u>Ph$_2$); 5.63 (s, 2H, 2-C<u>H</u>Ph$_2$, 6-<u>C</u>HPh$_2$); 6.48 (s, 2 H, H(3), H(5)); 6.87—6.93 (m, 4 H, H_o, 4-CHPh); 7.00—7.06 (m, 8 H, 2-CHPh, 6-CHPh$_2$); 7.10—7.31 (m, 18 H, H_m, H_p, <u>C</u>HPh$_2$). ^{13}C NMR, δ: 51.15 (2-<u>C</u>HPh$_2$, 6-<u>C</u>HPh$_2$); 55.70 (4-<u>C</u>HPh$_2$); 125.89 (2C$_p$, 4-<u>C</u>HPh$_2$); 126.53 (4 C$_p$, 2-CHPh$_2$, 6-CHPh$_2$); 128.01 (2 C(2)); 128.43 (8 C$_m$, 2-CHPh$_2$, 6-CHPh$_2$); 129.11 (4 C$_m$, 4-CHPh$_2$); 129.23 (8 C$_o$, 2-CHPh$_2$, 6-CHPh$_2$); 130.06 (4 C$_o$, 4-CHPh$_2$); 130.58 (2 C(3), C(5)); 135.17 (C(4)); 142.54 (4 C$_{ipso}$, 2-CHPh$_2$, 6-CHPh$_2$); 144.40 (2 C$_{ipso}$, 4-CHPh$_2$); 149.75 (COH). MS (EI, 70 eV), m/z (I_{rel}(%)): 425 [M − CHPh$_2$]$^+$ (3), 347 [M — CHPh$_2$ — PhH]$^+$ (1), 269 [M − CHPh$_2$ − 2 PhH]$^+$ (2), 252 (2), 241 (5), 218 (12), 202 (4), 191 (5), 179 (21), 167 [CHPh$_2$]$^+$ (100), 152 (25), 115 (13), 105 (19), 91 [M − 3 CHPh$_2$]$^+$ (36), 77 [Ph]$^+$ (10), 40 (12). Found (%): C, 91.20; H, 6.23. $C_{45}H_{36}O$. Calculated (%): C, 91.22; H, 6.08.

A paramagnetic solution containing 2,4,6-tribenzhydrylphenoxyl radical is formed on treatment of phenol **5** in toluene with lead dioxide. The ESR spectrum of the phenoxyl radical (g ≈ ≈ 2.004270) is an incompletely resolved doublet of triplets of triplets with the hiperfine coupling constants 8.9 (methine proton of the *p*-benzhydryl group), 4.2 (methine protons of the *o*-benzhydryl groups), and 1.7 G (*m*-protons of the central benzene ring).

B. Acid **2b** was subjected to oxidative destruction under similar conditions. Phenol **5** was obtained in a yield of 0.16 g (17%) from 1.73 g (6 mmol) of this acid; m.p. 165 °C (Pr^{i}OH—MeOH—MeCN). The IR spectrum of the compound is identical to that of the samples obtained using method ***A***, the mixing probe shows no melting point depression.

C. In a similar synthesis 0.44 g (47%) compound **5**, m.p. 166—168 °C (Pr^{i}OH—MeOH), was obtained from 1.5 g (6 mmol) of nitrile **2c**.

D. A solution of peroxytrifluoroacetic acid (1.6 mL) in CF_3COOH, prepared according to the procedure described

above, was gradually added with vigorous stirring at the temperature about 10 °C to a solution of benzhydrol (1.16 g, 6.3 mmol) in CF_3COOH (5 mL). Then the reaction was carried out as in experiments ***A*—*C***. The yield of phenol **5** was 0.26 g (24%), m.p. 166—168 °C (MeCN).

Action of trifluoroacetic acid on amide 2a. Compound **2a** (0.40 g, 1.6 mmol) was treated with CF_3COOH (1.5 mL), and the mixture was kept for 10 min at 40 °C. Then water (30 mL) was added, and the precipitate was filtered off, washed with a solution of $NaHCO_3$, and dried. The intial compound was recovered in an amount of 0.39 g (97%), m.p. 108—110 °C (EtOAc—petroleum ether). The IR spectrum of the isolated substance is identical to that of the initial compound.

Oxidation of sulfoxide 4a with PTFA in trifluoroacetic acid. A solution of PTFA (0.8 mL) in trifluoroacetic acid, prepared according to the procedure presented above, was added to a solution of sulfoxide **4a** (0.86 g, 3.2 mmol) in CF_3COOH (2.5 mL) at ambient temperature. After 10 min, the reaction mixture was treated with water (30 mL) and aqeuous ammonia (10 mL). The viscous product was separated and dried. According to the TLC data, the product contained no phenol **5**. Then the obtained substance was triturated with 2-propanol—petroleum ether (1 : 1, 5 mL), and the precipitate was filtered off and recrystallized from ethanol. The yield of benzhydryl sulfanyl acetamide was 0.06 g (6.7%), m.p. 198—200 °C.[72] The mixing probe with authentic sample of the compound showed no melting point depression. The IR spectra of both samples are identical.

Oxidation of sulfide 2d to sulfoxide 4d with PTFA. A solution of PTFA (1.6 mL) in CF_3COOH, prepared according to the procedure described above, was added dropwise for ~10 min with vigorous stirring at 10 °C to a solution of benzhydrylmethyl sulfide (1.46 g, 6.3 mmol) in CF_3COOH (5 mL). After 0.5 h, the reaction mixture was diluted with water (40 mL) and alkalized with aqueous ammonia to a weakly alkaline pH value. The oil precipitated was extracted with chloroform. Then the extract was washed with water, and the solvent was evaporated. The formed oil crystallized slowly. The obtained crude product was washed with petroleum ether. The yield was 1.1 g (79%), m.p. 109—110 °C (Pr^iOH—petroleum ether) (*cf.* Ref. 73: 112—114 °C). ^1H NMR, δ, 2.38 (s, 3 H, Me); 4.75 (s, 1 H, CH); 7.30—7.50 (m, 10 H, 2 Ph).[73] Found (%): C, 73.00; H, 6.31; S, 13.75. $C_{14}H_{14}OS$. Calculated (%): C, 73.01; H, 6.13; S, 13.92.

Oxidation of amide 2a with nitrosonium perchlorate. Amide **2a** (2.57 g, 10 mmol) was added at 0—10 °C to a vigorously stirred suspension of nitrosonium perchlorate (2.76 g, 20 mmol) in acetonitrile (6 mL). The mixture was kept at ambient temperature for 24 h and treated with water (50 mL). The precipitate of acetamide **10** was filtered off, dried, and purified by chromatography on alumina using chloroform as an eluent (R_f 0.5). The yield was 1.1 g (46%), m.p. 148—150 °C (PhMe) (*cf.* Ref. 74: 149 °C). ^1H NMR, δ: 2.06 (s, 1 H, CH_3); 6.21 (d, 1 H, CH, J_{vic} = = 7.6 Hz); 6.40 (strongly br.d, 1 H, NH); 7.18—7.36 (m, 10 H, 2 Ph). Upon deuteration, the signal from the proton of the NH group at δ 6.40 disappears and the doublet of the proton of the CH group gains the shape of a singlet. Found (%): C, 80.12; H, 6.80; N, 6.20. $C_{15}H_{15}NO$. Calculated (%): C, 79.97; H, 6.71; N, 6.22.

Oxidation of nitrile 2c with nitrosonium perchlorate. The reaction was conducted similarly using nitrile **2c** (2.55 g, 10.7 mmol), nitrosonium perchlorate (2.76 g, 21.4 mmol), and acetonitrile (15 mL). Acetamide **10** was obtained in a yield of 0.9 g (37%), m.p. 148—150 °C (PhMe). The mixing probe with the sample from the previous experiment shows no melting point depression.

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References

1. K. A. Bilevich, O. Yu. Okhlobystin, *Russ. Chem. Rev.*, 1968, **37**, 954.
2. A. S. Morkovnik, *Russ. Chem. Rev.*, 1988, **57**, 144.
3. L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, New York, 1987, 234 pp.
4. J. H. Ridd, *Chem. Soc. Rev.*, 1991, **20**, 149.
5. Z. V. Todres, *Ion-Radical Organic Chemistry. Principles and Applications*, 2nd ed., CRC Press, Taylor and Francis Group, 2009, 475 pp.
6. K. K. Kalninsh, *Chem. Phys. Lett.*, 1981, **79**, 427.
7. A. Peluso, G. Del Re, *J. Phys. Chem.*, 1996, **100**, 5303.
8. X. F. Xu, S. Zilberg, Y. Haas, *J. Phys. Chem. A*, 2010, **114**, 4924.
9. E. J. Behrman, J. O. Edwards, *Phys. Org. Chem.*, 1967, **4**, 93.
10. M. A. P. Dankleff, C. Ruggero, J. O. Edwards, H. Y. Pyun, *J. Am. Chem. Soc.*, 1968, **90**, 3209.
11. D. G. Pobedimskii, A. L. Buchachenko, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1968, **17**, 2579 [*Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1968, 2720].
12. Y. Watanabe, T. Iyanagi, S. Oae, *Tetrahedron Lett.*, 1980, **21**, 3685.
13. W. Adam, N. E. Gonzalez, *Tetrahedron*, 1991, **47**, 3773.
14. E. Baciocchi, O. Lanzalunga, F. Marconi, *Tetrahedron Lett.*, 1994, **35**, 9771.
15. E. Bosch, J. K. Kochi, *J. Chem. Soc., Perkin Trans. 1,* 1995, 1057.
16. W. Adam, J. E. Argüello, A. B. Pecécory, *J. Org. Chem.*, 1998, **63**, 3905.
17. E. Baciocchi, M. F. Gerini, O. Lanzalunga, A. Lapi, M. Grazia Lo Piparo, *Org. Biomol. Chem.*, 2003, **1**, 422.
18. S. M. Bonesi, M. Fagnoni, A. Albini, *J. Sulfur Chem.*, 2008, **29**, 367.
19. H. Lund, O. Hammerich, *Organic Electrochemistry*, Marcel Dekker, New York—Basel, 4th ed., 2001, p. 991.
20. M. A. P. Dankleff, R. Curci, J. O. Edwards, H. Pyun, *J. Am. Chem. Soc.*, 1968, **90**, 3209.
21. R. D. Bach, in *The Chemistry of Peroxides. The Chemistry of Functional Groups*, *S. Patai Series*, Ed. Z. Rappoport, Vol. **2**, Part 1, Wiley-VCH Verlag GmbH, Weinheim, 2006, 1.
22. J. Chu, B. L. Trout, *J. Am. Chem. Soc.*, 2004, **126**, 900.
23. A. V. Bicherov, A. R. Akopova, V. I. Spiglazov, A. S. Morkovnik, *Russ. Chem. Bull.* (*Int. Ed.*), 2010, **59**, 91

[*Izv. Akad. Nauk*, *Ser. Khim*., 2010, 92] and references cited therein.
24. C. G. Overberger, R. W. Cummins, *J. Am. Chem. Soc.*, 1953, **75**, 4250.
25. G. Modena, P. E. Todesco, *J. Chem. Soc*., 1962, 4920.
26. T. M. Ramond, S. J. Blanksby, S. Kato, V. M. Bierbaum, G. E. Davico, R. L. Schwartz, W. C. Lineberger, G. B. Ellison, *J. Phys. Chem. A*, 2002, **106**, 9641.
27. S. J. Blanksby, T. M. Ramond, G. E. Davico, M. R. Nimlos, S. Kato, V. M. Bierbaum, W. C. Lineberger, G. B. Ellison, M. Okumura, *J. Am. Chem. Soc*., 2001, **123**, 9585.
28. L. S. Wang, C. F. Ding, X. B. Wang, J. B. Nicholas, B. Nicholas, *Phys. Rev. Lett*., 1998, **81**, 2667.
29. H. Shi, Z. Zhang, Y. Wang, *J. Mol. Catal. A: Chem.*, 2005, **238**, 13.
30. E. T. McBee, G. W. Calundann, C. J. Morton, T. Hodgins, E. P. Wesseler, *J. Org. Chem.*, 1972, **37**, 3140.
31. E. H. Prilezhaeva, *Reaktsiya Prilezhaeva. Elektrofil´noe okislenie* [*Prileschajew Reaction. Electrophilic Oxidation*], Nauka, Moscow, 1974, p. 34 (in Russian).
32. V. G. Nenajdenko, A. E. Gavryushin, E. S. Balenkova, *Tetrahedron Lett.*, 2001, **42**, 4397.
33. J. Lou, J. Chang, J. Jorgensen, D. M. Lemal, *J. Am. Chem. Soc*., 2002, **124**, 15302.
34. U. Frommer, V. Ulrich, *Z. Naturforsch.*, 1971, **26**, 322.
35. N. C. Deno, L. A. Messer, *J. Chem. Soc., Chem. Commun.*, 1976, 1051.
36. L. V. Gurvich, G. Z. Karachevtsev, V. N. Kondrat´ev, Yu. A. Lebedev, V. A. Medvedev, V. K. Potapov, Yu. S. Khodeev, *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* [*Energies of Chemical Bond Cleavage. Ionization Potentials and Electron Affinity*], Nauka, Moscow, 1974, p. 255 (in Russian).
37. G. Merényi, J. Lind, L. Engman, *J. Phys. Chem*., 1996, **100**, 8875.
38. E. Baciocchi, M. F. Gerini, P. J. Harvey, O. Lanzalunga, S. Mancinelli, *Eur. J. Biochem*., 2000, **267**, 2705.
39. E. Baciocchi, T. Del Giacco, M. F. Gerini, O. Lanzalunga, *Org. Lett.*, 2006, **8**, 641.
40. T. Fuchigami, K. Yamamoto, Y. Nakagawa, *J. Org. Chem*., 1991, **56**, 137.
41. R. S. Glass, in *Topics in Current Chemistry*, Springer, Berlin—Heidelberg, 1999, **205**, p. 1.
42. E. Baciocchi, M. Bietti, O. Lanzalunga, *J. Phys. Org. Chem.*, 2006, **19**, 467.
43. D. M. Camaioni, J. T. Bays, W. J. Shaw, J. C. Linehan, J. C. Birnbaum, *J. Org. Chem.*, 2001, **66**, 789.
44. Van Alphen, *J. Rec. Trav. Chim. Pays-Bas Belg.*, 1927, **46**, 799; *Chem. Abstr.*, 1928, **22**, 3405.
45. E. Müller, A. Rieker, K. Scheffler, *Justus Liebigs Ann. Chem.*, 1961, **645**, 92.
46. M. Freccero, R. Gandolfi, M. Sarzi-Amadè, A. Rastelli, *J. Org. Chem.*, 1999, **64**, 3853.
47. M. Freccero, R. Gandolfi, M. Sarzi-Amadè, A. Rastelli, *J. Org. Chem.*, 2004, **69**, 7479.
48. R. Criegge, *Chem. Ber.*, 1944, **77**, 722.
49. R. Criegge, *Lieb. Ann. Chem.*, 1948, **560**, 127.
50. P. A. Krasutsky, I. V. Kolomitsyn, S. G. Krasutsky, P. Kiprof, *Org. Lett.*, 2004, **6**, 2539.
51. A. Soriano, E. Silla, I. Tunon, *J. Chem. Phys.*, 2002, **116**, 6102.
52. I. Photaki, J. Taylor-Papadimitriou, C. Sakarellos, P. Mazarakis, L. Zervas, *J. Chem. Soc., C*, 1970, 2683.
53. P. Buckus, *Russ. Chem. Rev.*, 1983, **52**, 1203.
54. T. Masaki, K. Yuko, U. Eijiro, I. Katsuyoshi, T. Atsushi, Sh. Seiji, *Bioorg. Med. Chem*., 1998, **6**, 1641.
55. A. R. Groenhof, A. W. Ehlers, K. Lammertsma, *J. Phys. Chem. A,* 2008, **112**, 12855.
56. M. Freccero, R. Gandolfi, M. Sarzi-Amadé, A. Rastelli, *Tetrahedron*, 2001, **57**, 9843.
57. J. Grafenstein, A. M. Hjerpe, D. Cremer, E. Kraka, *J. Phys. Chem.*, 2000, **104**, 1748.
58. R. D. Bach, O. Dmitrenko, *J. Org. Chem*., 2010, **75**, 3705.
59. O. A. Reutov, A. L. Kurts, K. P. Butin, *Organicheskaya khimiya. Klassicheskii uchebnik dlya universitetov* [*Organic Chemistry. Classical Textbook for Universities*], Vol. **4**, Binom, Moscow, 2010, p. 94 (in Russian).
60. P. D. Sullivan, *J. Am. Chem. Soc*., 1968, **90**, 3618.
61. Y. Watanabe, T. Numata, T. Iyanagi, S. Oae, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1163.
62. M. Kimura, K. Koie, Sh. Matsubara, Y. Sawaki, H. Iwamura, *Chem. Commun.*, 1987, 122.
63. E. Baciocchi, C. Rol, E. Scamosci, G. V. Sebastiani, *J. Org. Chem.*, 1991, **56**, 5498.
64. A. A. Granovsky, http://classic.chem.msu.su/gran/firefly/index.html.
65. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
66. K. K. Irikura, R. D. Johnson, III, R. N. Kacker, *J. Phys. Chem. A*, 2005, **109**, 8430.
67. G. M. Sheldrick, *Acta Crystallogr., Sect A: Found. Crystallogr.*, 2008, **64**, 112.
68. W. O. Foye, J. M. Kauffman, *J. Pharm. Sci.*, 1968, **57**, 1614.
69. T. Prisinzano, J. Podobinski, K. Tidgewell, M. Luo, D. Swenson, *Tetrahedron: Asymmetry*, 2004, **15**, 1053.
70. Ger. Pat., DE2642511; http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=DE&NR=2642511A1&KC=A1&FT=D&date=19770414&DB=EPODOC&locale=en_EP.
71. H. Ikehira, Sh. Tanimoto, T. Oida, M. Okano, *J. Org. Chem.*, 1983, **48**, 1120.
72. N. Chatterjie, J. P. Stables, H. Wang, G. J. Alexander, *Neurochem. Res.*, 2004, **29**, 1481.
73. I. D. Etwistle, *J. Chem. Soc., C*, 1967, 302.
74. *Dictonary of Organic Compounds*, 5th ed., New York—London—Toronto, **2**, 2323.

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