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Generation of Cyclopropanediazonium and Its Chemical Transformations in the Presence of Phenol*

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Abstract—The reaction of phenol with cyclopropanediazonium ion generated *in situ* from *N*-cyclopropyl-*N*-nitrosourea by the action of K_2CO_3 or Cs_2CO_3 was studied. The main reaction pathway is diazo coupling of cyclopropanediazonium with phenol to give 4-(cyclopropyldiazenyl)phenol, and only traces of isomeric 2-(cyclopropyldiazenyl)phenol were formed. The reaction was accompanied by partial denitrogenation of the diazonium ion with formation of cyclopropyl and allyl cations which gave rise to a number of by-products. All transformation products were characterized by the ^1H and ^{13}C NMR spectra with detailed signal assignment.

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Our recent studies [2, 3] have shown that cyclopropanediazonium ion (**I**) generated *in situ* in the presence of active azo components, e.g., naphthalen-2-ol, gives rise to the corresponding cyclopropyldiazenylarenes in high yield. The observed behavior of intermediate **I** is not typical of aliphatic diazonium ions [4] which usually readily lose nitrogen molecule to form the corresponding carbocations.

However, the number of compounds capable of reacting with ion **I** to give diazo coupling products remains strongly limited. In particular, reasons for the failure of **I** to form diazo coupling products with such active substrates as aniline and phenol are so far unclear. For example, Feldman and Kirmse [5] performed a detailed study on the chemical transformations of intermediate **I** and found that neither phenol nor phenoxide ion gave diazo coupling products with cyclopropanediazonium; on the other hand, the authors did not specify transformation products of diazonium ion **I**. It should be noted that, depending on the nature of the trapping species, cyclopropanediazonium (**I**) can react along several pathways with both retention of the diazo group and loss of nitrogen molecule [6].

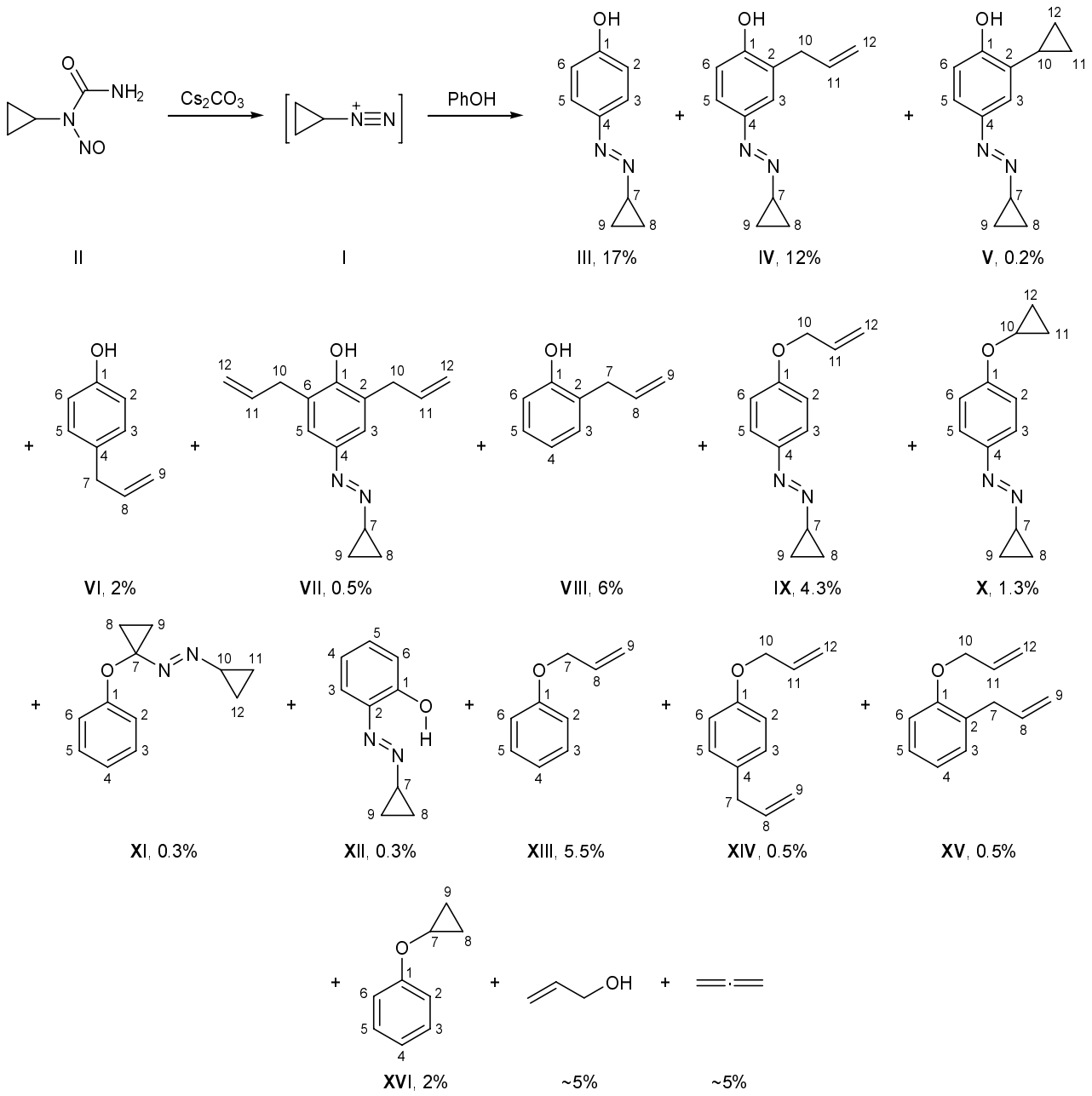
In the present work we studied in detail chemical transformations of ion **I** generated *in situ* from *N*-cyclopropyl-*N*-nitrosourea (**II**) in the presence of phenol, isolated and identified products of these transformations, and defined the main reaction pathways.

Decomposition of nitrosourea **II** is usually promoted by the action of such bases as MeONa, LiOH, KOH, and K_2CO_3 in methylene chloride, methanol, or their mixtures. It is advisable to use K_2CO_3 containing ~20% of water and perform the reaction at 0–7°C in methylene chloride [3]. Our first experiments on reaction of phenol with ion **I** generated *in situ* under the above conditions showed that a complex mixture of products is formed [2]. Presumably, diazonium ion **I** readily loses nitrogen molecule with formation of allyl and cyclopropyl cations (see, e.g., [7]) capable of alkylating the substrate. In the reaction with active traps, e.g., naphthalen-2-ol, no such alkylation products are formed, and the yield of the diazo coupling product attains 90% [2].

In order to optimize the reaction conditions, we performed a series of experiments where different bases were added to a solution of *N*-cyclopropyl-*N*-nitrosourea (**II**) and phenol in CD_2Cl_2 or CD_3OD, cooled to ~5°C, and the progress of the reaction was monitored by ^1H NMR spectroscopy. Decomposition of compound **II** by the action of a suspension of moist K_2CO_3 in CD_2Cl_2 in the presence of phenol was accompanied by appearance of strong signals in the ^1H NMR spectrum at δ 0.7–0.8, 1.3–1.5, and 3.6–3.8 ppm, which are typical of a monosubstituted cyclopropane ring. In addition, the region δ 3.3–4.6 ppm contained no less than 5 doublets of triplets corresponding to the methylene fragment of an allyl system (CH_2=CHC**H**$_2$X). The singlet at δ 4.69 ppm belongs to allene [8] which is

* For preliminary communication, see [1].

Scheme 1.



formed from diazonium ion **I** in ~10% yield as a result of deprotonation and elimination of nitrogen molecule, followed by cyclopropylidene–allene rearrangement. The complete decomposition of compound **II** required 8 h, though the reaction in the presence of other substrates, e.g., naphthalen-2-ol, was generally complete in 1.5–2 h [2].

When CD_2Cl_2 was replaced by CD_3OD, the reaction was complete in 5–10 min, and the products were almost exclusively 2-deutero-1-(trideuteromethoxy)-prop-2-ene and 1-deutero-1-(trideuteromethoxy)cyclopropane; they were formed from ion **I** and CD_3OD according to the mechanism proposed in [7]. Obviously, deuterated methanol successfully competes with phenol, so that the latter has no chance to react with diazonium ion **I**. We can conclude that methylene chloride is preferred for the diazo coupling reaction.

Insofar as the decomposition of **II** by the action of K_2CO_3 in CH_2Cl_2 in the presence of phenol was slow and nonselective, we tried cesium carbonate as a base. In this case, approximately a half of intermediate **I** reacted with phenol to give products containing a cyclo-

propane ring, while the other part of **I** was converted into allyl cation. Although the major products were almost the same as in the reaction with K_2CO_3, the amount of minor products was considerably smaller, and the yield of allene decreased by half. Moreover, in the presence of cesium carbonate the reaction time shortens to 10 min; therefore, Cs_2CO_3 is more advantageous than K_2CO_3.

The product mixture was separated by column chromatography on silica gel using gradient elution with toluene to toluene–ethyl acetate (10 : 1). Several fractions were collected. One of these contained excess unreacted phenol, another fraction contained the target product, 4-(cyclopropyldiazenyl)phenol (**III**), and the remaining fractions were complex mixtures of products. Each of the latter was subjected to additional chromatographic separation on silica gel; depending on the nature of compounds to be separated, toluene, petroleum ether–toluene, cyclohexane–toluene, and toluene–ethyl acetate at different ratios (see Experimental) were used as eluent. As a result, we isolated 14 compounds, 8 of which were not reported previously. Almost all products obtained from ion **I** and phenol may be divided into two main groups, the first of which includes *ortho*- and/or *para*-substituted phenols, and the second, *O*-allyl and *O*-cyclopropyl derivatives (Scheme 1; the compounds are numbered in the order of increasing R_f value on silica gel).

Compound **III** turned out to be adsorbed most efficiently by the silica surface. After first chromatographic separation, followed by recrystallization from pentane–benzene (3 : 10), it was isolated as large yellow crystals which displayed a broad absorption band at λ_{max} 379 nm (with a shoulder extending to the visible region) in the UV spectrum. The intensity of that band is quite low (ε = 750), while the corresponding band for the diazo adducts of ion **I** with naphthalen-2-ol is characterized by a molar absorption coefficient of about 6000 [6]; presumably, the reason is the longer conjugation chain in cyclopropyldiazenylnaphthols.

In the ^{1}H NMR spectrum of **III**, protons in the cyclopropane ring characteristically give rise to a triplet of triplets at δ 3.67 ppm (7-H) and two multiplets at δ 1.46 (*trans*-8-H, *trans*-9-H) and 1.22 ppm (*cis*-8-H, *cis*-9-H). In the downfield region we observed an *AA'BB'* system typical of a *para*-substituted benzene ring (two multiplets at δ 6.84 and 7.56 ppm). The two-dimensional NOESY spectrum revealed coupling between the hydroxy proton (δ 5.64 ppm, br.s) and protons in the *ortho* position with respect to the hydroxy group. Therefore, the multiplet at δ 6.84 ppm was assigned to 2-H and 6-H. For detailed assignment of signals in the ^{1}H and ^{13}C NMR spectra, see Experimental.

Compound **III** can be stored for a long time at 20°C in the absence of oxygen; however, like most other diazo adducts isolated in the present work, compound **III** undergoes slow oxidation on exposure to air. Taking this into account, all the isolated diazo coupling products were subjected to additional purification just before analysis to obtain satisfactory analytical data.

Electrophilic substitution of hydrogen in the phenol molecule by diazonium ion **I** and allyl cation (the sequence of these processes is not discussed here) leads to 2-allyl-4-(cyclopropyldiazenyl)phenol (**IV**) which was isolated as thin yellow needles. The appearance of the cyclopropane fragment of **IV** in the ^{1}H and ^{13}C NMR spectra was similar to that observed for compound **III**. The allyl CH_2 group in the *ortho* position with respect to the hydroxy group gave a doublet of triplets at δ 3.45 ppm in the ^{1}H NMR spectrum and a signal at δ_C 34.47 ppm in the ^{13}C NMR spectrum. Isomeric 2-cyclopropyl-4-(cyclopropyldiazenyl)phenol (**V**) is characterized by a higher R_f value as compared to allylphenol **IV**. In the ^{1}H NMR spectrum of **V**, signals from protons of the cyclopropane ring attached to the aromatic ring were located at δ 1.83 (1H), 1.00 (2H), and 0.70 ppm (2H); the cyclopropyldiazenyl group gave signals at δ 3.65, 1.47, and 1.22 ppm (cf. the data for compound **III**).

Among cyclopropyldiazenylphenols we also identified a double-allylation product, 2,6-diallyl-4-(cyclopropyldiazenyl)phenol (**VII**). Its ^{1}H NMR spectrum was fairly simple due to its symmetric structure (the two allyl groups and two aromatic protons are equivalent). The allyl CH_2 groups gave rise to a doublet of triplets at δ 3.44 ppm, which is typical of *o*-allylphenols.

The formation of appreciable amounts of 4-allylphenol (**VI**) and 2-allylphenol (**VIII**) implies that conventional electrophilic alkylation occurs; unlike diazo coupling, allylation at the *ortho* position predominates: the **VI**/**VIII** isomer ratio is about 1 : 3. The ^{1}H and ^{13}C NMR spectra of isomeric allyl phenols **VI** and **VIII** are consistent with published data [9–11]. Although we failed to purify compound **VI** from initial phenol (their R_f values were very similar), we nevertheless succeeded in reliably assigning signals of **VI** in the NMR spectra.

One of the isolated fractions contained a compound whose R_f value was slightly greater than that of 2-allylphenol (**VIII**). This compound showed in the ^{1}H NMR spectrum signals typical of a cyclopropane ring attached to an aromatic ring. Taking into account the presence of a triplet of triplets at δ 1.81 ppm (CH, $^3J_{cis}$ = 8.2, $^3J_{trans}$ = 5.4 Hz) and two multiplets at δ 0.97 and 0.65 ppm (CH_2CH_2), the product was assumed to have the structure of 2-cyclopropylphenol; however, its amount was too small (~1 mg) to perform unambiguous identification.

The other group of compounds formed in the reaction of ion **I** with phenol includes aryl allyl and aryl cyclopropyl ethers. Specifically, 1-allyloxy-4-(cyclopropyldiazenyl)benzene (**IX**) and 1-(cyclopropyldiazenyl)-4-cyclopropyloxybenzene (**X**) were formed in appreciable amounts (4.3 and 1.3%, respectively). These compounds are likely to originate from cyclopropyldiazenylphenol **III** via alkylation of the hydroxy group with allyl or cyclopropyl cation. The reverse reaction sequence (O-alkylation of phenol followed by diazo coupling) seems to be improbable, for successful diazo coupling requires the presence of a free hydroxy group in the azo component (see, e.g., [12]). In fact, by special experiment we showed that methoxybenzene is incapable of trapping ion **I** under analogous conditions.

Despite a small difference in the R_f values of isomers **IX** and **X**, we succeeded in isolating two fractions (by preparative thin-layer chromatography), one of which was enriched in isomer **X** (ratio **IX**:**X** = 2:3), and the other, in **IX** (ratio **IX** : **X** = 3 : 1). The ^{1}H and ^{13}C NMR spectra of these isomer mixtures allowed us to unambiguously assign signals to both isomers. In addition, satisfactory elemental analyses were obtained for the second fraction. In the ^{1}H NMR spectrum, signals from protons in the cyclopropyldiazenyl fragment of isomers **IX** and **X** coincided, while the cyclopropyloxy group in ether **X** gave rise to multiplets at δ 0.80 (CH_2CH_2) and 3.77 ppm (CH). The latter signal is displaced by 0.11 ppm downfield relative to the signal from the corresponding proton in the cyclopropyldiazenyl group. An analogous downfield shift is observed in the ^{13}C NMR spectrum: the cyclopropane carbon atoms attached to oxygen and nitrogen are characterized by chemical shifts of δ_C 51.21 and 50.47 ppm, respectively.

Among the identified compounds, the formation of 1-cyclopropyl-2-(1-phenoxycyclopropyl)diazene (**XI**) was the most difficult to rationalize. The ^{1}H and ^{13}C NMR spectra of **XI** contained signals from the phenoxy group, cyclopropyldiazenyl fragment, and 1,1-disubstituted cyclopropane ring; the quaternary carbon atom in the latter resonated at δ_C 82.42 ppm.

Apart from cyclopropyldiazenyl derivatives **III**–**V**, **VII**, **IX**, and **X** which were formed via attack by diazonium ion **I** at the *para* position of phenol molecule, we isolated a small amount of 2-(cyclopropyldiazenyl)-phenol (**XII**). This result is consistent with the data of [13] for the diazo coupling of benzenediazonium with phenol: the fraction of the corresponding *ortho* isomer was about ~1%. The hydroxy proton in phenol **XII** is involved in intramolecular hydrogen bond with one nitrogen atom of the diazenyl group, and it appears in the ^{1}H NMR spectrum as a broadened signal at δ 11.7 ppm; this pattern is typical of aromatic azo compounds having a hydroxy group in the *ortho* position with respect to the –N=N– moiety [2]. Intramolecular hydrogen bonding hampers adsorption of phenol **XII** on the silica surface, as compared to its *para*-substituted isomer **III**, and exerts a considerable stabilizing effect; as a result, compound **XII** was the only isolated product which was fairly stable to oxidation on exposure to air.

Allyl aryl ethers **XIII**–**XV** and phenyl cyclopropyl ether **XVI** are very similar in chemical nature; therefore, we failed to isolate them as individual substances by chromatography on silica gel. The yields were estimated on the basis of the ^{1}H NMR data. Using two-dimensional COSY and HSQC techniques we refined the assignment of some signals of previously reported compounds **XIII**, **XV**, and **XVI** [11, 14–16] and specified ^{1}H and ^{13}C signals belonging to compound **XIV**.

A doublet of triplets at δ 4.15 ppm in the ^{1}H NMR spectrum of the product mixture was attributed to the OCH_2 group of allyl alcohol (the same signal is observed in the spectrum of an authentic sample of allyl alcohol). Taking into account its intensity, the yield of allyl alcohol was estimated at ~5%. Allyl alcohol can be formed by reaction of allyl cation with water which is present in cesium carbonate and is liberated by decomposition of nitrosourea **II**.

Thus we have identified all main products formed in the reaction of phenol with cyclopropanediazonium (**I**) generated *in situ* from *N*-cyclopropyl-*N*-nitrosourea (**II**). The overall yield of the identified products is ~62%. The poor yields of the isolated compounds (or their mixtures) may partially result from oxidation of the diazo adducts and high volatility of those containing no diazenyl fragment (they could be lost in part during evaporation of fractions obtained by chromato-

graphic separation). The main reaction pathway is diazo coupling with formation of 4-(cyclopropyldiazenyl)phenol (**III**). However, phenol is a considerably less reactive azo component than naphthalen-1- and -2-ols, so that the contribution of elimination of nitrogen molecule from diazonium ion **I** to give allyl and cyclopropyl cations becomes appreciable. These cations give rise to a broad spectrum of C- and O-alkylation products from compounds present in the reaction mixture. We cannot rule out that the major product, 4-(cyclopropyldiazenyl)phenol (**III**), reacts with allyl and cyclopropyl cations more actively than does initial phenol.

EXPERIMENTAL

The ^{1}H NMR spectra were measured on a Bruker AM-300 spectrometer (300 MHz) from solutions in $CDCl_3$ containing 0.05% of tetramethylsilane as internal reference. The ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer (62.9 MHz) from solutions in $CDCl_3$ (δ_C 77.1 ppm); two-dimensional COSY, NOESY, and HSQC experiments were performed on a Bruker DRX-500 instrument (500 MHz). The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer with direct sample admission into the ion source. The UV spectra were measured on a Specord M-40 spectrometer. The elemental compositions were determined on a Perkin–Elmer Series II 2400 CHN analyzer.

N-Cyclopropyl-*N*-nitrosourea (**II**) was prepared according to the procedure described in [17]. Potassium carbonate of chemically pure grade contained ~20% of water; phenol of analytical grade and anisole and Cs_2CO_3 with a purity of 99% were used. Analytical and preparative thin-layer chromatography was performed on silica gel plates (Silufol, Merck). Silica gel 60 (0.040–0.063 mm, Merck) was used for column chromatography.

General procedure for carrying out reactions in NMR ampules. A solution of 6.5 mg (0.05 mmol) of *N*-cyclopropyl-*N*-nitrosourea (**II**) and 6.6 mg (0.07 mmol) of phenol in 0.4 ml of CD_2Cl_2 or CD_3OD was cooled to 5–7°C, and 17.3 mg (0.1 mmol) of K_2CO_3 or 32.6 mg (0.1 mmol) of Cs_2CO_3 was added. The progress of the reaction was monitored by ^{1}H NMR at 5°C; the results were discussed above.

Decomposition of *N*-cyclopropyl-*N*-nitrosourea (II) by the action of cesium carbonate in the presence of phenol. A solution of 1.14 g (8.8 mmol) of nitrosourea **II** and 1.15 g (12.3 mmol) of phenol in 30 ml of methylene chloride was cooled to 5–8°C, and 5.86 g (18 mmol) of cesium carbonate was added under stirring. Vigorous gas evolution was observed over a period of 10 min. The mixture was stirred for an additional 40 min, maintaining the temperature at 5–8°C. The precipitate was filtered off and washed with methylene chloride (2 × 10 ml), and the solvent was distilled off under reduced pressure (100 mm) to obtain 1.73 g of an orange–brown semicrystalline material which was dissolved in a minimal amount of toluene and subjected to column chromatography on silica gel. The column was eluted first with toluene and then with toluene–ethyl acetate mixtures with increasing concentration of the latter up to a PhMe–EtOAc ratio of 10 : 1. Individual compounds were isolated from fractions containing several products by additional chromatography and crystallization (see below).

4-(Cyclopropyldiazenyl)phenol (III) was isolated by recrystallization from pentane–benzene (3 : 1). Yield 241 mg (17%), yellow prisms, mp 93–94°C. UV spectrum (Et_2O): λ_{max} 379 nm (ε = 750). ^{1}H NMR spectrum, δ, ppm: 7.56 m (2H, 3-H, 5-H), 6.84 m (2H, 2-H, 6-H), 5.64 br.s (1H, OH), 3.67 t.t (1H, 7-H, J_{trans} = 3.4, J_{cis} = 7.1 Hz), 1.46 m (2H, *trans*-8-H, *trans*-9-H, J_{trans} = 3.4 Hz), 1.22 m (2H, *cis*-8-H, *cis*-9-H, J_{cis} = 7.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 158.22 (C^1), 145.18 (C^4), 123.71 (C^3, C^5), 115.95 (C^2, C^6), 50.23 (C^7), 9.89 (C^8, C^9). Mass spectrum, *m*/*z* (I_{rel}, %): 162 (14) $[M]^+$, 134 (3) $[M - N_2]^+$, 122 (9) $[M - C_3H_4]^+$, 107 (29) $[M - C_3H_5N]^+$, 93 (38) $[M - C_3H_5N_2]^+$, 39 (100). Found, %: C 66.75; H 6.40; N 17.38. $C_9H_{10}N_2O$. Calculated, %: C 66.65; H 6.21; N 17.27.

2-Allyl-4-(cyclopropyldiazenyl)phenol (IV) was isolated by double column chromatography (toluene to toluene–ethyl acetate, 20 : 1), followed by recrystallization from pentane–benzene (5 : 1). Yield 106 mg (12%), thin yellow needles, mp 89–90°C. ^{1}H NMR spectrum, δ, ppm: 7.45 m (2H, 3-H, 5-H), 6.84 m (1H, 6-H), 6.03 m (1H, 11-H, $J_{10,11}$ = 6.4, $J_{11,12\text{-}cis}$ = 9.5, $J_{11,12\text{-}trans}$ = 17.6 Hz), 5.38 br.s (1H, OH), 5.22–5.14 m (2H, *cis*-12-H, *trans*-12-H), 3.67 t.t (1H, 7-H, J_{trans} = 3.3, J_{cis} = 7.0 Hz), 3.45 d.t (2H, 10-H, $J_{10,12\text{-}trans} \approx J_{10,12\text{-}cis}$ = 1.6, $J_{10,11}$ = 6.4 Hz), 1.47 m (2H, *trans*-8-H, *trans*-9-H, J_{trans} = 3.3 Hz), 1.22 m (2H, *cis*-8-H, *cis*-9-H, J_{cis} = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 156.25 (C^1), 145.34 (C^4), 135.96 (C^{11}), 127.06 (C^2), 123.54 (C^3), 122.06 (C^5), 116.29 (C^{12}), 115.55 (C^6), 50.19 (C^7), 34.47 (C^{10}), 9.67 (C^8, C^9). Mass spectrum, *m*/*z* (I_{rel}, %): 202 (74) $[M]^+$, 174 (10) $[M - N_2]^+$, 162 (28) $[M - C_3H_4]^+$, 147 (31) $[M - C_3H_5N]^+$, 133 (30)

$[M - C_3H_5N_2]^+$, 39 (100). Found, %: C 71.29; H 7.01; N 13.80. $C_{12}H_{14}N_2O$. Calculated, %: C 71.26; H 6.98; N 13.85.

2-Cyclopropyl-4-(cyclopropyldiazenyl)phenol (V) was isolated as described above for compound **IV** and was then additionally purified by preparative thin-layer chromatography on silica gel using toluene–ethyl acetate (40:1) as eluent. Yield 2 mg (0.2%). Yellow oily substance with a purity of 90–95% (according to the ^{1}H NMR data). ^{1}H NMR spectrum, δ, ppm: 7.45 d.d (1H, 5-H, $J_{3,5}$ = 2.5, $J_{5,6}$ = 8.5 Hz), 7.40 d.d (1H, 3-H, $J_{3,10}$ = 0.8, $J_{3,5}$ = 2.5 Hz), 6.89 d (1H, 6-H, $J_{5,6}$ = 8.5 Hz), 5.66 br.s (1H, OH), 3.65 t.t (1H, 7-H, J_{trans} = 3.3, J_{cis} = 7.0 Hz), 1.83 d.t.t (1H, 10-H, $J_{3,10}$ = 0.8, J_{trans} = 5.2, J_{cis} = 8.3 Hz), 1.47 m (2H, *trans*-8-H, *trans*-9-H, J_{trans} = 3.3 Hz), 1.22 m (2H, *cis*-8-H, *cis*-9-H, J_{cis} = 7.0 Hz), 1.00 m (2H, *cis*-11-H, *cis*-12-H, J_{cis} = 8.3 Hz), 0.70 m (2H, *trans*-11-H, *trans*-12-H, J_{trans} = 5.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 157.02 (C^1), 146.09 (C^4), 129.52 (C^2), 122.50 (C^3), 121.80 (C^5), 114.92 (C^6), 50.41 (C^7), 9.45 (C^8, C^9, C^{10}), 5.70 (C^{11}, C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 202 (69) $[M]^+$, 174 (7) $[M - N_2]^+$, 162 (18) $[M - C_3H_4]^+$, 147 (36) $[M - C_3H_5N]^+$, 133 (28) $[M - C_3H_5N_2]^+$, 39 (100).

4-Allylphenol (VI) was isolated by repeated column chromatography (toluene–cyclohexane, 1:1 to 2:1) as a mixture with phenol. Yield ~24 mg, ratio ~2:1 (2% of **VI**). ^{1}H NMR spectrum, δ, ppm: 7.04 m (2H, 3-H, 5-H), 6.75 m (2H, 2-H, 6-H), 5.93 m (1H, 8-H, $J_{7,8}$ = 6.7, $J_{8,9\text{-}cis}$ = 9.5, $J_{8,9\text{-}trans}$ = 17.5 Hz), 4.98 br.s (1H, OH), 5.06–4.98 m (2H, *cis*-9-H, *trans*-9-H), 3.31 d.t (2H, 7-H, $J_{7,9\text{-}trans} \approx J_{7,9\text{-}cis}$ = 1.5, $J_{7,8}$ = 6.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 153.77 (C^1), 137.91 (C^8), 132.33 (C^4), 129.81 (C^3, C^5), 115.60 (C^9), 115.33 (C^2, C^6), 39.42 (C^7).

2,6-Diallyl-4-(cyclopropyldiazenyl)phenol (VII) was isolated as described above for compound **VI** and was additionally purified by preparative thin-layer chromatography on silica gel using benzene as eluent. Yield 4 mg (0.5%). Yellow oily substance with a purity of ~95% (according to the ^{1}H NMR data). ^{1}H NMR spectrum, δ, ppm: 7.35 s (2H, 3-H, 5-H), 6.02 m (1H, 11-H, $J_{10,11}$ = 6.4, $J_{11,12\text{-}cis}$ = 9.5, $J_{11,12\text{-}trans}$ = 17.7 Hz), 5.41 br.s (1H, OH), 5.22–5.14 m (2H, *cis*-12-H, *trans*-12-H), 3.66 t.t (1H, 7-H, J_{trans} = 3.4, J_{cis} = 7.0 Hz), 3.44 d.t (2H, 10-H, $J_{10,12\text{-}trans} \approx J_{10,12\text{-}cis}$ = 1.6, $J_{10,11}$ = 6.4 Hz), 1.47 m (2H, *trans*-8-H, *trans*-9-H, J_{trans} = 3.4 Hz), 1.21 m (2H, *cis*-8-H, *cis*-9-H, J_{cis} = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 154.41 (C^1), 145.93 (C^4), 136.14 (C^{11}), 126.06 (C^2, C^6), 122.59 (C^3, C^5), 116.97 (C^{12}), 50.47 (C^7), 35.38 (C^{10}), 9.44 (C^8, C^9). Mass spectrum, *m*/*z* (I_{rel}, %): 242 (100) $[M]^+$, 214 (8) $[M - N_2]^+$, 202 (33) $[M - C_3H_4]^+$, 39 (50).

2-Allylphenol (VIII) was isolated as described above for compound **VI**. Yield ~70 mg (6%). Yellow oily substance with a purity of 90–95% (according to the ^{1}H NMR data). ^{1}H NMR spectrum, δ, ppm: 7.12 m (2H, 3-H, 5-H), 6.89 d.t (1H, 4-H, $J_{4,6}$ = 1.2, $J_{3,4}$ = $J_{4,5}$ = 7.4 Hz), 6.81 d.d (1H, 6-H, $J_{4,6}$ = 1.2, $J_{5,6}$ = 7.9 Hz), 6.02 m (1H, 8-H, $J_{7,8}$ = 6.3, $J_{8,9\text{-}cis}$ = 9.7, $J_{8,9\text{-}trans}$ = 17.6 Hz), 5.20–5.12 m (2H, *cis*-9-H, *trans*-9-H), 5.00 br.s (1H, OH), 3.42 d.t (2H, 7-H, $J_{7,9\text{-}trans} \approx J_{7,9\text{-}cis}$ = 1.7, $J_{7,8}$ = 6.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 154.16 (C^1), 136.45 (C^8), 130.51 (C^3), 127.98 (C^5), 125.30 (C^2), 121.01 (C^4), 116.58 (C^9), 115.87 (C^6), 35.22 (C^7).

1-(4-Allyloxyphenyl)-2-cyclopropyldiazene (IX) and 1-(4-cyclopropyloxyphenyl)-2-cyclopropyldiazene (X) were isolated as described above for compound **VI**, followed by preparative thin-layer chromatography on silica gel using petroleum ether–benzene (2:1) as eluent. Two closely located chromatographic zones were obtained; according to the ^{1}H and ^{13}C NMR data, they contained compounds **IX** amd **X** at ratios of ~3:1 and 2:3. Yellow oily substance. Compound **IX**. Yield ~38 mg (4.3%). ^{1}H NMR spectrum, δ, ppm: 7.59 m (2H, 3-H, 5-H), 6.94 m (2H, 2-H, 6-H), 6.05 d.d.t (1H, 11-H, $J_{10,11}$ = 5.3, $J_{11,12\text{-}cis}$ = 10.5, $J_{11,12\text{-}trans}$ = 17.3 Hz), 5.42 d.q (1H, *trans*-12-H, $J_{10,12\text{-}trans} \approx J_{12\text{-}trans,12\text{-}cis}$ = 1.6, $J_{11,12\text{-}trans}$ = 17.3 Hz), 5.30 d.q (1H, *cis*-12-H, $J_{10,12\text{-}cis} \approx J_{12\text{-}trans,12\text{-}cis}$ = 1.4, $J_{11,12\text{-}cis}$ = 10.5 Hz), 4.57 d.t (2H, 10-H, $J_{10,12\text{-}trans} \approx J_{10,12\text{-}cis}$ = 1.5, $J_{10,11}$ = 5.3 Hz), 3.66 t.t (1H, 7-H, J_{trans} = 3.3, J_{cis} = 7.0 Hz), 1.46 m (2H, *trans*-8-H, *trans*-9-H, J_{trans} = 3.3 Hz), 1.22 m (2H, *cis*-8-H, *cis*-9-H, J_{cis} = 7.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 159.99 (C^1), 146.36 (C^4), 132.95 (C^{11}), 123.44 (C^3, C^5), 118.01 (C^{12}), 114.82 (C^2, C^6), 69.06 (C^{10}), 50.47 (C^7), 9.49 (C^8, C^9).

Compound **X**. Yield ~12 mg (1.3%). ^{1}H NMR spectrum, δ, ppm: 7.59 m (2H, 3-H, 5-H), 7.07 m (2H, 2-H, 6-H), 3.77 m (1H, 10-H), 3.66 t.t (1H, 7-H, J_{trans} = 3.3, J_{cis} = 7.0 Hz), 1.46 m (2H, *trans*-8-H, *trans*-9-H, J_{trans} = 3.3 Hz), 1.22 m (2H, *cis*-8-H, *cis*-9-H, J_{cis} = 7.0 Hz), 0.80 m (4H, 11-H, 12-H). ^{13}C NMR spectrum, δ_C, ppm: 160.43 (C^1), 146.54 (C^4), 123.33 (C^3, C^5), 115.14 (C^2, C^6), 51.21 (C^{10}), 50.47 (C^7), 9.49 (C^8, C^9), 6.39 (C^{11}, C^{12}). Mass spectrum of the first fraction, *m*/*z* (I_{rel}, %): 202 (12) $[M]^+$, 161 (100) $[M - C_3H_5]^+$, 41 (71) $[C_3H_5]^+$. Found, %: C 71.13; H 7.31; N 13.89. $C_{12}H_{14}N_2O$. Calculated, %: C 71.26; H 6.98; N 13.85.

1-Cyclopropyl-2-(1-phenoxycyclopropyl)diazene (XI) was isolated as described above for compound **IX**. Yield 3 mg (0.3%). Colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 7.24 d.d (2H, 3-H, 5-H, $J_{3,4} = J_{4,5} = 7.4$, $J_{2,3} = J_{5,6} = 8.8$ Hz), 6.96 t.t (1H, 4-H, $J_{2,4} = J_{4,6} = 1.1$, $J_{3,4} = J_{4,5} = 7.4$ Hz), 6.85 m (2H, 2-H, 6-H, $J_{2,4} = J_{4,6} = 1.1$, $J_{2,3} = J_{5,6} = 8.8$ Hz), 3.52 t.t (1H, 10-H, $J_{trans} = 3.2$, $J_{cis} = 7.1$ Hz), 1.62 m (2H, 8-H, 9-H), 1.46 m (2H, 8-H, 9-H), 1.25 m (2H, *trans*-11-H, *trans*-12-H, $J_{trans} = 3.2$ Hz), 1.07 m (2H, *cis*-11-H, *cis*-12-H, $J_{cis} = 7.1$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 156.81 (C^1), 128.94 (C^3, C^5), 121.24 (C^4), 116.13 (C^2, C^6), 82.42 (C^7), 49.52 (C^{10}), 17.87 (C^8, C^9), 8.77 (C^{11}, C^{12}). Mass spectrum, *m*/*z* (I_{rel}, %): 202 (3) $[M]^+$, 201 (11) $[M - H]^+$, 174 (2) $[M - N_2]^+$, 133 (16), 105 (25), 94 (38) $[C_6H_6O]^+$, 77 (43) $[C_6H_5]^+$, 39 (100).

2-(Cyclopropyldiazenyl)phenol (XII) was isolated by preparative thin-layer chromatography on silica gel using toluene as eluent. Yield 4 mg (0.3%). Yellow crystals, mp 43–44°C. ^{1}H NMR spectrum, δ, ppm: 11.73 br.s (1H, OH), 7.74 d.d (1H, 3-H, $J_{3,5} = 1.8$, $J_{3,4} = 7.9$ Hz), 7.27 d.d.d (1H, 5-H, $J_{3,5} = 1.8$, $J_{4,5} = 7.3$, $J_{5,6} = 8.2$ Hz), 7.00 d.d.d (1H, 4-H, $J_{4,6} = 1.3$, $J_{4,5} = 7.3$, $J_{3,4} = 7.9$ Hz), 6.94 d.d (1H, 6-H, $J_{4,6} = 1.3$, $J_{5,6} = 8.2$ Hz), 3.71 t.t (1H, 7-H, $J_{trans} = 3.7$, $J_{cis} = 6.8$ Hz), 1.46 m (2H, *cis*-8-H, *cis*-9-H, $J_{cis} = 6.8$ Hz), 1.34 m (2H, *trans*-8-H, *trans*-9-H, $J_{trans} = 3.7$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 152.44 (C^1), 136.31 (C^2), 131.89 (C^5), 131.33 (C^3), 119.68 (C^4), 117.94 (C^6), 49.20 (C^7), 10.72 (C^8, C^9). Mass spectrum, *m*/*z* (I_{rel}, %): 162 (100) $[M]^+$, 134 (59) $[M - N_2]^+$. Found, %: C 66.86; H 6.28; N 16.94. $C_9H_{10}N_2O$. Calculated, %: C 66.65; H 6.21; N 17.27.

Allyloxybenzene (XIII), 1-allyl-4-(allyloxy)benzene (XIV), 1-allyl-2-(allyloxy)benzene (XV), and cyclopropyloxybenzene (XVI) were isolated as a mixture (93 mg) by column chromatography from the initial product mixture. According to the ^{1}H NMR data, the yields were ~5.5% of **XIII**, ~0.5% of **XIV** and **XV** each, and ~2% of **XVI**.

Compound **XIII**. ^{1}H NMR spectrum, δ, ppm: 7.28 m (2H, 3-H, 5-H), 6.93 m (3H, 2-H, 4-H, 6-H), 6.06 d.d.t (1H, 8-H, $J_{7,8} = 5.3$, $J_{8,9\text{-}cis} = 10.5$, $J_{8,9\text{-}trans} = 17.2$ Hz), 5.41 d.q (1H, *trans*-9-H, $J_{7,9\text{-}trans} \approx J_{9\text{-}trans,9\text{-}cis} = 1.6$, $J_{8,9\text{-}trans} = 17.2$ Hz), 5.28 d.q (1H, *cis*-9-H, $J_{7,9\text{-}cis} \approx J_{9\text{-}trans,9\text{-}cis} = 1.4$, $J_{8,9\text{-}cis} = 10.5$ Hz), 4.53 d.t (2H, 7-H, $J_{7,9\text{-}trans} \approx J_{7,9\text{-}cis} = 1.5$, $J_{7,8} = 5.3$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 158.58 (C^1), 133.38 (C^8), 129.40 (C^3, C^5), 120.80 (C^4), 117.46 (C^9), 114.72 (C^2, C^6), 68.65 (C^7).

Compound **XIV**. ^{1}H NMR spectrum, δ, ppm: 7.09 m (2H, 3-H, 5-H), 6.92 m (2H, 2-H, 6-H), 6.06 d.d.t (1H, 11-H, $J_{10,11} = 5.3$, $J_{11,12\text{-}cis} = 10.5$, $J_{11,12\text{-}trans} = 17.2$ Hz), 5.95 m (1H, 8-H, $J_{7,8} = 6.7$, $J_{8,9\text{-}cis} = 10.2$, $J_{8,9\text{-}trans} = 16.9$ Hz), 5.42 d.q (1H, *trans*-12-H, $J_{10,12\text{-}trans} \approx J_{12\text{-}trans,12\text{-}cis} = 1.6$, $J_{11,12\text{-}trans} = 17.2$ Hz), 5.27 d.q (1H, *cis*-12-H, $J_{10,12\text{-}cis} \approx J_{12\text{-}trans,12\text{-}cis} = 1.4$, $J_{11,12\text{-}cis} = 10.5$ Hz), 5.09–5.01 m (2H, *cis*-9-H, *trans*-9-H), 4.54 d.t (2H, 10-H, $J_{10,12\text{-}trans} \approx J_{10,12\text{-}cis} = 1.5$, $J_{10,11} = 5.3$ Hz), 3.32 d.t (2H, 7-H, $J_{7,9\text{-}trans} \approx J_{7,9\text{-}cis} = 1.5$, $J_{7,8} = 6.7$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 157.01 (C^1), 137.84 (C^8), 133.48 (C^{11}), 132.22 (C^4), 129.83 (C^3, C^5), 116.78 (C^{12}), 115.40 (C^9), 111.63 (C^2, C^6), 68.65 (C^{10}), 39.38 (C^7).

Compound **XV**. ^{1}H NMR spectrum, δ, ppm: 7.16 m (2H, 5-H, 6-H), 6.84 m (2H, 3-H, 4-H), 6.06 d.d.t (1H, 11-H, $J_{10,11} = 5.3$, $J_{11,12\text{-}cis} = 10.5$, $J_{11,12\text{-}trans} = 17.2$ Hz), 6.01 m (1H, 8-H, $J_{7,8} = 6.7$, $J_{8,9\text{-}cis} = 10.1$, $J_{8,9\text{-}trans} = 17.0$ Hz), 5.40 d.q (1H, *trans*-12-H, $J_{10,12\text{-}trans} \approx J_{12\text{-}trans,12\text{-}cis} = 1.6$, $J_{11,12\text{-}trans} = 17.2$ Hz), 5.26 d.q (1H, *cis*-12-H, $J_{10,12\text{-}cis} \approx J_{12\text{-}trans,12\text{-}cis} = 1.4$, $J_{11,12\text{-}cis} = 10.5$ Hz), 5.09–5.04 m (2H, *cis*-9-H, *trans*-9-H), 4.51 d.t (2H, 10-H, $J_{10,12\text{-}trans} \approx J_{10,12\text{-}cis} = 1.5$, $J_{10,11} = 5.3$ Hz), 3.42 d.t (2H, 7-H, $J_{7,9\text{-}trans} \approx J_{7,9\text{-}cis} = 1.4$, $J_{7,8} = 6.7$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 156.21 (C^1), 136.99 (C^8), 133.54 (C^{11}), 129.65 (C^2), 129.40 (C^3), 127.22 (C^5), 121.14 (C^4), 116.78 (C^{12}), 115.36 (C^9), 112.39 (C^6), 68.81 (C^{10}), 34.47 (C^7).

Compound **XVI**. ^{1}H NMR spectrum, δ, ppm: 7.28 m (2H, 3-H, 5-H), 7.05 m (2H, 2-H, 6-H), 6.93 m (1H, 4-H), 3.72 m (1H, 7-H), 0.76 m (4H, 11-H, 12-H). ^{13}C NMR spectrum, δ_C, ppm: 158.92 (C^1), 129.32 (C^3, C^5), 120.90 (C^4), 114.97 (C^2, C^6), 50.63 (C^7), 6.23 (C^8, C^9).

Decomposition of *N*-cyclopropyl-*N*-nitrosourea (II) by the action of cesium carbonate in the presence of anisole. A solution of 6.5 mg (0.05 mmol) of compound **II** and 8.3 mg (0.08 mmol) of anisole in 0.4 ml of CD_2Cl_2 was cooled to 5–7°C, and 32.6 mg (0.1 mmol) of Cs_2CO_3 was added. Slow gas evolution started and was over in 3 h; the ^{1}H NMR spectrum of the mixture contained no signals which could indicate transformation of initial anisole; the only decomposition products were allyl alcohol (its ^{1}H NMR spectrum coincided with that of an authentic sample) and allene (δ 4.69 ppm, s [8]).

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