Russian Journal of Organic Chemistry, Vol. 40, No. 8, 2004, pp. 1098–1112. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 8, 2004, pp. 1146–1160.

Cyclopropyl- and Allyl-substituted Arenes in Reaction with Dinitrogen Tetroxide. Effect of Substrate Oxidation Potential on Reaction Direction

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Received December 12 , 2003

Abstract—A correlation was found between oxidation potentials of acylcyclopropanes in solution (in CH_2Cl_2 and CH_3CN) and their HOMO energies calculated by semiempirical (AM1) and nonempirical (HF/6-31G and HF/6-31G**) methods. The correlation provides a possibility to forecast the reaction direction of the mentioned substrates and N_2O_4. The correlation possesses a general character. It was established for instance that arylcyclopropanes, cyclopropylmethyl- and allylbenzenes oxidized at more positive potentials than reduction potential of NO^+ and having more positive ε_{HOMO} than –9.0 eV (AM1), –8.4 eV (HF/6-31G), and –8.3 eV (HF/6-31 G**) reacted with N_2O_4 following the mechanism "electron transfer – radical pair recombination" affording nitroaromatic derivatives retaining the cyclopropane (or allyl) fragments. Substrates of the same type where the electron transfer to NO^+ should be endothermic process and whose HOMO values are less than the above critical numbers react with N_2O_4 by the mechanism of electrophilic cyclopropane ring opening (with aryl and benzylcyclopropanes) or by electrophilic addition across the double C=C bond (with allylbenzenes).

It was shown previously that reaction with dinitrogen tetroxide (N_2O_4) of phenylcyclopropane and its *para*-alkyl- or *para*-bromo-substituted analogs in dichloromethane occurred solely at the three-membered carbon ring [1, 2]. On the contrary 6-cyclopropyl-1,4-benzodioxane and its 7-bromo-substituted analog under the same conditions reacted with N_2O_4 at the aromatic ring with conservation of the cyclopropane moiety [2, 3].

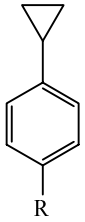
This difference in behavior of arylated cyclopropanes was rationalized [1–3] as dissimilar relation of the initial substrates with respect to nitrozyl cation initiating the reaction. It was implied that in the first case the nitrosyl cation played the role of an electrophilic agent reacting with the three-carbon ring along the standard electrophilic addition route, whereas in the second instance the nitrosyl cation functioned as oxidant initiating the nitration of the aromatic ring by one-electron transfer mechanism.

We attempted in this study to test this assumption, to determine the frontier criteria where we should expect the alteration in the reaction pathway originating from the change in its mechanism from electrophilic addition to electron transfer, and also to apply the data obtained to performing new syntheses.

It was shown recently [4] that the nitrosyl cation having reduction potential E_{red} 1.48 V (with respect to saturated calomel electrode, normal electrode) efficiently oxidized in dichloromethane aromatic compounds possessing oxidation potential below 1.45 V, but with substrates having oxidation potential over 1.60 V it only formed charge-transfer complexes. From these data we presumed that cyclopropyl-substituted substrates with an oxidation potential below 1.48 V would be oxidized with dinitrogen tetroxide into the corresponding cation-radical that further through ion-radical reaction with $\cdot NO_2$ would furnish a product of substitution in the aromatic ring.

The data on oxidation potentials of arylcyclopropanes are scanty up till now. Nonetheless, the available experimental data confirm our assumption. For instance, it was established experimentally that phenylcyclopropane and 4-methylphenylcyclopropane (oxidation potentials 1.78 and 1.60 V respectively) (Table 1), react with N_2O_4 only with the opening of the cyclopropane

Table 1. Calculated values of HOMO energies of arylcyclopropanes **I–V**, experimental values of their oxidation potentials in dichloromethane and acetonitrile, and of their ionization potentials



Compd. no.	R	$-\varepsilon_{HOMO}$, eV			*IP*, eV	E_{OX}, V	
		AM1	HF/6-31G	HF/6-31G**		MeCN [10]	CH_2Cl_2 [11]
I	MeO	8.82	8.19	8.06	8.05 [9]	1.42	1.35
II	Me	9.10	8.45	8.40	8.27 [11]	1.57	1.60
III	H	9.21	8.44	8.39	8.61 [12], 8.66 [9]	1.83	1.78
IV	Cl	9.33	9.07	8.81	8.64 [9]	1.86	
V	CN	9.74	9.35	9.32		2.17	

ring. In contrast, 4-anisylcycloprpoane having oxidation potential of 1.35 V (Table 1) reacted with N_2O_4 with conservation of the three-memberd ring [2].

Aiming at developing criteria for distinguishing between cyclopropyl-containing substrates capable of one-electron oxidation to furnish products of nitration into the aromatic ring or those capable of electrophilic opening of the cyclopropyl ring we planned to use quantum-chemical calculation of various cyclopropylbenzenes properties in comparison with available experimental data on their oxidation potentials in solution. The quantum-chemical calculations were carried out with the use of software package GAUSSIAN 98 [5] applying three procedures: semiempirical method AM1 [6] and *ab initio* method in the basis HF/6-31G with accounting for polarization functions and without it [7, 8].

As seen from Table 1, experimental values of ionization potentials of arylcycloprppanes are in good agreement with the ε_{HOMO} values calculated by nonempirical procedure with the use of HF/6-31G** basis. On the other hand a better correlation with the oxidation potentials in solution is observed at the use of semiempirical AM1 procedure for calculation of HOMO energy (which according to Kupmans theorem [13] correspond to ionization potentials of the compound):

$$E_{OX}\,(MeCN)\ -0.838\varepsilon_{HOMO} - 5.97,\ r\ 0.978 \qquad (1)$$

$$E_{OX}\,(CH_2Cl_2)\ -1.06\varepsilon_{HOMO} - 8.02,\ r\ 0.988 \qquad (2)$$

Interestingly both equations give consistent results: oxidation potential of arylcyclopropane would be below 1.48 V if the $-\varepsilon_{HOMO}$ value calculated by AM1 procedure be smaller than 9.0 eV [8.9 and 8.96 eV according to equations (1) and (2) respectively]. At the use of the calculations by HF/6-31G and HF/6-31G** methods the corresponding frontier values equal approximately to 8.4 and 8.3 eV. For comparison we mention the values of $-\varepsilon_{LUMO}(NO^+)$ calculated by procedures HF/6-31G (8.36 eV) and MP2/6-31G** (8.31 eV).

The correlation analysis performed suggests that arylcyclopropanes whose ionization potential calculated by methods AM1, HF/6-31G, and HF/6-31G** is below respectively 9.0, 8.4, and 8.3 eV should react with N_2O_4 according to electron transfer mechanism, retaining the cyclopropane fragment and giving products of nitration into the aromatic ring, whereas the compounds with larger value of the calculated ionization potentials should react along the electrophilic mechanism of the cyclopropane ring opening.

To prove these conclusions we first calculated the energy of the frontier orbitals for cyclopropylarenes whose behaviour in reactions with dinitrogen tetroxide had been already studied before.

The data of Table 2 show that the calculated HOMO energies of these substrates really conform to our suggestion: 4-bromophenylcyclopropane (**VI**) having ionization potential higher than the frontier value reacts with N_2O_4 with the opening of cyclopropane ring (as shown in [1]), and 6-cyclopropyl-1,4-benzodioxane (**VII**)

Table 2. Calculated values of HOMO energy for arylcyclopropanes **VI–IX**

Compd. no.	$-\varepsilon_{HOMO}$, eV		
	AM1	HF/6-31G	HF/6-31G**
VI	9.39	8.90	8.74
VII	8.52	8.25	8.02
VIII	8.95	8.47	8.19
IX	8.49	7.87	7.72

Table 3. Calculated values of HOMO energy for substituted benzylcyclopropanes **XIV–XXIV**

Compd. no.	$-\varepsilon_{HOMO}$, eV		
	AM1	HF/6-31G	HF/6-31G**
XIV	9.37	8.73	8.67
XV	8.82	8.17	8.04
XVI	8.49	7.85	7.70
XVII	8.81	8.23	8.00
XVIII[a]	8.96	8.51	8.22
XIX	9.58	9.20	8.85
XX[b]	9.58	9.13	8.99
XXI	8.94	8.42	8.32
XXII	8.65	8.16	7.96
XXIII	8.97	8.56	8.27
XXIV	9.72	9.51	9.10

[a] 6-Bromo-7-cyclopropylmethyl-1,4-benzodioxane.

[b] 1,1-Dichloro-2-benzylcyclopropane.

with the ionization potential below the frontier value affords product of benzene ring nitration [3, 14]. 6-Bromo-7-cyclopropyl-1,4-benzodioxane (**VIII**) is an intermediate case: its HOMO energy turned out to be larger than the frontier value when calculated by procedure HF/6-31G, but both other calculation methods give figures slightly lower than the frontier value permitting the occurrence of one-electron transfer. Inasmuch as the experiment demonstrated [3, 14] that under the chosen conditions the reaction afforded the product nitrated into the aromatic ring, it was possible to conclude that the results of calculation by AM1 or HF/6-31G** methods possess better power for forcasting the reaction direction than the data of HF/6-31G calculations. Nonetheless we use further all the three calculation procedures.

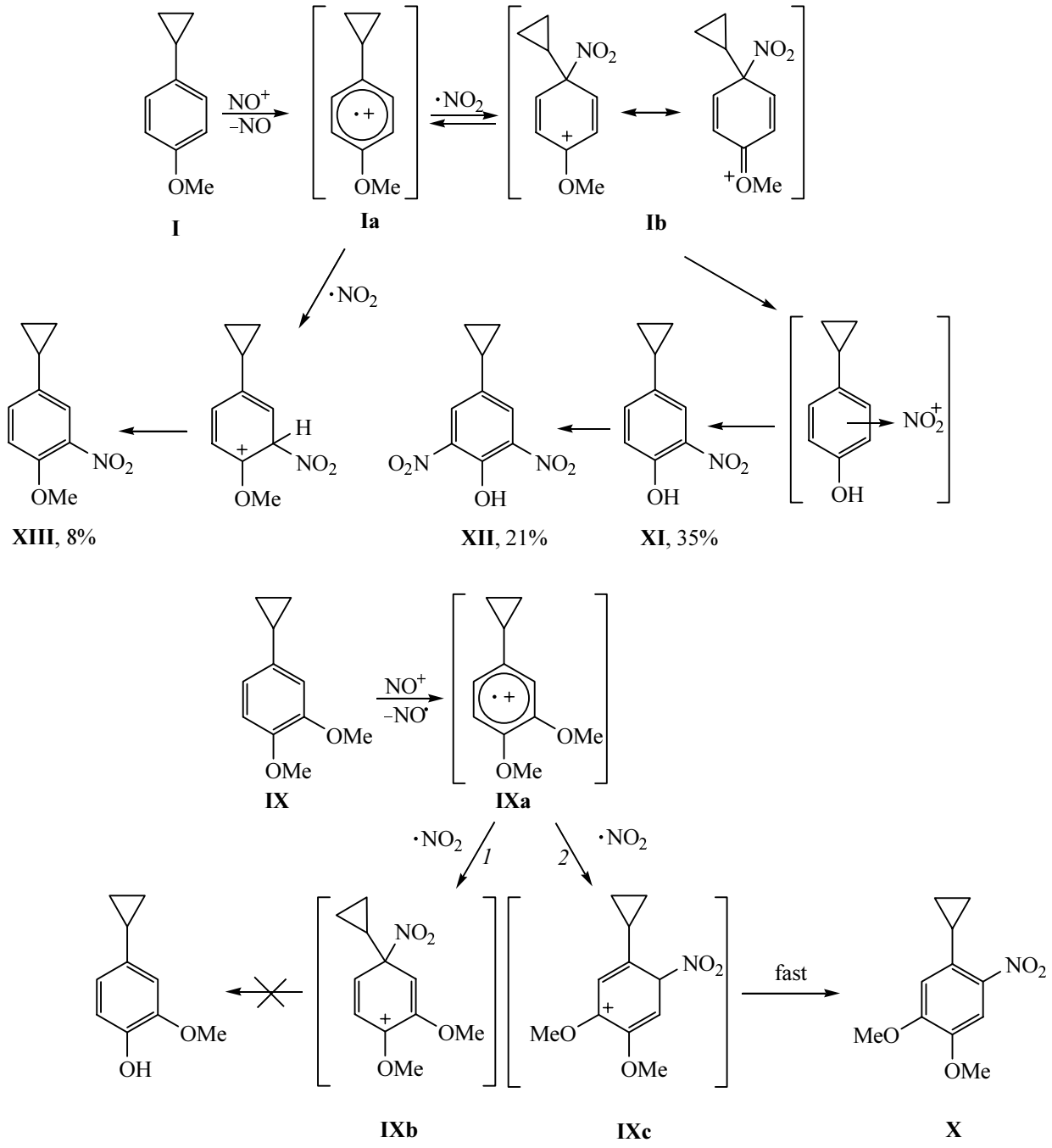
In Table 2 the calculated HOMO values are also presented for 3,4-dimethoxyphenylcyclopropane whose reaction with N_2O_4 has not been previously studied. On comparison of these energies with the frontier values that determine the direction of arylcyclopropane reactions with N_2O_4 we concluded that compound **IX** would be nitrated by dinitrogen tetroxide into the benzene ring without opening of the cyclopropane ring. To prove this conclusion 3,4-dimethoxyphenylcyclopropare was prepared, and its reaction with N_2O_4 was investigated.

It turned out really that compound **IX** reacted with N_2O_4 in dichloromethane to yield exclusively 4,5-dimethoxy-2-nitrophenylcyclopropane (**X**). Interestingly that unlike reaction of 4-methoxyphenylcyclopropane (**I**) with N_2O_4 occurring by *SET*-mechanism with the rupture of the ether O–Me bond, in this case no demethylation product was obtained. Apparently in reaction of compound **I** the electron transfer from substrate to nitrosonium ion leads to formation of a cation-radical species **Ia** (Scheme 1) where the radical site is localized mainly of the carbon atoms attached to methoxy and cyclopropyl substituents (as confirmed by our own and published [15] nonempirical calculations of such cation-radicals). The subsequent *ipso*-attack of NO_2-radical on the C^1 carbon results in benzolonium ions of **Ic** type that are known to be responsible for formation of nitrophenols **XI** and **XII** at 4-anisylcyclopropane (**I**) nitration with nitric acid in acetic anhydride. In the case of dimethoxy derivative **IX** the arising cation-radical **IXa** is characterized by higher degree of delocalization of the charge as well as spin density. As a result the attack of $\cdot NO_2$ on the *ipso*-position competes with its addition to C^6 carbon. Whereas the arising *ipso*-σ-complex **IXb** has relatively longer lifetim, and its formation is reversible, σ-complex **IXc** eliminates proton rapidly and irreversibly affording the final product of aromatic substitution **X**.

So far the correlation of ε_{HOMO} for cyclopropyl-substituted substrate with the pathway taken by their reaction with N_2O_4 was limited to arylcyclopropanes where the small ring is conjugated with the benzene one. We anticipated that if the calculated ε_{HOMO} values of cyclopropylmethylbenzenes would fit to criteria governing the cyclopropyl ring conservation in phenylcyclopropane reactions with N_2O_4, then the similar reactions of benzylcyclopropanes also would proceed with retention of the cyclopropane moiety, notwithstanding the fact that here the cyclopropyl ring removed from the benzene one by one methylene group was more capable to open under the action of electrophilic reagents [17]. Therefore we performed quantum-chemical calculations of frontier orbitals for a series of benzylcyclopropanes, both substituted in the aromatic and cyclopropane rings (Table 3).

The calculation results show that the ε_{HOMO} values exceeding the limit permitting the reaction of

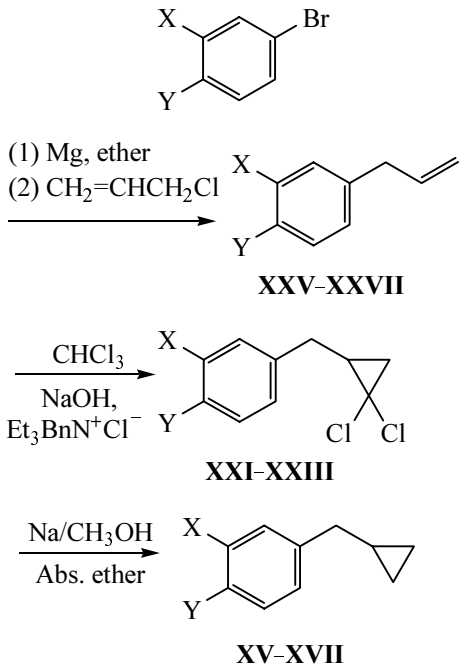
Scheme 1.



cyclopropyl-containing substrates with N_2O_4 to proceed through *SET*-mechanism correspond to compounds **XV–XVIII**, and **XXII**. Unlike that, the ε_{HOMO} value of benzylcyclopropane (**XIV**) and those of compounds **XIX, XX,** and **XXIV** lie below the indicated frontier values, and these compounds should react with dinitrogen tetroxide following the ionic mechanism and consequently yielding products of cyclopropane ring opening. As to compounds **XVIII, XXI**, and **XXIII**, their ε_{HOMO} values fall into the frontier region, and these compounds may presumably react with N_2O_4 along both possible routes.

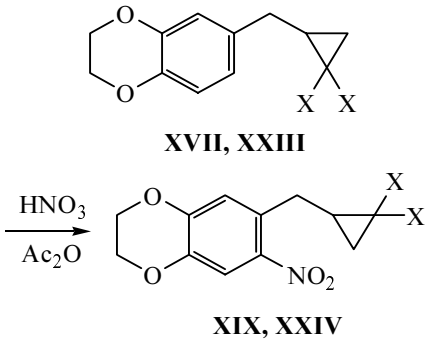
To test our assumption we synthesized a series of substituted benzylcyclopropanes whose reaction with N_2O_4 was expected to take the route "electron transfer–recombination of the radical pair", and also some

Scheme 2.



X = H, Y = MeO (**XV, XXI, XXV**); X = Y = MeO (**XVI, XXII, XXVI**); X, Y = OCH_2CH_2O (**XVII, XXIII, XXVII**).

Scheme 3.



X = H (**XVII, XIX**), X = Cl (**XXIII, XXIV**).

benzylcyclopropanes where the electron transfer would be thermodynamically unfavorable. The synthesis of model compounds was carried out along Schemes 2 and 3.

The study of reaction of dinitrogen tetroxide with substituted benzylcyclopropanes whose calculated ε_{HOMO} values (Table 3) suggested that the process would proceed by the mechanism "electron transfer–recombination of the radical pair" demonstrated that the conversion of these cyclopropane substrates actually occurred along the predicted pathway. Therewith the trends observed in the reaction of phenylcyclopropyl substrates with N_2O_4 by *SET*-mechanism were also valid for their structural analogs from the benzylcyclopropane series although with some distinctions. For instance, the common feature of reactions between N_2O_4 and 4-anisylcyclopropane (**I**) and 4-methoxybenzylcyclopropane (**XV**) possessing virtually identical ionization potentials (Tables 1 and 3) is the process proceeding through the stage of an *ipso*-σ-complexes **Ib** (Scheme 1) and **XVb** (Scheme 4) formation. However the further transformation of these σ-complexes is different. Thus as shown in [2] the *ipso*-benzolonium ions arising in the reaction of 4-anisylcyclopropane (**I**) with N_2O_4 were converted under the reaction conditions into cyclopropyl-substituted nitro- and dinitrophenols **XI** and **XII** (Scheme 1), whereas the *ipso*-benzolonium ions **XVb** inevitably forming under the same conditions from 4-methoxybenzylcyclopropane (**XV**) transformed mainly into products of intramolecular cyclopropylation and nitration into the aromatic ring **XXVIII** and **XXIX** (Scheme 4) as was demonstrated in this study.

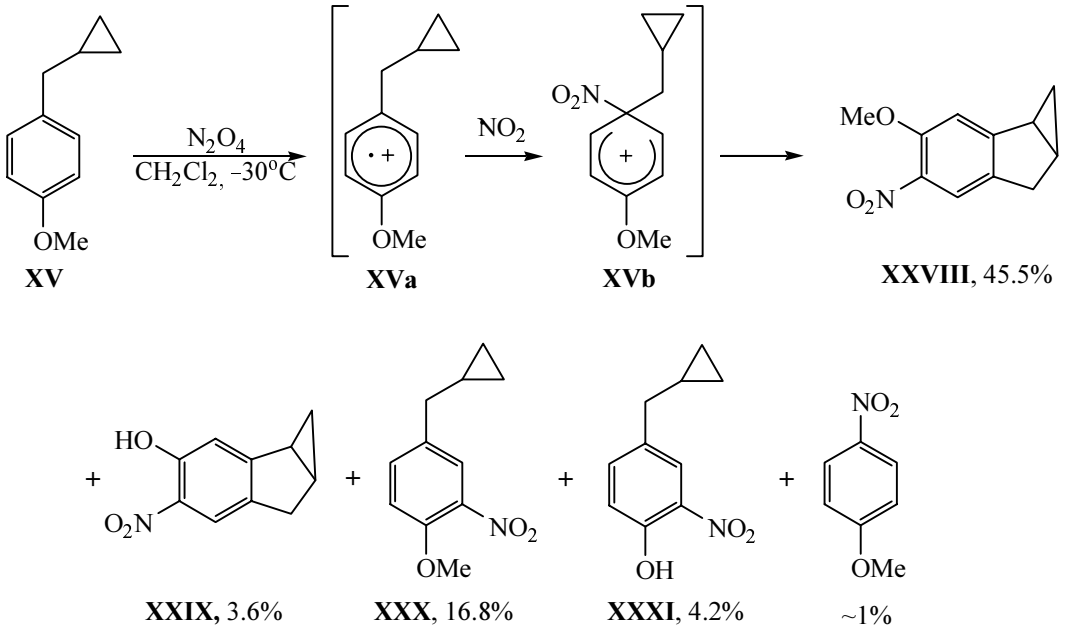
Interestingly the 2-(4-methoxybenzyl)-1,1-dichlorocyclopropane (**XXI**) possessing ionization potential (ε_{HOMO}) corresponding to the frontier region reacted with N_2O_4 under the given conditions still by the *SET*-mechanism affording in contrast to the nonchlorinated analog **XV** only nitro-substituted benzylcyclopropanes **XXXII** and **XXXIII** (Scheme 5).

It is interesting to note that although the reaction of compound **XXI** with N_2O_4 [like that of 4-methoxybenzylcyclopropane (**XV**)] proceeded through *ipso*-σ-complexes **XXIc** as shows nitrophenol **XXXIII** formationβ no tricyclic compounds, like **XXXIV**, were obtained similar to those arising in the process with nonchlorinated analog **XV** (Scheme 3).

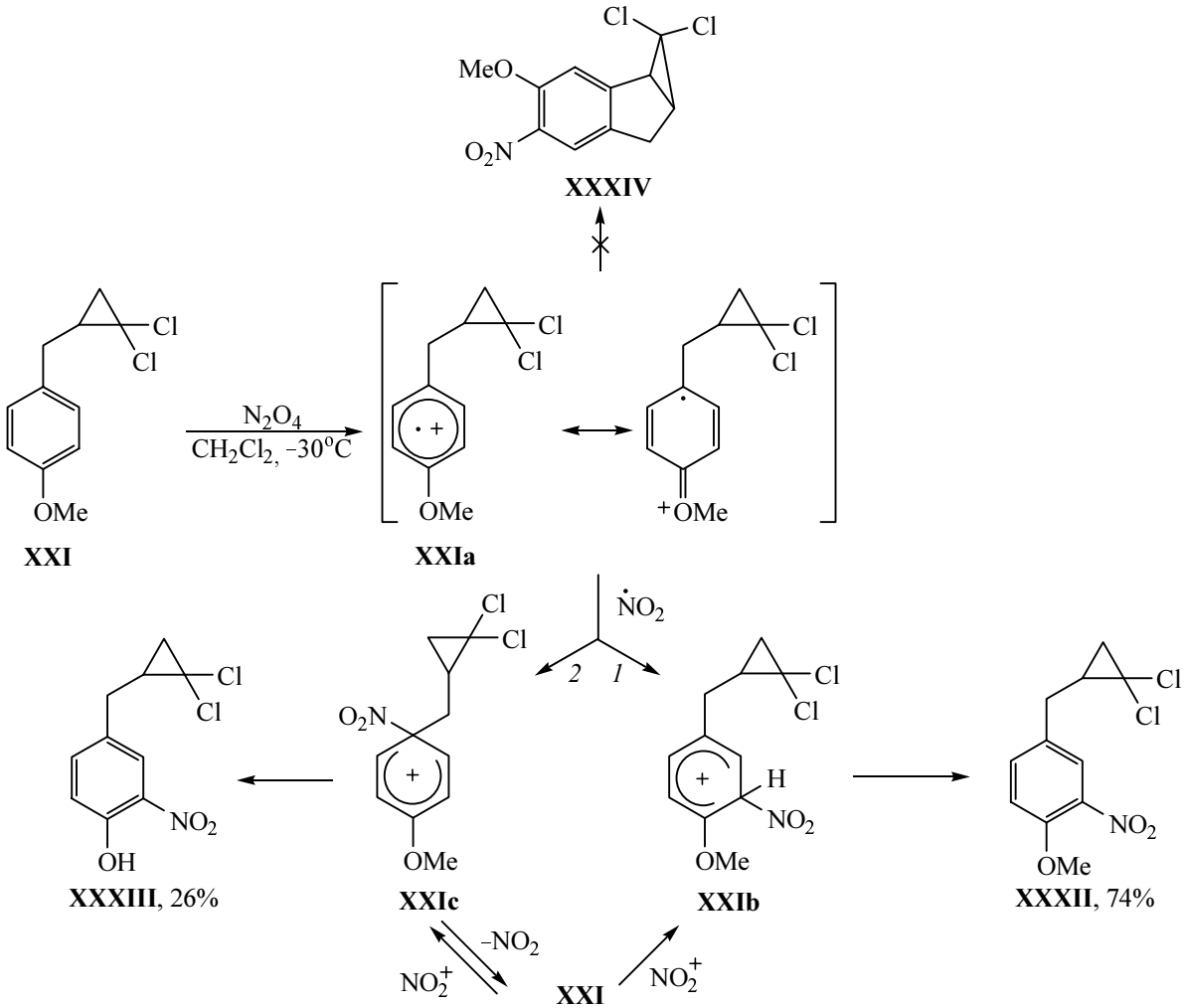
As we anticipated, unsubstituted benzylcyclopropane (**XIV**) having ε_{HOMO} value significantly smaller than the HOMO energy of, e.g., 4-methoxybenzylcyclopropane (**XV**) reacted with N_2O_4 solely at the three-membered ring furnishing a multicomponent mixture of highly labile addition products.

Interestingly, compounds **XIX**, **XX**, and **XXIV** with HOMO situated deeper than that of benzylcyclopropane (**XIV**) (Table 3) under the given conditions do not react with N_2O_4 and are quantitatively recovered from the reaction mixture. At the same time benzylcyclopropanes **XVII**, **XXII**, and **XXIII** whose calculated ε_{HOMO} values we close to those of ε_{HOMO} for 3,4-dimethoxy-phenyl-

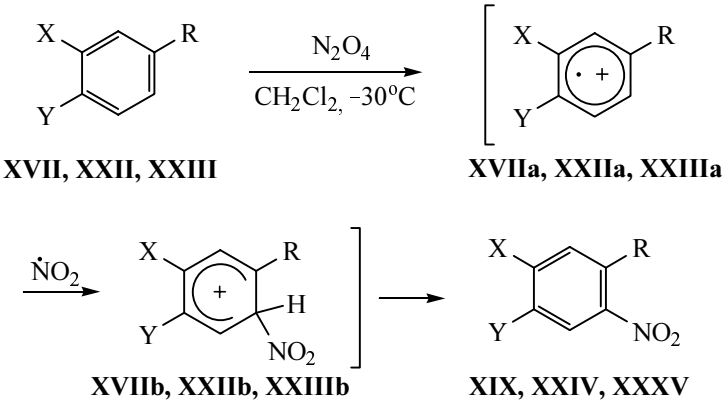
Scheme 4.



Scheme 5.

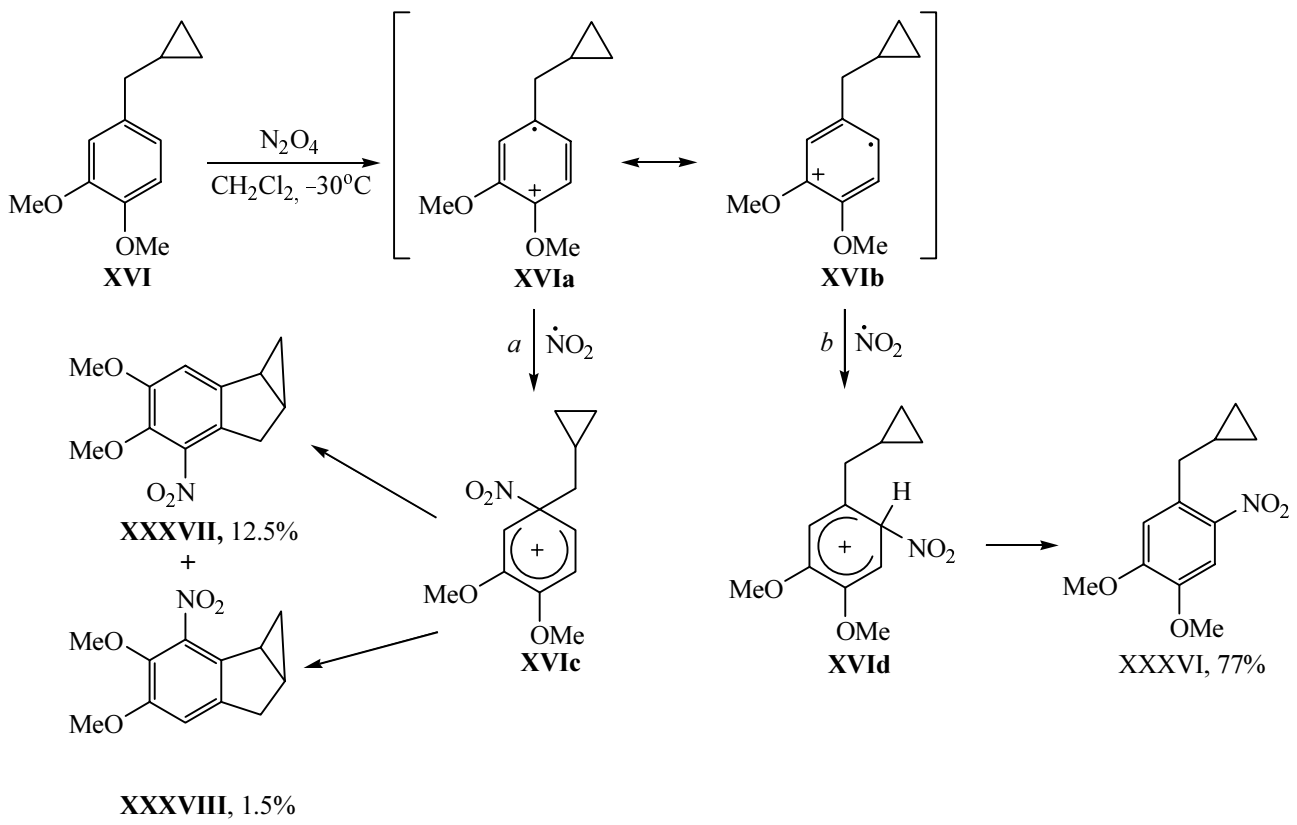


Scheme 6.



X, Y = OCH_2CH_2O, R = cyclopropylmethyl (**XVII, XVIIa, XIX**); X = Y = OMe, R = 2,2-dichlorocyclopropylmethyl (**XXII, XXIIa**, **XXXV**); X, Y = OCH_2CH_2O, R = 2,2-dichlorocyclopropylmethyl (**XXIII, XXIIIa, XXIV**).

Scheme 7.



cyclopropane (**IX**) and 6-cyclopropyl-1,4-benzodioxane (**VII**) (Tables 2 and 3) behaved in the reaction under consideration as expected completely identical to **IX** and **VII**: in high yields only the corresponding 2-nitro-substituted benzylcyclopropanes **XIX**, **XXIV**, and **XXXV** are obtained (Scheme 6).

In contrast to compounds **VII, IX, XVII, XXII**, and **XXIII** 3,4-dimethoxtbenzylcyclopropane whose ε_{HOMO} value suggested that reaction with N_2O_4 should have occurred by the mechanism "electron transfer–recombination of the radical pair" reacted actually ambiguously: apart from the main product corresponding

to the general trends of the reaction, 4,5-dimethoxy-2-nitrobenzylcyclopropane (**XXXVI**), we identified in the reaction mixture also 3,4-dimethoxy-5-nitro-1,1a,6,6a-tetrahydrocyclopropa[a]indene (**XXXVII**) and its 2-nitro isomer **XXXVIII** (Scheme 7).

The formation of cyclopropaindenes **XXVIII** and **XXIX** in reaction of 4-methoxybenzylcyclopropane (**XV**) and cyclopropaindenes **XXXVII** and **XXXVIII** in reaction of 3,4-dimethoxybenzylcyclopropane (**XVI**) evidences by and large the general character of the intramolecular cyclopropylation process in the series of benzylcyclopropanes. For generation of these tricyclic compounds may be responsible the corresponding *ipso*-σ-complexes of **XVb** or **XVIc** type (Schemes 4 and 7). The latter assumption is confirmed, e.g., by the fact that the yield of cyclization products **XXXVII** and **XXXVIII** in the reaction of 3,4-dimethoxybenzylcyclopropane (**XVI**) is considerably smaller than the yield of their analog **XXVIII** in the reaction of 4-methoxybenzylcyclopropane (**XV**). Apparently in the process involving 3,4-dimethoxybenzylcyclopropane (**XVI**) the recombination of the ion-radical pair follows preferably the pathway *b* than the path *a* (Scheme 7). Consequently *ipso*-σ-complexes **XVIc** necessary for the substrate transformation into cyclopropa[a]indenes **XXXVII** and **XXXVIII** are formed in a lesser amount.

The results obtained give convincible proof of the possibility to retain the susceptible to electrophilic attack cyclopropyl ring of benzylcyclopropanes in reactions following the mechanism "electron transfer–recombination of the radical pair" that can be achieved when ε_{HOMO} of the initial substrates has values necessary for reactions taking this pathway (i.e., the HOMO must be situated higher than the mentioned critical values).

It is known [18], that styrene and its alkyl-substituted analogs in reaction with dinitrogen tetroxide afford only products of the electrophilic addition to the double bond. Taking into consideration these data it was presumable that the reaction between N_2O_4 and allylbenzenes should also give addition products at the double bond, and the reaction should go as easily as with alkylenes [19–21] since the vinyl moiety was not conjugated with the benzene ring. At the same time we have demonstrated in this study that the cyclopropyl ring of benzylcyclopropanes prone to reactions of electrophilic addition can be conserved in the reaction with N_2O_4 when the ε_{HOMO} of the initial substrates fits in the range of values ensuring reaction occurring via mechanism "electron transfer–recombination of the radical pair".

We suggested that the direction of allylbenzenes reaction with N_2O_4 would also depend first of all on the

Table 4. Calculated values of HOMO energy for allylbenzenes **XXV**–**XXVII**, and **XXXIX**

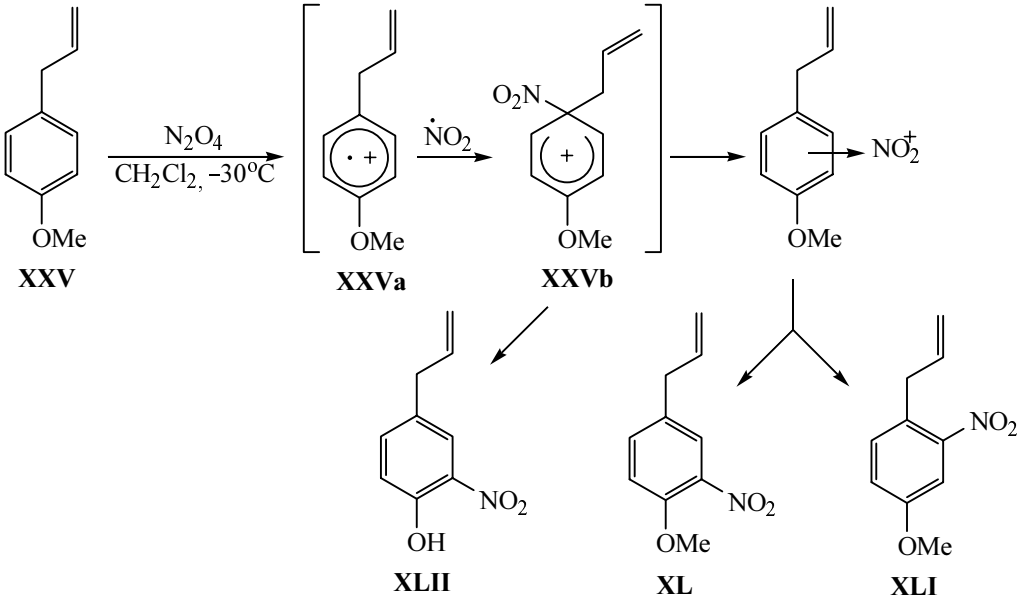
Compd. no.	$-\varepsilon_{HOMO}$, eV		
	AM1	HF/6-31G	HF/6-31G**
XXV	8.86	8.21	8.08
XXVI	8.52	7.86	7.74
XXVII	8.83	8.30	8.07
XXXIX	9.42	8.78	8.71

ε_{HOMO} values of the substrates in question. To test the validity of this assumption we calculated ε_{HOMO} for some substituted allylbenzenes (Table 4), compared the calculated ε_{HOMO} values with the corresponding data for cyclopropane analogs, and studied the behavior in reaction with N_2O_4 of unsaturated compounds whose ε_{HOMO} values were close to those of the respective benzylcyclopropanes reacting with dinitrogen tetroxide by the *SET*-mechanism.

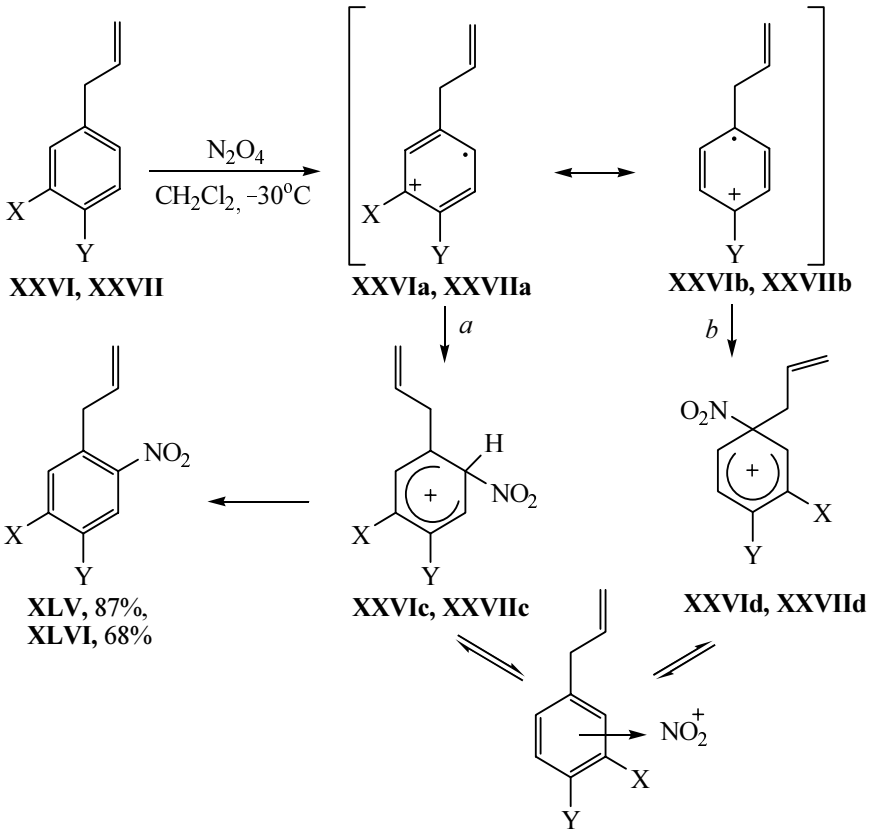
As seen from Tables 3 and 4 the ε_{HOMO} values for 4-methoxybenzylcyclopropane (**XV**) and 4-methoxyallylbenzane (**XXV**) calculated, for instance, by *ab initio* calculations in the HF/6-31G basis are practically equal (–8.17 and –8.21 eV respectively). It proved that the behavior of substrates **XV** and **XXV** under conditions of the staudy was also similar. Although the reaction of 4-methoxyallylbenzane (**XXV**) with N_2O_4 unlike that of compound **XV** was more complicated, and a considerable part of the substrate still was converted into labile products of addition to the double bond, yet three compounds **XL–XLII** were isolated in an overall yield of ~35% with structures unambiguously demonstrating that allylbenzenes also can react with dinitrogen tetroxide along the *SET*-mechanism to afford nitroaromatic compounds with the retained allyl substituent (Scheme 8).

This is essentially the first example of aromatic nitration of alkenylbenzenes effected by N_2O_4 occurring with retention of the electron-donor double bond in the side chain. It was important that we failed to identify in the reaction mixture obtained from 3,4-dimethoxyallylbenzene and N_2O_4 any products which could have formed via *ipso*-σ-complexes of **XXVId** type (Scheme 9). Apparently in contrast to reaction of 3,4-dimethoxybenzylcyclopropane (**XVI**) the second reaction stage (radical pair recombination) with 3,4-dimethoxyallylbenzene (**XXVI**) proceeded rather along path *a* (Scheme 9) than path *b*. An alternative possibility consists in reduction of the demethylation rate of *ipso*-σ-complex **XXVId** as compared to **XXVb** induced by the presence of the second methoxy group, and therefore the main

Scheme 8.



Scheme 9.



X = Y = OMe (**XXVI, XXVIa–d, XLV**); X, Y = OCH_2CH_2O (**XXVII, XXVIIa–d, XLVI**).

transformation route of the former leads to isomeric σ-complex **XXVIId** and to the final product of aromatic nitration at C^6 atom. Similar difference was found in behavior of 4-methoxy- and 3,4-dimethoxyphenylcyclopropanes (**I** and **IX**) (Scheme 1).

Hence in this study we demonstrated that application of relatively simple quantum-chemical calculations of the frontier orbitals energy permitted forecasting of direction in N_2O_4 reactions with cyclopropyl-, cyclopropylmethyl-, and allylbenzenes in solvents of low polarity, like dichloromethane. In particular, substrates possessing more positive calculated ε_{HOMO} values than –9.0 eV (method AM1), –8.4 eV (method HF/6-31G), and –8.3 eV (method HF/6-31G**) should react with N_2O_4 via mechanism "electron transfer–recombination of the radical pair" with subsequent stabilization of the adduct of ion-radical recombination.

EXPERIMENTAL

^{1}H NMR spectra were registered on spectrometers Bruker AW-300 (operating frequency 300 MHz) and Varian BXR-400 (400 MHz) in $CDC1_3$ using TMS as internal reference. Mass spectra were measured on Finnigan SSQ-7000 instrument, GC-MS type equipped with a capillary column (30 m, liquid phase DB-1, carrier gas helium), oven temperature programmed from 50 to 300°C at a rate 10 deg/min. Ionizing electrons energy 70 eV. The preparative separation of reaction mixtures was carried out on plates with $A1_2O_3$ of the II activity grade in a thin layer, eluent systems: A , ethyl ether–petroleum ether (40–70°C), 1:3; B, ether–chloroform–petroleum ether (40–70°C), 1:1:3.

6-Bromo-1,4-benzodioxane was prepared as described in [22], yield 74%, bp 150–151°C (20 mm Hg), n_D^{20} 1.5914.

3,4-Dimethoxyphenylcyclopropane (IX) was synthesized from 3,4-dimethoxyacetophenone similarly to a described procedure for preparation of 4-methoxyphenylcyclopropane [23], yield 64% (calculated with respect to Mannich base), bp 155–156°C (19 mm Hg), n_D^{20} 1.5485. ^{1}H NMR spectrum, δ, ppm: 0.66 m (2H), 0.93 m (2H) and 1.87 m (1H): cyclopropane ring protons, 3.83 s (3H, OCH_3), 3.86 s (3H, OCH_3), 6.62 d.d (1H, ArH^6, J_o 8.0, J_m 2 Hz), 6.64 d (1H, ArH^2, J_m 2 Hz), 6.76 d (1H, ArH^5, J 8.0 Hz). Found, %: C 73.99, 74.02; H 7.77, 7.83. $C_{11}H_{14}O_2$. Calculated, %: C 74.13; H 7.92.

4-Allylanisole (XXVI) was prepared as described in [24], yield 91%, bp 122–124°C (22 mm Hg), n_D^{20} 1.5210.

4-Allyl-1,2-dimethoxybenzene (XXV) was prepared as described in [25], yield 79%, bp 128–130°C (10 mm Hg), n_D^{20} 1.5344.

6-Allyl-1,4-benzodioxane (XXVII). To a solution of Grignard reagent prepared from 4.1 g of Mg and 32.5 g (0.151 mol) of 6-bromo-1,4-benzodioxane in 70 ml of ether at 10°C while stirring was added dropwise a cooled solution of 19.6 g (0.162 mol) of allyl bromide in 30 ml of ether. The mixture was warmed to 20°C and then heated at reflux for 3 h. Then the reaction mixture was poured on a mixture of 100 g of ice and 50 ml of 2 N HCl, the ether layer was separated, the water layer was extracted with ether (2×30 ml). The combined ether solution was washed with 2 N solution of K_2CO_3, with water, and dried on $MgSO_4$. The solution was evaporated, the residue was subjected to vacuum distillation. Yield 14.1 g (53%), bp 138–139°C (14 mm Hg), n_D^{20} 1.5534. ^{1}H NMR spectrum, δ, ppm: 3.28 d (2H, CH_2, J 7.8 Hz), 4.23 s (4H, OCH_2CH_2O), 5.08 m (2H, $C\underline{H}_2$=CH), 5.96 m (1H, CH_2 =C<u>H</u>), 6.64 d.d (1H, arom, J_O 8.8, J_m 1.8 Hz), 6.71 d (1H, arom, J_m 1.8 Hz), 6.81 d (1H, arom, J_O 8.8 Hz). Found, %: C 74.88, 74.96; H 6.68, 6.77. $C_{11}H_{12}O_2$. Calculated, %: C 74.98; H 6.86.

Dichlorocarbenylation of allylbenzenes XXV–XXVII. Standard procedure: To a solution of 0.1 mol of allylbenzene **XXV–XXVII** and 0.5 g of Et_3BnNCl in 70 ml of $CHC1_3$ was gradually added at stirring 60 ml of 50% NaOH solution, the mixture was stirred for 3 h and poured into 200 ml of H_2O. The organic layer was separated, the water layer was extracted with $CHC1_3$ (3 × 5 0 ml), the combined organic solvents were washed with 2 N HC1, with water, and dried on $MgSO_4$. On removing 2/3 of solvent the residue was passed through a bed of $A1_2O_3$ of II activity grade, eluate was evaporated, and reaction product was subjected to distillation.

2-(4-Methoxybenzyl)-1,1-dichlorocyclopropane (XXI). From 14.8 g (0.1 mol) of 4-allylanisole (**XXV**) by the standard procedure was obtained 15.2 g (66%) of compound **XXI**, bp 169–170°C (12 mm Hg), n_D^{20} 1.5435. ^{1}H NMR spectrum, δ, ppm: 1.22 m (1H), 1.64 m (1H) and 1.83 m (1H): cyclopropane ring protons, 2.72 d.d (1H, CH_2Ar, J_1 14.4, J_2 14.4 Hz), 2.93 d.d (1H, CH_2Ar, J_1 14.4, J_2 7.7 Hz), 3.81 s (3H, OCH_3), 6.88 d (2H, arom, J_O 8.8 Hz), 7.21 d (2H, arom, J_O 8.8 Hz). Found, %: C 57.04, 57.11; H 5.19, 5.10. $C_{11}H_{12}C1_2O$. Calculated, %: C 57.16; H 5.23.

2-(3,4-Dimethoxybenzyl)-1,1-dichlorocyclopropane (XXII). Likewise from 17.8 g (0.1 mol) of 3,4-dimethoxyallylbenzene (**XXVI**) was obtained 18.1 g (69%) of compound **XXII**, bp 193–195°C (13 mm Hg), n_D^{20} 1.5526. ^{1}H NMR spectrum, δ, ppm: 1.23 m (1H), 1.65 m (1H) and 1.89 m (1H): cyclopropane ring protons, 2.78 d.d (1H, CH_2Ar, J_1 15.2, J_2 6.0 Hz), 2.95 d.d (1H, CH_2Ar, J_1 15.2, J_2 7.6), 3.86 s (3H, OCH_3) and 3.91 s (3H, OCH_3), 6.86 m (3H, arom). Found, %: C 54.92, 55.12; H 5.23, 5.32. $C_{12}H_{14}C1_2O_2$. Calculated, %: C 55.19; H 5.40.

6-(2,2-Dichlorocyclopropylmethyl)-1,4-benzodioxane (XXIII). Likewise from 17.8 g (0.1 mol) of 6-allyl-1,4-benzodioxane (**XXVII**) was obtained 16.1 g (62%) of dichlorocyclopropane **XXIII**, bp 193–194°C (15 mm рт.Ст), n_D^{20} 1.5645. ^{1}H NMR spectrum, δ, ppm: 1.19 d.d (1H, J_1 7.2, J_2 7.3 Hz), 1.63 d.d (1H, J_1 7.2, J_2 10.6 Hz), 1.81 m (1H): cyclopropane ring protons, 2.65 d.d (1H, CH_2Ar, J_1 14.8, J_2 7.3 Hz), 2.87 d.d (1H, CH_2Ar, J_1 14.8, J_2 9.9 Hz), 4.40 m (4H, OCH_2CH_2O), 6.73 d.d (1H, ArH^7, J_O 8.8, J_m 2.1 Hz), 6.79 d (1H, ArH^5, J_m 2.1 Hz), 6.81 d (1H, ArH^8, J_O 8.8 Hz). Found, %: C 55.57, 55.36; H 4.39, 4.41. $C_{12}H_{12}C1_2O_2$. Calculated, %: C 55.62; H 4.67.

Reduction of *gem*-dichlorocyclopropanes XXI–XXIII. To a suspension of 18.4 g (0.8 mol) of finely dispersed sodium in 200 ml of anhydrous ether was added dropwise at vigorous stirring 0.1 mol of an appropriate *gem*-dichlorocyclopropane **XXI–XXIII** in a mixture of 31 ml of methanol and 20 ml of anhydrous ether. The rate of addition was so controlled that the ether steadily boiled. After the completion of dichloride addition 12 ml of methanol was added dropwise to the reaction mixture, and it was stirred for 3 h. Into the reaction mixture that became thick was added first 100 ml of moist ether, and then gradually water till a transparent two-phase system arose. The ether layer was separated, the water layer was extracted with ether (2×50 ml), the combined ethereal solutions were washed with water till neutral washings, and dried on $MgSO_4$. The solvent was distilled off, the residue was subjected to distillation.

4-Methoxybenzylcyclopropane (XV). From 23.1 g (0.1 mol) of compound **XXI** by the above procedure was obtained 11.5 g (71%) of compound **XV**, bp 112–113°C (12 mm Hg), n_D^{20} 1.5348. ^{1}H NMR spectrum, δ, ppm: 0.29 m (2H), 0.62 m (2H), 1.02 m (1H): cyclopropane ring protons, 2.61 d (2H, CH_2Ar, J 7.7 Hz), 3.91 s (3H, OCH_3), 6.92 d (2H, arom, J_O 8.6), 7.26 d (2H, arom, J_O 8.6). Found, %: C 81.22, 81.31; H 8.61, 8.65. $C_{11}H_{14}O$. Calculated, %: C 81.44; H 8.70.

3,4-Dimethoxybenzylcyclopropane (XVI). From 26.1 g (0.1 mol) of compound **XXII** we obtained 14.1 g (73%) of compound **XVI**, bp 162–164°C (20 mm Hg), n_D^{20} 1.5354. ^{1}H NMR spectrum, δ, ppm: 0.21 m (2H), 0.53 m (2H), 0.98 m (1H): cyclopropane ring protons, 2.54 d (2H, CH_2Ar, J 9.8 Hz), 3.87 s (3H, OCH_3), 3.92 s (3H, OCH_3), 6.82 m (3H, arom). Found, %: C 74.81, 74.93; H 8.14, 8.35. $C_{12}H_{16}O_2$. Calculated, %: C 74.96; H 8.39.

6-Cyclopropylmethyl-1,4-benzodioxane (XVII). From 25.9 g (0.1 mol) of dichloride **XXIII** we obtained 11.8 g (62%) of compound **XVII**, bp 144–146°C (14 mm Hg), n_D^{20} 1.5503. ^{1}H NMR spectrum, δ, ppm: 0.14 m (2H), 0.48 m (2H), 0.92 m (1H): cyclopropane ring protons, 2.41 d (2H, CH_2Ar, J 10.2 Hz), 4.18 s (4H, OCH_2CH_2O), 6.61 m (3H, arom). Found, %: C 75.70, 75.72; H 7.16, 7.38. $C_{12}H_{14}O_2$. Calculated, %: C 75.57; H 7.42.

6-Nitro-7-cyclopropylmethyl-1,4-benzodioxane (XIX). To 15 ml of acetic anhydride at –50°C was added 1.3 ml of HNO_3 (d_4^{20} 1.51), at the same temperature was added dropwise a solution of 1.9 g (0.01 mol) of compound **XVII** in 3 ml of acetic anhydride. The reaction mixture was stirred for 2 h at –50°C and then poured into 150 ml of warm water. On cooling the precipitated oily product crystallized. The crystals were filtered off, washed with water, and recrystallized from ethanol. Yield 1.7 g (72%), mp 87°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 0.21 m (2H), 0.49 m (2H), 1.01 m (1H): cyclopropane ring protons, 2.71 d (2H, CH_2Ar, J 7.6 Hz), 4.46 m (4H, OCH_2CH_2O), 7.08 s (1H, ArH^5), 7.53 s (1H, ArH^8). Found, %: C 61.01, 61.17; H 5.41, 5.48; N 5.71, 6.06. $C_{12}H_{13}NO_4$. Calculated, %: C 61.27; H 5.57; N 5.95.

6-(2,2-Dichlorocyclopropylmethyl)-7-nitro-1,4-benzodioxane (XXIV). Nitration of compound **XXIII** was carried out as described above but at –30°C. From 2.6 g (0.01 mol) of dichloride **XXIII** we obtained 2.47 g (81%) of nitro compound **XXIV**, mp 81–82°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 1.23 d.d (1H, J_1 7.2, J_2 7.3 Hz), 1.64 d.d (1H, J_1 7.2, J_2 10.6 Hz), 1.97 m (1H): cyclopropane ring protons, 3.15 d.d (1H, CH_2Ar, J_1 7.3, J_2 14.7 Hz), 3.24 d.d (1H, CH_2Ar, J_1 8.3, J_2 14.7 Hz), 4.31 m (2H, OCH_2CH_2O), 4.39 m (2H, OCH_2CH_2O), 6.97 s (1H, ArH^5), 7.69 C (1H, ArH^8). Found, %: C 47.24, 47.31; H 3.47, 3.53; N 4.31, 4.54. $C_{12}H_{11}NC1_2O_4$. Calculated, %: C 47.39; H 3.65; N 4.61.

Reaction of substrates IX, XV–XVII, XIX, XXI–XXIII, XXV–XXVII with dinitrogen tetroxide. To a solution of 2.8 g (0.03 mol) of N_2O_4 in 30 ml of anhydrous CH_2C1_2 cooled to –30°C was added dropwise at this temperature a solution of 0.015 mol of an appropriate substrate in 15 ml of the same solvent. The reaction mixture was stirred for 1 h at –30°C, poured into 100 ml of water, the organic layer was separated, washed with 3% $NaHCO_3$ solution, with water, and dried with $MgSO_4$. on evaporating the solvent the target compounds were isolated: 1) by column chromatography on silica gel, 40/100, eluent ether–petroleum ether (40–70°C), 1:5; 2) by thin-layer chromatography on $A1_2O_3$ of II activity grade, eluent ether–chloroform–petroleum ether, 1:1:3.

From 2.67 g (0.015 mol) of 3,4-dimethoxyphenylcyclopropane (**IX**) and N_2O_4 with subsequent performance of column chromatography of the reaction mixture we obtained 3.07 g (92%) of **4,5-dimethoxy-2-nitrophenylcyclopropane (XIII),** mp 56–57°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 0.63 m (2H), 1.08 m (2H), 2.54 m (1H): cyclopropane ring protons, 3.93 s (3H, OCH_3), 3.95 s (3H, OCH_3), 6.62 s (1H, ArH^6), 7.57 C (1H, ArH^3). Mass spectrum, *m/z*, (I_{rel}, %): 223 (31.1) M^+, 206 (7.7), 189 (11.0), 162 (10.5), 151 (18.6), 136 (100), 119 (14.2), 108 (19.9), 103 (12.2), 91 (20.5), 77 (19.2), 65 (16.7), 51 (10.9). Found, %: C 58.98, 59.23; H 5.71, 5.82; N 6.03, 6.11. $C_{11}H_{13}NO_4$. Calculated, %: C 59.18; H 5.87; N 6.27.

Reaction of 4-methoxybenzylcyclopropane (XV) with N_2O_4 was carried out as described above. From 2.45 g (0.015 mol) of compound **XV** we obtained 2.63 g of reaction mixture. Chromatography on a plate with $A1_2O_3$ furnished 1.24 g (51%) of the initial reagent, 0.26 g (16.8%)* of **4-methoxy-3-nitrobenzyl-cyclopropane (XXX),** viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 0.22 m (2H), 0.58 (2H), 0.94 (1H): cyclopropane ring protons, 2.55 d (2H, CH_2Ar, *J* 5.7 Hz), 3.98 s (3H, OCH_3), 7.03 d (1H, ArH^5, J_O 8.8 Hz), 7.44 d.d (1H, ArH^6, J_O 8.8, J_m 2.4 Hz), 7.75 d (1H, ArH^2, J_m 2.4 Hz). Mass spectrum, *m/z* (I_{rel}, %): 207 (14.9) M^+, 190 (3.2), 179 (18.9), 166 (100), 161 (20.9), 146 (6.8), 135 (13.1), 132 (12.6), 115 (21.5), 103 (30.4), 91 (43.0), 90 (68,3), 89 (31.6), 77 (27.8), 63 (13.4), 51 (17.1). Found, %: C 63.41, 63.48; H 6.32, 6.39; N 6.38, 6.71. $C_{11}H_{13}NO_3$. Calculated, %: C 63.75; H 6.32; N 6.76;

0.69 g (45.5%)* of **3-methoxy-4-nitro-1,1a,6,6a-tetrahydrocyclopropa-[*a*]indene (XXVIII)**, mp 72–73°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 0.07 d.t (1H, H$^{1'}$, J_1 4.5, J_2 3.4 Hz), 1.14 d.τ (1H, H$^{1'}$, J_1 4.5, J_2 8.0 Hz), 1.94 m (1H, H^{6a}), 2.33 m (1H, H^{1a}), 2.84 d (1H, H$^{6'}$, J_1 16.8 Hz), 3.07 d.d (1H, H$^{6''}$, J_1 16.8, J_2 6.7 Hz), 3.88 s (3H, OCH_3), 6.97 s (1H, ArH^2), 7.58 s (1H, ArH^5). ^{13}C NMR spectrum, δ, ppm: 17.14 (C^1), 17.89 (C^{6a}), 24.46 (C^{1a}), 34.26 (C^6), 108.40 (C^5), 122.55 (C^2), 133.18 (C^3), 137.0 (C^{6a}), 152.6 (C^4), 155.0 (C$^{1\beta}$). Mass spectrum, *m/z* (I_{rel}, %): 205 (45.6) M^+, 158 (34.2), 144 (11.3), 129 (40.5), 128 (100), 127 (43.3), 115 (73.4), 114 (24.0), 103 (13.7), 91 (13.5), 89 (13.4), 77 (14.2), 65 (6.3), 63 (15.8), 51 (10.1). Found, %: C 64.41, 64.12; H 5.32, 5.29; N 6.68, 6.83. $C_{11}H_{11}NO_3$. Calculated, %: C 64.38; H 5.40; N 6.83;

0.11 g of a mixture of **3-hydroxy-4-nitro-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene (XXIX)** and **4-hydroxy-3-nitrobenzylcyclopropane (XXXI)** in 1:1.2 ratio as shown by a chromatogram obtained in the study of the reaction mixture by GC-MS method. Mass spectrum of compound **XXIX**, *m/z* (I_{rel}, %): 191 (35.4) M^+, 145 (27.2), 144 (18.9), 127 (6.3), 115 (100), 114 (22.8), 103 (6.3), 91 (16.2), 89 (11.4), 77 (13.3), 65 (6.2), 63 (11.3), 51 (10.1); of compound **XXXI**, *m/z* (I_{rel}, %): 193 (8.9) M^+, 165 (70.9), 152 (100), 119 (6.2), 106 (36.7), 91 (21.5), 77 (31.6), 65 (10.1), 51 (22.8), 39 (12.6).

Reaction of 1,1-dichloro-2-(4-methoxybenzyl)-cyclopropane (XXI) with N_2O_4. In reaction of 3.5 g (0.015 mol) of compound **XXI** with N_2O_4 carried out under standard conditions and followed by separation of the reaction mixture on plates with Al_2O_3 we obtained 2.7 g (78%) of initial compound **XXI**, 0.71 g (74%)** of **2-(4-methoxy-3-1,1-dichloronitrobenzyl)cyclopropane (XXXII**), viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.29 m (1H), 1.72 m (1H), 1.88 m (1H): cyclopropane ring protons, 2.86 d.d (1H, CH_2Ar, J_1 17.2, J_2 6.8 Hz), 2.96 d.d (1H, CH_2Ar, J_1 17.2, J_2 8.8 Hz), 3.97 s (3H, OCH_3), 7.04 d (1H, ArH^5, J_O 8.3 Hz), 7.46 d.d (1H, ArH^6, J_O 8.4, J_m 2.2 Hz), 7.72 d (1H, ArH^2, J_m 2.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 277 (5.1) ^{1}[*M*]$^+$, 275 (8.3) ^{2}[*M*]$^+$, 236 (3.5), 234 (5.8), 179 (57.2), 166 (100), 132 (18.6), 119 (13.5), 103 (24.3), 90 (37.2), 77 (20.2), 63 (8.2), 51 (12.7). Found, %: C 7.62, 47.79; H 3.89, 3.97; N 4.94, 4.98. $C_{11}H_{11}C_{I2}NO_3$. Calculated, %: C 47.84, H 4.02, N 5.07;

0.22 g (26%)* of **2-(3-nitro-4-hydroxybenzyl)-1,1-dichlorocyclopropane (XXXIII),** viscous oily substance. ^{1}H NMR spectrum, δ, ppm: 1.24 m (1H), 1.71

* Calculated on the reacted compound **XV**.

** Calculated on the reacted compound **XXI**.

m (1H), 1.82 m (1H): cyclopropane ring protons, 2.84 d.d (1H, CH_2Ar, J_1 17.6, J_2 10.6 Hz), 7.14 d (1H, ArH^5, J_o 9.0), 7.54 d.d (1H, ArH^6, J_O 9.0, J_m 2.22), 8.03 d (1H, ArH^3, J_m 2.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 263 (4.0) $^1[M]^+$, 261 (6.4) $^2[M]^+$, 165 (83.3), 152 (100), 115 (9.4), 106 (19.2), 91 (10.9), 77 (14.1), 63 (7.4), 51 (11.9).

Reaction of 6-cyclopropylmethyl-1,4-benzodioxane (XVII) with N_2O_4. From 2.85 g (0.015 mol) of compound **XVII** and two equiv of N_2O_4 under standard conditions followed by column chromatography on silica gel (40/100) we obtained 3.27 g (93%) of **6-nitro-7-cyclopropylmethyl-1,4-benzodioxane** (**XIX**), mp 87°C (EtOH). ^{1}H NMR spectrum was identical to that of an authentic sample, and the sample mixed with an authentic compound showed no melting point depression.

Reaction of 2-(3,4-dimethoxybenzyl)-1,1-dichlorocyclopropane (XXII) with N_2O_4. Reaction of 3.9 g (0.015 mol) of compound **XXII** under standard conditions followed by column chromatography afforded 4.3 g (95%) of **2-(4,5-dimethoxy-2-nitrobenzyl)-1,1-dichlorocyclopropanea (XXXV)**, mp 52–53°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 1.34 т (1H), 1.75 d.d (1H, J_1 14.4, J_2 3.4 Hz), 1.99 m (1H): cyclopropane ring protons, 3.12 d.d (1H, CH_2Ar, J_1 19.8, J_2 6.8 Hz), 3.14 d.d (1H, CH_2Ar, J_1 19.8, J_2 5.4 Hz), 3.98 s (3H, OCH_3), 4.04 s (3H, OCH_3), 7.04 s (1H, ArH^6), 7.69 s (1H, ArH^3). Mass spectrum, *m/z* (I_{rel}, %): 307 (9.9) $^1[M]^+$, 305 (16.1) $^2[M]^+$, 270 (15.9), 240 (18.2), 206 (17.2), 192 (53.2), 181 (32.1), 180 (100), 166 (98.1), 150 (43.6), 138 (33.3), 136 (33.2), 121 (16.0), 109 (19.5), 107 (18.6), 92 (18.5), 77 (36.5), 63 (23.2), 51 (24.9), 39 (14,6). Found, %: C 46.87, 47.01; H 4.08, 4.13; N 4.31, 4.49. $C_{12}H_{13}Cl_2NO_4$. Calculated, %: C 47.08; H 4.28; N 4.57.

Reaction of 6-(2,2-dichlorocyclopropylmethyl)-1,4-benzodioxane (XXIII) with N_2O_4. Reaction of 3.9 g (0.015 mol) of compound **XXIII** with two equiv of N_2O_4 followed by column chromatography furnished 4.25 g (93%) of nitro compound **XXIV**, mp 81–82°C (EtOH). ^{1}H NMR spectrum was identical to that of a sample obtained by nitration of compound **XXIII** with nitric acid in acetic anhydride.

Reaction of 3,4-dimethoxybenzylcyclopropane (XVI) with N_2O_4. Reaction of 4.8 g (0.025 mol) of cyclopropane **XVI** with 4.6 g (0.05 mol) N_2O_4 in 60 ml of CH_2Cl_2 at –30°C after standard workup of the reaction mixture followed by separation of the reaction mixture on plates with Al_2O_3 afforded 0.08 g (1.5%) of **3,4-dimethoxy-2-nitro-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene (XXXVIII)**, light-yellow crystals. ^{1}H NMR spectrum, δ, ppm: 0.87 m (1H, H'^1), 1.29 m (1H, H''^1), 1.64 m (1H, H^{6a}), 2.53 m (1H, H^{1a}), 2.96 d (1H, H'^6, J 17.8 Hz), 3.19 d.d (1H, H''^6, J_1 17.8, J_2 7.1 Hz), 3.94 s (3H, OCH_3), 4.01 s (3H, OCH_3), 7.33 s (1H, ArH^2). Mass spectrum, *m/z* (I_{rel}, %): 235 M^+. Found, %: C 60.94, 61.07; H 5.34, 5.47; N 5.69, 5.90. $C_{12}H_{13}NO_4$. Calculated, %: C 61.27; H 5.57; N 5.95;

0.73 g (12.5%) of **3,4-dimethoxy-5-nitro-1,1a,6,6a-tetrahydrocyclo-propa[*a*]indene (XXXVII)**, mp 99°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 0.18 m (1H, H'^1), 1.21 m (1H, H''^1), 1.99 m (1H, H^{6a}), 2.59 m (1H, H^{1a}), 3.43 d (1H, H'^6, J 19.2), 3.52 d.d (1H, H''^6, J_1 9.2, J_2 6.6 Hz), 3.92 s (3H, OCH_3), 4.07 s (3H, OCH_3), 7.55 s (1H, ArH^2). Mass spectrum, *m/z* (I_{rel}, %): 235 (13.4) M^+, 218 (100), 188 (24.8), 173 (14.7), 159 (9.2), 145 (10.4), 131 (12.3), 115 (16.8), 103 (18.1), 91 (7.7), 77 (21.9), 63 (7.8), 51 (10.6). Found, %: C 60.99, 61.03; H 5.38, 5.55; N 5.71, 5.76. $C_{12}H_{13}NO_4$. Calculated, %: C 61.27; H 5.57; N 5.95;

4.55 g (77%) of **4,5-dimethoxy-2-nitrobenzylcyclopropane (XXXVI)**, mp 75–76°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 0.24 m (1H), 0.55 m (1H), 1.11 m (1H): cyclopropane ring protons, 2.89 d (2H, CH_2Ar, J 6.8), 3.92 s (3H, OCH_3), 3.99 s (3H, OCH_3), 6.98 s (1H, ArH^6), 7.62 s (1H, ArH^3). Mass spectrum, *m/z* (I_{rel}, %): 237 (39.7) M^+, 220 (80.1), 190 (22.4), 176 (24.3), 165 (100), 148 (19.3), 136 (25.51), 121 (16.1), 115 (30.7), 103 (21.1), 91 (29.7), 77 (55.7), 69 (47.7), 63 (23.1), 51 (28.2), 39 (24.9). Found, %: C 60.46, 60.48; H 6.21, 6.30; N 5.71, 5.79. $C_{12}H_{15}NO_4$. Calculated, %: C 60.75; H 6.37; N 5.90.

Reaction of 4-allylanisole (XXV) with N_2O_4. Reaction of 2.96 g (0.02 mol) of compound **XXV** with 3.7 g (0.04 mol) of N_2O_4 was carried out by standard procedure. The separation of the reaction mixture on plates with Al_2O_3 afforded 1.69 g(57%) of initial 4-allylanisole (**XXV**) identified by ^{1}H and mass spectra; 0.1 g (6.1%) of **4-allyl-3-nitroanisole (XLI),** oily substance. ^{1}H NMR spectrum, δ, ppm: 3.43 d (2H, CH_2Ar, J 6.2 Hz), 3.99 s (3H, OCH_3), 5.12 m (2H, CH_2=CH), 5.95 m (1H, CH_2=CH), 6.92 d (1H, ArH^5, J_o 9.2 Hz), 8.06 d (1H, ArH^2, J_m 2.5 Hz), 8.14 d.d (1H, ArH^6, J_o 9.2, J_m 2.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 193 (71.8) M^+, 146 (12.4), 133 (15.4), 115 (100), 103 (39.7), 91 (75.6), 77 (39.1), 63 (18.6), 51 (25.1), 39 (15.5); 0.76 g (45.5%) of **4-allyl-2-nitroanisole (XL),** oily substance. ^{1}H NMR spectrum, δ, ppm: 3.38 d (2H, CH_2Ar, J 6.0 Hz), 3.95 s

* Calculated on the reacted compound **XXI**.

(3H, OCH_3), 5.14 m (2H, CH_2=CH), 5.93 m (1H, CH_2=CH), 7.03 d (1H, ArH^6, J_o 8.8 Hz), 7.37 d.d (1H, ArH^5, J_o 8.8, J_m 2.2 Hz), 7.67 d (1H, ArH^3, J_m 2.2 Hz). Mass spectrum, *m/z* (I_{rel}, %): 193 (100) M^+, 164 (6.4), 147 (17.3), 132 (47.3), 131 (46.7), 118 (37.8), 115 (39.1), 103 (41.1), 91 (39.2), 77 (33.9), 63 (16.1), 51 (18.6), 39 (10.2). Found, %: C 61.93, 62.07; H 5.59, 5.62; N 7.01, 7.11. $C_{10}H_{11}NO_3$. Calculated, %: C 62.16; H 5.74; N 7.25;

0.37 g (24.5%) of **4-allyl-2-nitrophenol (XLII)**, oily substance. ^{1}H NMR spectrum, δ, ppm: 3.35 d (2H, CH_2Ar, *J* 6.8 Hz), 5.19 m (2H, CH_2=CH), 5.92 m (1H, CH_2=CH), 7.11 d (1H, ArH^6, J_O 8.6 Hz), 7.44 d.d (1H, ArH^5, J_o 8.6, J_m 2.4 Hz), 7.94 d (1H, ArH^3, J_m 2.4 Hz), 10.51 s (1H, OH). Mass spectrum, *m/z* (I_{rel}, %): 179 (100) M^+, 162 (13.6), 133 (49.6), 116 (6.2), 103 (38.8), 91 (15.3), 84 (21.9), 77 (44.2), 63 (5.8), 51 (29.3), 49 (30.9), 39 (9.9).

Reaction of allyl-1,2-dimethoxybenzene (XXVI) with N_2O_4. From 2.67 g (0.015 mol) of compound **XXVI** we obtained 3.12 g (94%) of **4-allyl 1,2-dimethoxy-5-nitrobenzene (XLIII)**, mp 36–37°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 3.64 d (2H, CH_2Ar, *J* 7.1), 3.87 s (3H, OCH_3), 3.89 s (3H, OCH_3), 5.04 m (2H, CH_2=CH), 5.91 m (1H, CH_2=CH), 6.65 s (1H, ArH^3), 7.51 s (1H, ArH^6). Mass spectrum, *m/z* (I_{rel}, %): 223 (19.2) M^+, 206 (100), 189 (72.4), 176 (21.1), 162 (33.9), 147 (21.1), 133 (21.2), 118 (18.6), 103 (21.9), 91 (30.8), 77 (31.1), 65 (27.6), 63 (20.5), 55 (45.1), 51 (16.1), 39 (17.1). Found, %: C 58.96, 58.99; H 5.71, 5.84; N 6.03, 6.11. $C_{11}H_{13}NO_4$. Calculated, % : C 59.18; H 5.87; N 6.27 .

Reaction of 6-allyl-1,4-benzodioxane (XXVII) with N_2O_4. Reaction of 2.64 g (0.015 mol) of compound **XXVII** under standard conditions followed by separation of the reaction mixture by column chromatography on silica gel (40/100 μm) afforded 2.25 g (68%) of **6-allyl-7-nitro-1,4-benzodioxane (XLIV)**, mp 40–42°C (EtOH). ^{1}H NMR spectrum, δ, ppm: 3.59 d (2H, CH_2Ar, *J* 7.6 Hz), 4.33 m (4H, OCH_2CH_2O), 5.06 m (2H, CH_2=CH), 5.91 m (1H, CH_2=CH), 6.88 s (1H, ArH^5), 7.52 s (1H, ArH^8). Found, %: C 59.41, 59.67; H 4.88, 4.93; N 6.12, 6.27. $C_{11}H_{11}NO_4$. Calculated, % : C 59.72; H 5.01; N 6.33 .

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