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Transformations of *para*-Substituted Benzylcyclopropanes, Allylbenzenes, and Diphenylmethanes under Nitration with Nitric Acid in Acetic Anhydride

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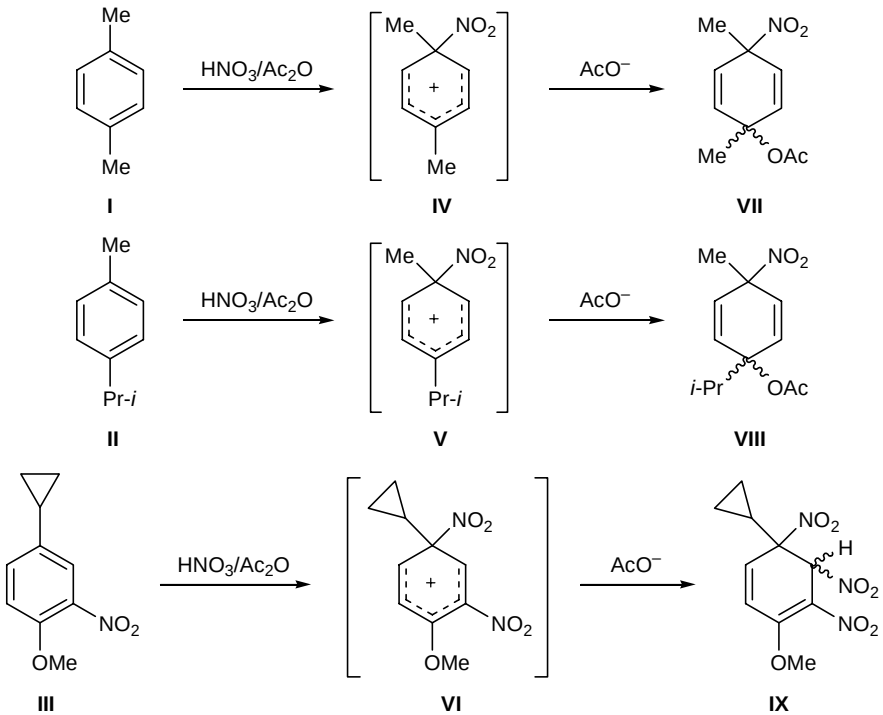
Abstract—Electrophilic nitration of benzylcyclopropanes, allylbenzenes, and diphenylmethanes containing *ortho*,*para*-orienting substituents in the *para* position of the benzene ring results mainly in replacement of the cyclopropylmethyl, allyl, or benzyl group, respectively (*ipso* substitution). The nitration of 4-cyclopropylallylbenzene is not accompanied by nitrodealkylation, and the products are only 2- and 3-nitro-4-cyclopropylallylbenzenes.

Up to now, direct proofs have been obtained that electrophilic nitration of *p*-alkyl- and *p*-alkoxy-substituted toluenes and phenylcyclopropanes **I**–**III** involves intermediate formation of *ipso*-σ-complexes **IV**–**VI** which are then converted into relatively stable cyclohexadiene adducts **VII**–**IX** (Scheme 1) [1–10]. Adducts like **VII**–**IX** can be isolated; however, they usually undergo acid-catalyzed transformations during the process. These transformations give rise to not only conventional electrophilic substitution products but

Scheme 1.



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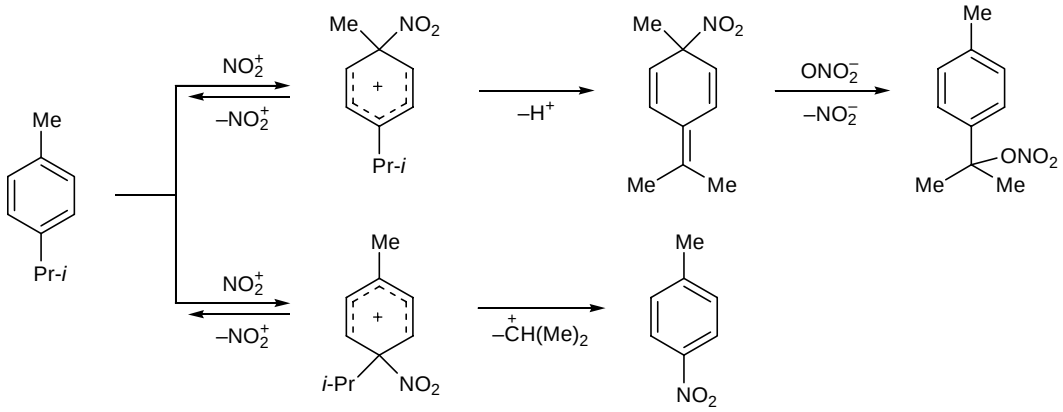
also so-called "anomalous" nitration products. The latter are formed from the corresponding *ipso*-σ-complexes **IV**–**VI**, e.g., via concurrent elimination of the alkyl group from the sp^3-hybridized carbon atom or modification of substituent in the *para*-position with respect to that carbon atom (Schemes 2, 3). It should be emphasized that electrophilic nitration of 1,4-dialkylbenzenes and 4-alkylphenylcyclopropanes is accompanied by *ipso*-substitution of methyl, ethyl, isopropyl, or *tert*-butyl group and that in no case *ipso*-substitution of cyclopropyl group was observed. The yield of the nitrodealkylation products in the above reactions did not exceed 10–17%, and it strongly depended on the conditions [9].

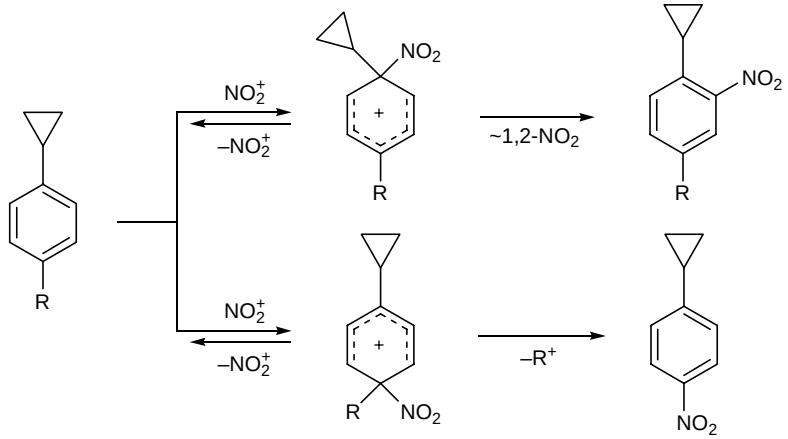
In continuation of our studies on the behavior of 1,4-dialkylbenzenes under conditions of electrophilic nitration, in the present work we examined transformations of *para*-substituted benzylcyclopropanes in reactions with nitric acid in acetic anhydride. We previously showed [11] that the nitration of unsubstituted benzylcyclopropane with nitric acid in acetic anhydride occurs in a way similar to phenylcyclopropane: the reaction takes place at low temperature, and the acidophobic cyclopropylmethyl fragment is retained. However, the ratio of the resulting *o*- and *p*-nitrobenzylcyclopropanes (1.1:1) sharply differed from the ratio of the corresponding isomeric nitrophenylcyclopropanes obtained from phenylcyclopropane under the same conditions (4.5:1) [12].

Taking the above results into account, we presumed that benzylcyclopropanes having an isopropyl or *tert*-butyl group or a halogen atom in the *para* position should behave similarly to analogous phenylcyclopropane derivatives under the nitration conditions reported for unsubstituted benzylcyclopropane [11]. As shown in [13–15], the nitration of substituted phenylcyclopropanes yields mainly the corresponding 2-nitro derivatives. However, in the reactions of 4-isopropyl-, 4-*tert*-butyl-, and 4-chlorobenzylcyclopropanes **X**–**XII** with nitric acid in acetic anhydride, the respective

Scheme 2.

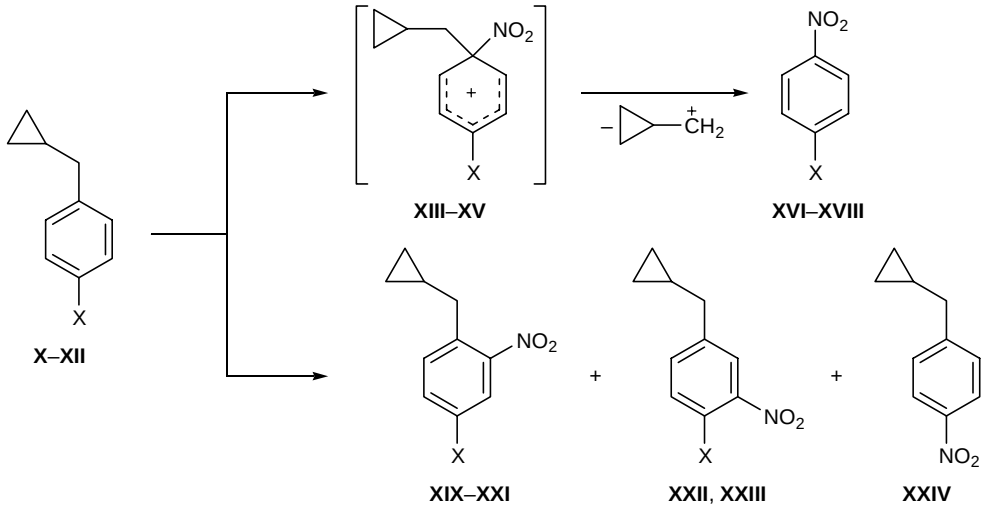


Scheme 3.



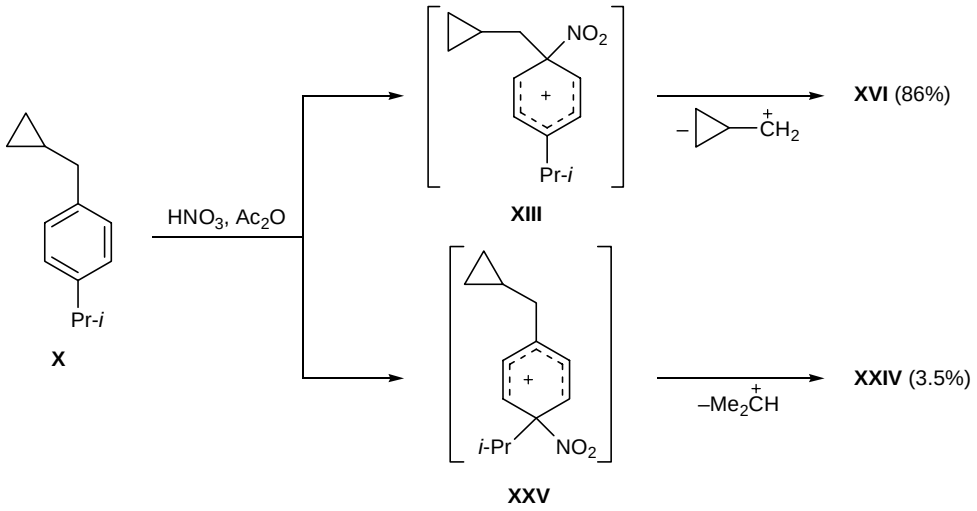
R = Me, Et, *i*-Pr, *t*-Bu.

Scheme 4.



X, **XIII**, **XVI**, **XIX**, **XXII**, **XXIV**, X = *i*-Pr; **XI**, **XIV**, **XVII**, **XX**, X = *t*-Bu; **XII**, **XV**, **XVIII**, **XXI**, **XXIII**, X = Cl.

Scheme 5.



nitroaromatic compounds were formed in a poor yield (9–17%), while the main reaction direction was replacement of the cyclopropyl substituent by nitro group (*ipso* substitution; Scheme 4).

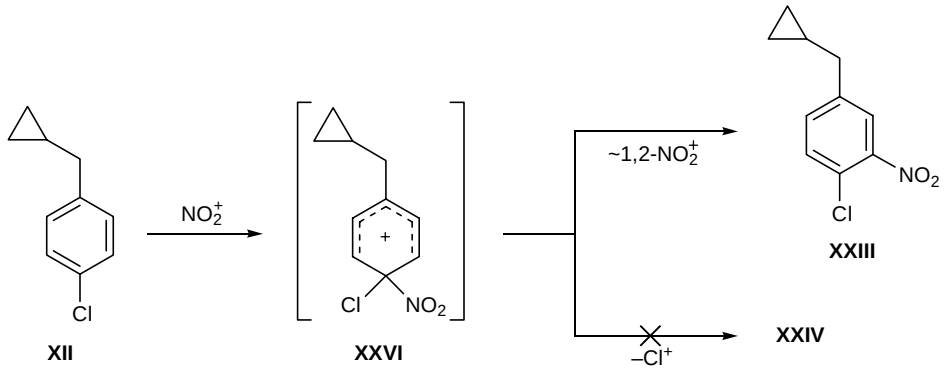
The high yield of the nitrodealkylation products (see table) convincingly shows that (1) predominant *ipso*-attack by nitronium ion observed for *para*-substituted alkylbenzenes is also typical of analogous benzylcyclopropanes and (2) (what is the most important) σ-complexes **XIII**–**XV** containing both cyclopropylmethyl group and nitro group in the geminal entity are formed more readily and they more readily eliminate the respective alkyl cation, as compared to alternative σ-complexes having a different alkyl group in the same position. The latter statement follows, e.g., from the ratio of the nitrodealkylation products formed by nitration of 4-isopropylbenzylcyclopropane (**X**) (Scheme 5).

Interestingly, the nitration of 4-chlorobenzylcyclopropane (**XII**), in addition to σ-complex **XV** responsible for the nitrodealkylation pathway, also gives rise

Nitration of *para*-substituted benzylcyclopropanes **X**–**XII** with nitric acid in acetic anhydride

Compound no.	Products (yield, %)
X	**XVI** (86), **XIX** (4), **XXII** (5.5), **XXIV** (3.5)
XI	**XVII** (90), **XX** (8)
XII	**XVIII** (76), **XXI** (6), **XXIII** (11)

Scheme 6.



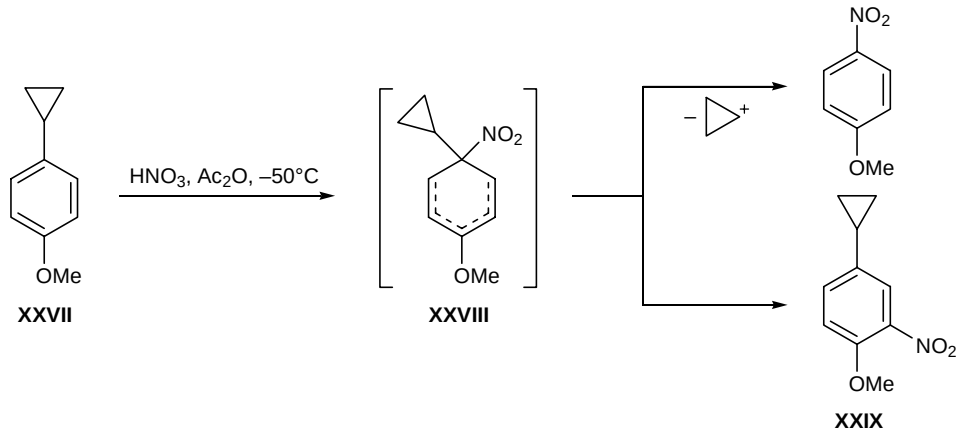
to complex **XXVI** having both chlorine atom and nitro group at the sp^3-carbon atom (Scheme 6). However, insofar as σ-complex **XXVI** (like analogous complexes derived from 4-chlorotoluene [16]) is likely to be incapable of eliminating chlorine as positively charged species, it is converted into 4-chloro-3-nitrobenzylcyclopropane (**XXIII**) via 1,2-shift of the nitro group. This also follows from the anomalously high ratio of nitrobenzylcyclopropanes **XXIII** and **XXI**.

We previously showed [17] that the nitration of 4-methoxyphenylcyclopropane (**XXVII**) with anhydrous nitric acid in acetic anhydride gives 4-methoxy-3-nitrophenylcyclopropane (**XXIX**) in almost quantitative yield. According to the data of [9, 18], the transformation of **XXVII** into nitro compound **XXIX** involves initial formation of a considerable amount (no less than 70%) of σ-complex **XXVIII** (Scheme 7). Without going into details how σ-complex **XXVIII** is converted into the final product (this problem has not been solved unambiguously as yet), we can state with a high degree of certainty that cyclopropyl group cannot be eliminated from the geminal entity in σ-complex **XXVIII** under the given conditions.

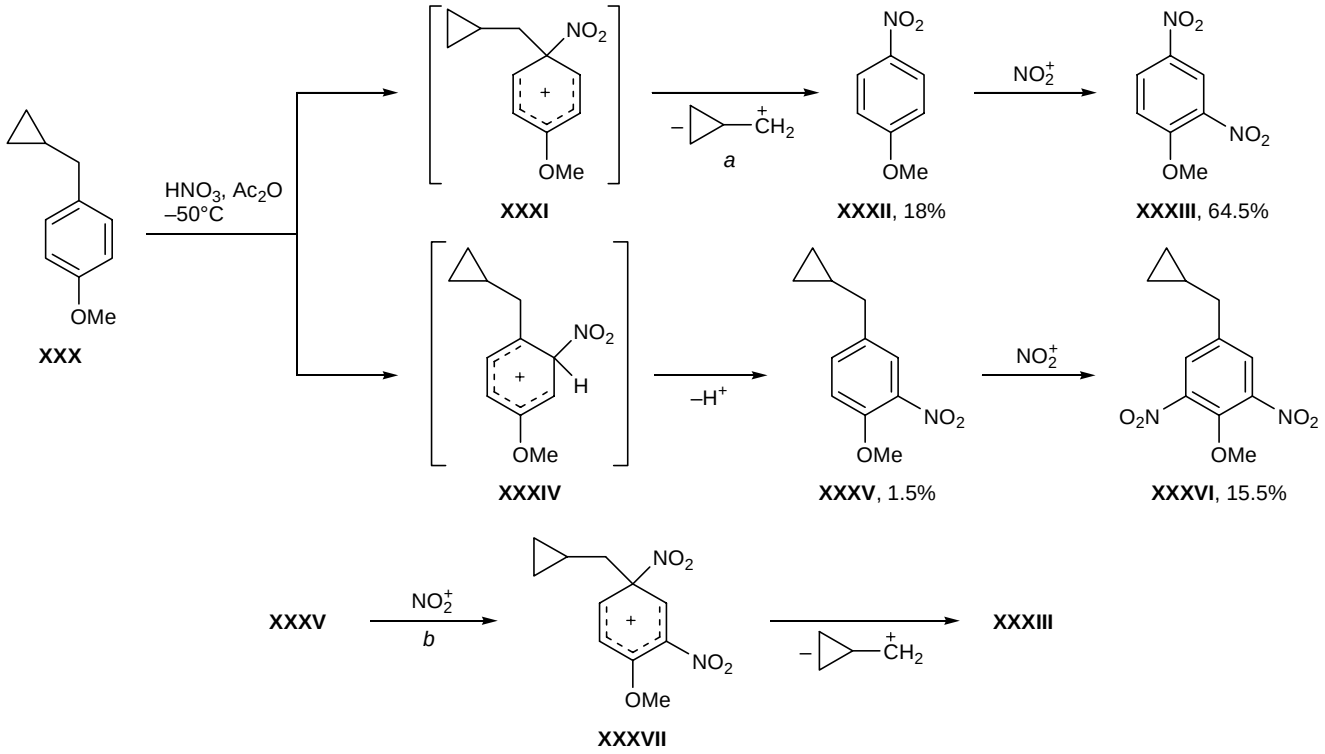
The nitration of 4-metoxybenzylcyclopropane (**XXX**) which is homologous to **XXVII** also involves formation of σ-complex **XXXI** which is analogous to **XXVIII**. However, unlike **XXVIII**, σ-complex **XXXI** readily eliminates the alkyl moiety, yielding 4-nitro- and 2,4-dinitroanisoles **XXXII** and **XXXIII**, whereas normal electrophilic aromatic substitution products are formed in considerably smaller amounts (Scheme 8; see Experimental). Taking into account that mononitrobenzylcyclopropane (**XXXV**) was detected only in trace amount (~1.5%), there are grounds to believe that this compound underwent not only further nitration to dinitro derivative **XXXVI** but also *ipso*-substitution along pathway *b* to afford dinitroanisole **XXXIII**. This assumption is confirmed, e.g., by the fact that a homolog of **XXXV**, 4-cyclopropyl-3-nitroanisole (**III**), under analogous conditions is converted in high yield into the corresponding *ipso*-adduct with the cyclopropyl and nitro groups attached to the sp^3-hybridized carbon atom (Scheme 1) [10].

Obviously, relatively facile elimination of the cyclopropylmethyl fragment from σ-complexes like **XIII**–**XV** is favored by the greater stability of cyclo-

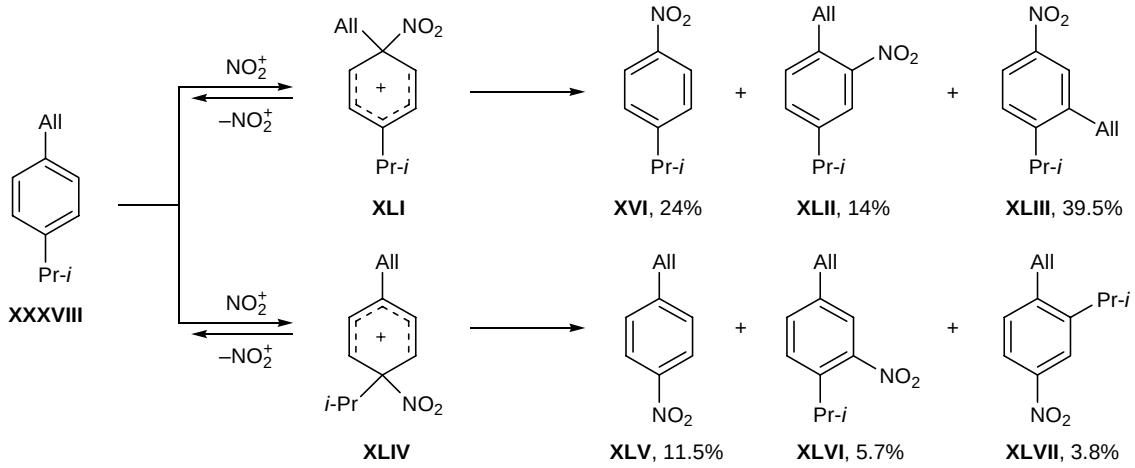
Scheme 7.



Scheme 8.



Scheme 9.



propylmethyl cation as compared to alkyl or cyclopropyl cation; the stability of the former is likely to be comparable with the stability of allyl or benzyl cation. Generally speaking, this suggests that the nitration of *para*-substituted allylbenzenes and diphenylmethanes under the same conditions as for *para*-substituted benzylcyclopropanes **X**–**XII** and **XXX** should follow the nitrodeallylation or nitrodebenzylation path. In order to verify this assumption we examined the nitration of 4-isopropyl- and 4-*tert*-butylallylbenzenes **XXXVIII** and **XXXIX** and 4,4'-difluorodiphenylmethane (**XL**) with nitric acid in acetic anhydride. In fact, the predominant transformation pathway of compounds **XXXVIII**–**XL** was nitrodealkylation as shown in Schemes 9–12. It was quite interesting that no nitrodealkylation products were obtained from 4-cyclopropylallylbenzene (**LV**) which is structurally related to 4-isopropylallylbenzene (**XXXVIII**); from the reaction mixture we isolated only 3- and 2-nitro-4-cyclopropylallylbenzenes **LVIII** and **LIX** (Scheme 12). The absence of the expected 4-nitrophenylcyclopropane (**LX**) among the products indicates (1) that the corre-

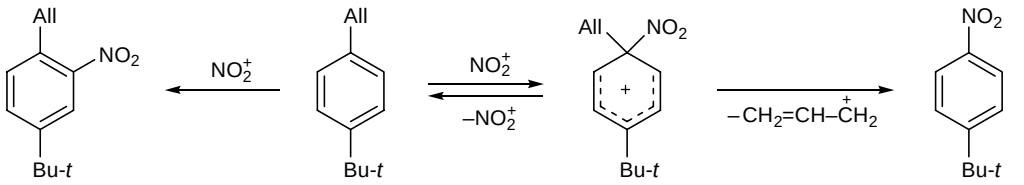
sponding precursor, σ-complex **LVII**, is formed in a considerably smaller amount, as compared to isomeric σ-complex **LVI**, and (2) that σ-complex **LVII** cannot be converted into nitrodeallylation product **LX** at an appreciable rate since the cyclopropane substituent effectively stabilizes the positive charge therein thus hindering elimination of the allyl group.

It should be emphasized that in the nitration of compound **LV** the fraction of product **LVIII** having a nitro group in the *ortho* position with respect to the cyclopropyl radical is greater by a factor of ~6 than the fraction of isomeric compound **LIX** in which the nitro group is neighboring to the allyl substituent. Presumably, the cyclopropane ring in **LV** activates *ipso*-attack by NO_2^+ cation to a considerably stronger extent than does the allyl group; therefore, σ-complex **LVI** is mainly formed. Insofar as the latter cannot eliminate the cyclopropyl group, it is converted into 4-allyl-2-nitrophenylcyclopropane (**LVIII**) via ~1,2-shift of the nitro group. This assumption is supported by the data of [18] according to which the relative contribution of *ipso*-attack by NO_2^+ ion on the cyclopropyl-substituted carbon atom in 4-cyclopropylanisole is considerably greater than the relative contribution of *ipso*-attack on the methyl-substituted position in 4-methylanisole. On the other hand, the nitration of compound **LV** according to the classical electrophilic substitution mechanism (Scheme 12) cannot be ruled out.

Comparison of the results of nitration of benzylcyclopropanes **X** and **XI** and allylbenzenes **XXXVIII** and **XXXIX** revealed the following relations holding in their transformations under the action of nitric acid in acetic anhydride. Steric shielding by the *tert*-butyl group in **XI** and **XXXIX** hinders the corresponding *ipso*-attack, and these substrates give rise almost exclusively to σ-complexes **XIV** and **XLIX**, respectively, having cyclopropyl or allyl and nitro groups at the sp^3-carbon atom; elimination of the alkyl groups from these complexes occurs at comparable rates (judging by the yields of the nitrodealkylation products formed within a specified period); the behaviors of 4-isopropylbenzylcyclopropane (**X**) and 4-isopropylallylbenzene (**XXXVIII**) under standard nitration conditions differ considerably, though the overall yield of the nitrodealkylation product and that formed as a result of anomalous modification of σ-complex (e.g., in the reaction with **XXXVIII**) is fairly high.

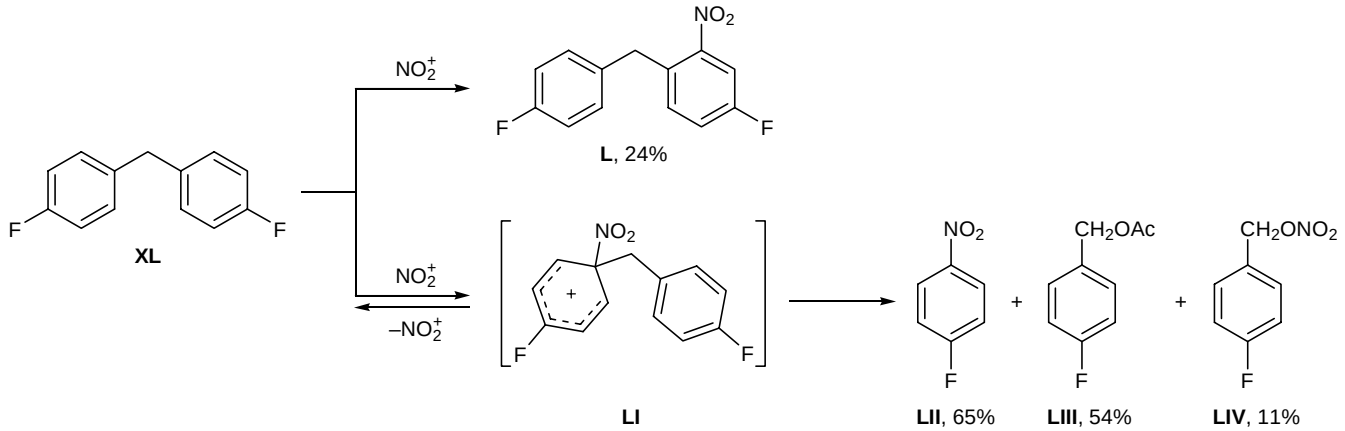
Taking into account similar electronic and steric properties of the substituents in the benzene ring, the relative contributions of *ipso*-attacks on both positions in structures **X** and **XXXVIII** should be similar. In fact, this is confirmed by comparing the overall yields of products formed in the nitration of substrates **X** and **XXXVIII** from the corresponding σ-complexes (**XIII**, 86%; **XLI**, 77.5%; **XXV**, 3.5%; **XLIV**, 21%; Schemes 4, 9).

Scheme 10.



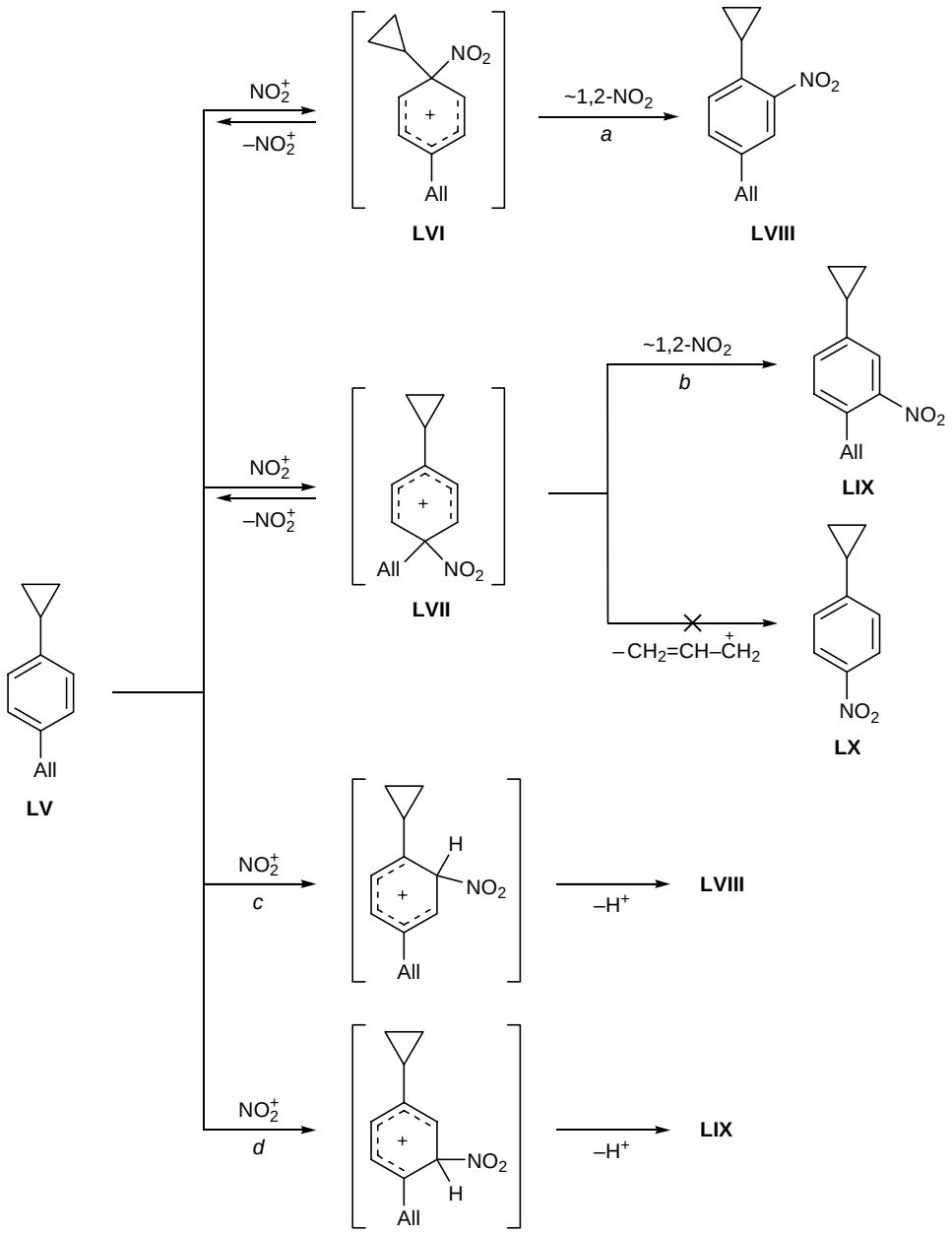
XLVIII **XXXIX** **XLIX** **XVII**, 84%

Scheme 11.



XL **L**, 24% **LI** **LII**, 65% **LIII**, 54% **LIV**, 11%

Scheme 12.



As follows from the yields of the *ipso*-substitution products obtained from **X** and **XXXVIII** (86 and 77.5%, respectively), the rates of elimination of cyclopropylmethyl cation and allyl cation from the corresponding σ-complexes differ insignificantly. Therefore, a strong difference in the behaviors of compounds **X** and **XXXVIII** should be attributed to the different abilities of the alkyl fragments liberated from σ-complexes **XIII** and **XXXXI** to participate in further transformations, specifically in the alkylation of 4-nitroisopropylbenzene (**XVI**) formed by nitrodealkylation of **X** and **XXXVIII**. Most probably, the ability of the liberated cyclopropylmethyl cation to undergo multivariant isomerizations and the lack of such ability in allyl cation are responsible for the observed transformation pathways of cyclopropylmethyl- and allylisopropylbenzenes **X** and **XXXVIII**. It should be noted that the absence of allylation products of 4-nitro-*tert*-butylbenzene (**XXVII**) together with the large contribution (84%) of *ipso*-substitution (and hence strong release of allyl cation) in the nitration of 4-*tert*-butyl-1-allylbenzene (**XXXIX)** suggest an important role of steric factor (hindered alkylation at the *ortho* position with respect to the bulky *tert*-butyl group.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker AW-300 (300 MHz) and Varian BXR-400 (400 MHz) instruments using $CDCl_3$ as solvent and TMS as internal reference. The mass spectra were obtained on a Finnigan SSQ-7000 GC–MS system (DB-1 capillary column, 30 m×2 mm; carrier gas helium, flow rate 40 ml/min; oven temperature programming from 50 to 300°C at 10 deg/min; energy of ionizing electrons 70 eV). The reaction mixtures were separated by column or thin-layer chromatography on aluminum oxide (Brockman activity grade II) using the following solvent systems as eluent: A: diethyl ether–petroleum ether (40–70°C), 1:3 (by volume); B: diethyl ether–chloroform–petroleum ether (40–70°C), 1:1:3 (by volume).

(4-Isopropylbenzyl)cyclopropane (X) was obtained by reduction of 1,1-dichloro-2-(4-isopropylbenzyl)-cyclopropane according to the procedure described in [19]. Yield 74%, bp 142–143°C (50 mm), n_D^{20} = 1.5120. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.12 m (2H), 0.39 m (2H), and 0.86 m (1H) (cyclopropane); 1.18 d (6H, CH_3); 2.42 d (2H, C**H**$_2$C$_6$H$_4$, *J* = 4.8); 2.77 sept [1H, C**H**$(CH_3)_2$]; 7.11 d (2H, *J* = 8.0) and 7.16 d (2H, *J* = 8.0) (H_{arom}). Found, %: C 89.28; H 10.22. $C_{13}H_{18}$. Calculated, %: C 89.59; H 10.41.

(4-*tert*-Butylbenzyl)cyclopropane (XI) was synthesized in a similar way from 2-(4-*tert*-butylbenzyl)-1,1-dichlorocyclopropane. Yield 64%, bp 99–101°C (10 mm), n_D^{20} = 1.5087. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.22 m (2H), 0.54 m (2H), and 1.01 m (1H) (cyclopropane); 1.29 s (9H, CH_3); 2.53 d (2H, C**H**$_2$C$_6$H$_4$, *J* = 5.4); 7.23 d (2H, *J* = 8.4) and 7.32 d (2H, *J* = 8.4) (H_{arom}). Found, %: C 88.98; H 10.42. $C_{14}H_{20}$. Calculated, %: C 89.30; H 10.70.

(4-Chlorobenzyl)cyclopropane (XII) was synthesized by the procedure described in [20]. Yield 68%, bp 94–95°C (11 mm), n_D^{20} = 1.5309.

(4-Methoxybenzyl)cyclopropane (XXI) was synthesized by the procedure described in [21]. Yield 73%, bp 114–115°C (12 mm), n_D^{20} = 1.5352.

1-Allyl-4-cyclopropylbenzene (LV) was synthesized by reaction of 4-cyclopropylphenylmagnesium bromide with an equimolar amount of allyl chloride. Yield 56%, bp 128–129°C (12 mm), n_D^{20} = 1.5442. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.63 m (2H), 0.92 m (2H), and 1.84 m (1H) (cyclopropane); 3.31 d (2H, C**H**$_2$C$_6$H$_4$, *J* = 5.8); 5.03 m (2H, C**H**$_2$=CH); 5.95 m (1H, CH_2=C**H**); 6.98 d (2H, *J* = 8.2) and 7.08 d (2H, *J* = 8.2) (H_{arom}). Found, %: C 90.91; H 8.81. $C_{12}H_{14}$. Calculated, %: C 91.08; H 8.92.

Reactions of compounds X–XII, XXX, XXXVIII–XL, and LV with nitric acid in acetic anhydride (*general procedure*). Nitric acid (d = 1.5 g/cm^3), 2.5 ml (0.06 mol), was added at –50°C to 20 ml of acetic anhydride, and a solution of 0.02 mol of compound **X**–**XII**, **XXX**, **XXXVIII**–**XL**, or **LV** in 6 ml of acetic anhydride was added dropwise under stirring, maintaining the temperature at –50°C. The mixture was stirred for 1 h at that temperature, poured into 150 ml of warm water (~40–50°C), and extracted with diethyl ether. The extract was washed with water, a 2 N solution of Na_2CO_3, and water again, dried over $MgSO_4$, and evaporated, and the residue was subjected to column or thin-layer chromatography on Al_2O_3.

Nitration of (4-isopropylbenzyl)cyclopropane (X). The nitration of 3 g (0.02 mol) of compound **X** gave 3.6 g of a mixture of products; by column chromatography we isolated 0.37 g (9.5%) of a mixture of (4-isopropyl-2-nitrobenzyl)cyclopropane (**XIX**) and (4-isopropyl-3-nitrobenzyl)cyclopropane (**XXII**), 0.12 g (3.5%) of (4-nitrobenzyl)cyclopropane (**XXIV**), and 2.84 g (86%) of 1-isopropyl-4-nitrobenzene (**XVI**).

Compound **XIX**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.06 m (2H), 0.41 m (2H), and 0.69 m (1H, cyclopropane); 0.98 d (6H, CH_3); 2.55 sept [1H, C**H**$(CH_3)_2$]; 2.62 d (2H, C**H**$_2$C$_6$H$_3$, *J* = 7.0); 7.06 (1H, J_o = 7.4), 7.60 d (1H, J_m = 1.6), and 7.82 d.d (1H, J_o = 7.4, J_m = 1.6) (H_{arom}).

Compound **XXII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.04 m (2H), 0.39 m (2H), 0.68 m (1H, cyclopropane); 1.02 d (6H, CH_3); 2.18 d (2H, C**H**$_2$C$_6$H$_3$, *J* = 7.0); 2.91 sept [1H, C**H**$(CH_3)_2$]; 6.89 d (1H, J_o = 7.2), 7.04 d.d (1H, J_o = 7.2, J_m = 1.8), and 7.19 d (1H, J_m = 1.8) (H_{arom}). Found for mixture **XIX**/**XXII**, %: C 70.93; H 7.67; N 6.18. $C_{13}H_{17}NO_2$. Calculated %: C 71.20; H 7.82; N 6.39.

Compound **XXIV**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.01 m (2H), 0.36 m (2H), and 0.63 m (1H) (cyclopropane); 2.32 d.d (2H, C**H**$_2$C$_6$H$_4$, J_1 = 12.3, J_2 = 8.8); 6.97 d (2H, J_o = 8.0) and 7.92 d (2H, J_o = 8.0) (H_{arom}). Found, %: C 67.68; H 6.17; N 7.81. $C_{10}H_{11}NO_2$. Calculated, %: C 67.77; H 6.27; N 7.91.

Compound **XVI**. bp 106–107°C (11 mm), n_D^{20} = 1.5380 [21].

Nitration of (4-*tert*-butylbenzyl)cyclopropane (XI). The nitration of 7.5 g (0.04 mol) of compound **XI** according to the standard procedure gave 7.95 g of

a mixture of products; by column chromatography on aluminum oxide we isolated 0.74 g (8%) of (4-*tert*-butyl-2-nitrobenzyl)cyclopropane (**XX**) and 6.37 g (90%) 1-*tert*-butyl-4-nitrobenzene (**XVII**).

Compound **XX**. Viscous oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.09 m (2H), 0.36 m (2H), and 0.92 m (1H) (cyclopropane); 1.05 m [9H, $(CH_3)_3C$]; 2.65 d (2H, C**H**$_2$C$_6$H$_3$, J = 5.9); 7.12 d (1H, 6-H, J_o = 8.2); 7.28 d.d (1H, 5-H, J_o = 8.2, J_m = 2.0); 7.86 d (1H, 3-H, J_m = 2.0). Found, %: C 71.85; H 8.02; N 5.81. $C_{14}H_{19}NO_2$. Calculated, %: C 72.07; H 8.21; N 6.00.

Compound **XVII**. bp 138–139°C (15 mm) (cf. [21]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.09 s [9H, $(CH_3)_3C$], 6.98 d (2H, 2-H, 6-H, J_o = 8.6), 7.88 d (2H, 3-H, 5-H, J_o = 8.6). Mass spectrum, *m*/*z* (I_{rel}, %): 179 (93) $[M]^+$, 164 (100), 136 (13.7), 118 (15.3), 106 (15.1), 91 (22.6), 77 (12.9), 63 (5.0), 51 (5.9).

Nitration of (4-chlorobenzyl)cyclopropane (XII). The nitration of 3.3 g (0.02 mol) of compound **XII** according to the standard procedure gave 3.25 g of a mixture of products; by preparative thin-layer chromatography on aluminum oxide we isolated 2.38 g (76%) of 1-chloro-4-nitrobenzene (**XVIII**) (mp 84–85°C), 0.25 g (6%) of (4-chloro-2-nitrobenzyl)cyclopropane (**XXI**), and 0.47 g (11%) of (4-chloro-3-nitrobenzyl)cyclopropane (**XXIII**).

Compound **XXI**. Oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.05 m (2H), 0.37 m (2H), and 0.74 m (1H) (cyclopropane); 2.48 d (2H, C**H**$_2$C$_6$H$_3$, J = 6.5); 6.76 d (1H, 6-H, J_o = 8.4), 7.08 d.d (1H, 5-H, J_o = 8.4, J_m = 2.0); 7.38 d (1H, 3-H, J_m = 2.0). Found, %: C 56.41; H 4.52; N 6.33. $C_{10}H_{10}ClNO_2$. Calculated, %: C 56.75; H 4.76; N 6.62.

Compound **XXIII**. Oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.02 m (2H), 0.35 m (2H), and 0.57 m (1H) (cyclopropane); 2.05 d (2H, C**H**$_2$C$_6$H$_3$, J = 6.9); 6.92 d (1H, 5-H, J_o = 8.2); 7.05 d.d (1H, 6-H, J_o = 8.2, J_m = 2.0), 7.17 d (1H, 2-H, J_m = 2.0). Found, %: C 56.75; H 8.02; N 6.62. $C_{10}H_{10}ClNO_2$. Calculated, %: C 56.75; H 4.76; N 6.62.

Nitration of (4-methoxybenzyl)cyclopropane (XXX). The nitration of 3.25 g (0.02 mol) of compound **XXX** according to the standard procedure gave 4.18 g of a mixture of products; by preparative thin-layer chromatography on aluminum oxide we isolated 0.6 g of a mixture of *p*-nitroanisole (**XXXII**) and (4-methoxy-3-nitrobenzyl)cyclopropane (**XXXV**) at a ratio of 9:1 (according to the GC–MS data), 0.78 g (15.5%) of (4-methoxy-3,5-dinitrobenzyl)cyclopropane (**XXXVI**), and 2.6 g (65%) of 2,4-dinitroanisole.

Compound **XXXII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.92 s (3H, OMe), 6.97 d (2H, H_{arom}, J_o = 8.8), 8.21 d (2H, H_{arom}, J_o = 8.8). Mass spectrum, *m*/*z* (I_{rel}, %): 153 (100) $[M]^+$, 123 (46.8), 107 (9.4), 95 (15.6), 92 (48.1), 77 (54.4), 74 (6.2), 64 (31.2), 63 (25.0), 50 (11.2), 38 (5.6).

Compound **XXXV**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.22 m (2H), 0.54 m (2H), and 0.97 m (1H) (cyclopropane); 2.55 d (2H, C**H**$_2$C$_6$H$_3$, J = 5.6); 3.94 s (3H, OMe); 7.04 d (1H, 5-H, J_o = 8.7); 7.45 d.d (1H, 6-H, J_o = 8.7, J_m = 2.5), 7.77 d (1H, 2-H, J_m = 2.5). Mass spectrum, *m*/*z* (I_{rel}, %): 207 (7.3) $[M]^+$, 179 (7.9), 166 (100), 161 (6.7), 135 (6.1), 132 (3.1), 118 (2.0), 90 (18.8).

Compound **XXXVI**. Viscous oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.29 m (2H), 0.69 m (2H), and 1.03 m (1H) (cyclopropane); 2.66 d (2H, C**H**$_2$C$_6$H$_2$, J = 6.4); 3.84 s (3H, OMe); 7.93 d (2H, 2-H, 6-H, J_m = 0.8). Mass spectrum, *m*/*z* (I_{rel}, %): 252 (10.9) $[M]^+$, 235 (6.7), 224 (22.1), 211 (100), 206 (8.3), 194 (6.3), 180 (21.8), 135 (8.9), 115 (11.5), 105 (19.2), 89 (16.0), 77 (30.1), 63 (12.8), 51 (13.5), 39 (12.2);

2,4-Dinitroanisole. mp 85°C [22]. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.18 s (3H, OMe), 7.29 d (1H, 6-H, J_o = 9.2), 8.48 d.d (1H, 5-H, J_o = 9.2, J_m = 2.4), 8.77 d (1H, 3-H, J_m = 2.4). Mass spectrum, *m*/*z* (I_{rel}, %): 198 (71.1) $[M]^+$, 168 (99.0), 151 (100), 138 (10.1), 122 (17.7), 105 (18.9), 92 (25.9), 79 (68.5), 76 (82.9), 63 (56.6), 51 (29.1), 50 (29.7), 39 (15.8).

Nitration of 1-allyl-4-isopropylbenzene (XXXVIII). The nitration of 3.2 g (0.02 mol) of compound **XXXVIII** according to the standard procedure gave 4.11 g of a mixture of products; by preparative thin-layer chromatography on aluminum oxide we isolated 0.81 g of a mixture of 2- and 3-nitro-4-isopropyl-1-allylbenzenes **XLII** and **XLVI** at a ratio of ~2:1 (according to the ^{1}H NMR data), 2.4 g of a mixture of 1-isopropyl-4-nitrobenzene (**XVI**) and 1-allyl-2-isopropyl-5-nitrobenzene (**XLIII**) at a ratio of 1:1.7 (^{1}H NMR), and 0.5 g of a mixture of 1-allyl-4-nitrobenzene (**XLV**) and 1-allyl-2-isopropyl-4-nitrobenzene (**XLVII**) at a ratio of 3:1 (^{1}H NMR).

Compound **XLII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.28 d (6H, CH_3, J = 7.7), 2.97 sept [1H, C**H**$(CH_3)_2$], 3.65 d (2H, C**H**$_2$C$_6$H$_3$, J = 6.8), 5.16 m (2H, CH=C**H**$_2$), 5.96 m (1H, C**H**=CH_2), 7.28 d (1H, 6-H, J_o = 8.4), 7.41 d.d (1H, 5-H, J_o = 8.4, J_m = 2.1), 7.77 d (1H, 3-H, J_m = 2.1). Mass spectrum, *m*/*z*

(I_{rel}, %): 205 (21.6) $[M - 1]^+$, 204 (26.8), 188 (63.9), 172 (39.8), 162 (37.6), 146 (86.4), 134 (62.3), 128 (88.1), 115 (100), 103 (21.1), 91 (66.9), 77 (36.3), 65 (21.1), 63 (19.2), 55 (32.4), 51 (19.1).

Compound **XLVI**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.29 d (6H, CH_3, *J* = 7.7), 3.38 sept [1H, C**H**$(CH_3)_2$], 3.42 d (2H, C**H**$_2C_6H_3$, *J* = 6.8), 5.14 m (2H, CH=C**H**$_2$), 5.91 m (1H, C**H**=CH_2), 7.36 d.d (1H, 6-H, J_o = 8.2, J_m = 2.0), 7.38 d (1H, 5-H, J_o = 8.2), 7.52 d (1H, 2-H, J_m = 2.0). Mass spectrum, *m*/*z* (I_{rel}, %): 205 (7.9) $[M]^+$, 188 (10.3), 170 (7.1), 160 (34.8), 147 (66.8), 129 (25.3), 128 (51.6), 115 (100), 93 (22.1), 91 (84.8), 77 (45.1), 65 (33.9), 63 (26.1), 55 (9.9), 51 (31.3).

Compound **XVI**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 d (6H, CH_3, *J* = 7.0), 3.03 sept [1H, C**H**$(CH_3)_2$], 7.37 d (2H, 2-H, 6-H, J_o = 8.8), 8.14 d (2H, 3-H, 5-H, J_o = 8.8). Mass spectrum, *m*/*z* (I_{rel}, %): 165 (47.5) $[M]^+$, 150 (100), 120 (18.7), 104 (31.7), 91 (42.9), 77 (30.2), 65 (9.4), 63 (8.6), 51 (15.8).

Compound **XLIII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.25 d (6H, CH_3, *J* = 6.9), 3.24 sept [1H, C**H**$(CH_3)_2$], 3.51 d (2H, C**H**$_2C_6H_3$, *J* = 6.4), 5.01 m and 5.19 m (2H, CH=C**H**$_2$), 5.99 m (1H, C**H**=CH_2), 7.42 d (1H, 3-H, J_o = 8.6), 8.02 d (1H, 6-H, J_m = 2.3), 8.05 d.d (1H, 4-H, J_o = 8.6, J_m = 2.3). Mass spectrum, *m*/*z* (I_{rel}, %): 205 (9.1) $[M]^+$, 190 (100), 173 (11.2), 144 (46.3), 129 (53.7), 115 (36.4), 103 (6.3), 91 (17.5), 77 (12.5), 63 (8.1), 51 (8.6).

Compound **XLV**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.48 d (2H, C**H**$_2C_6H_4$, *J* = 6.8), 5.16 m (2H, CH=C**H**$_2$), 5.93 m (1H, C**H**=CH_2), 7.29 d (2H, 2-H, 6-H, J_o = 8.6), 8.15 d (2H, 3-H, 5-H, J_o = 8.6). Mass spectrum, *m*/*z* (I_{rel}, %): 163 (100) $[M]^+$, 146 (10.8), 133 (12.9), 116 (29.1), 115 (61.9), 91 (15.8), 89 (6.5), 77 (3.3), 65 (2.7), 63 (2.6), 51 (1.9).

Compound **XLVII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.30 d (6H, CH_3, *J* = 6.8), 3.23 sept [1H, C**H**$(CH_3)_2$], 3.53 d (2H, C**H**$_2C_6H_3$, *J* = 6.4), 5.07 m (2H, CH=C**H**$_2$), 5.91 m (1H, C**H**=CH_2), 7.30 d (1H, 6-H, J_o = 8.6), 7.76 d (1H, 3-H, J_m = 2.3), 7.97 d.d (1H, 5-H, J_o = 8.6, J_m = 2.3). Mass spectrum, *m*/*z* (I_{rel}, %): 205 (4.8) $[M]^+$, 190 (100), 173 (10.2), 144 (56.9), 129 (70.1), 115 (49.6), 103 (6.1), 91 (28.3), 47 (22.5), 63 (16.2), 51 (20.1).

Nitration of 1-allyl-4-*tert*-butylbenzene (XXXIX). The nitration of 6.96 g (0.04 mol) of compound **XXXIX** according to the standard procedure gave 8.3 g of a mixture of products; by column chromatography we isolated 1.3 g (15%) of 1-allyl-4-*tert*-butyl-2-nitrobenzene (**XLVIII**) and 6.1 g (85%) of 1-*tert*-butyl-4-nitrobenzene (**XVII**); compound **XVII** was identical to a sample obtained by nitration of **XI** (see above).

Compound **XLVIII**. Viscous oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.05 s [9H, C$(CH_3)_3$], 3.67 d (2H, C**H**$_2C_6H_3$, *J* = 6.6), 5.14 m (2H, CH=C**H**$_2$), 6.01 m (1H, C**H**=CH_2), 7.21 d (1H, 6-H, J_o = 8.1), 7.33 d.d (1H, 5-H, J_o = 8.2, J_m = 2.0), 7.83 d (1H, 3-H, J_m = 2.0). Mass spectrum, *m*/*z* (I_{rel}, %): 219 (2.5) $[M]^+$, 204 (11.2), 187 (2.0), 173 (6.1), 162 (78.7), 143 (67.2), 128 (77.1), 116 (96.7), 115 (100), 103 (3.4), 91 (25.4), 77 (8.2), 63 (6.6), 57 (80.6), 51 (3.3), 43 (43.4).

Nitration of bis(4-fluorophenyl)methane (XL). The nitration of 4.1 g (0.02 mol) of compound **XL** according to the standard procedure gave 5.4 g of a mixture of products; by column chromatography we isolated 1.28 g (65%) of 1-fluoro-4-nitrobenzene (**LII**), bp 80–81°C (10 mm), n_D^{20} = 1.5310 [23]; 1.29 g (54%) of 4-fluorobenzyl acetate (**LIII**); 0.27 g of (11%) of 4-fluorobenzyl nitrate (**LIV**); and 0.85 g (24%) of 4,4'-difluoro-2-nitrodiphenylmethane (**L**).

Compound **LIV**. ^{1}H NMR spectrum, δ, ppm: 5.41 m (2H, C**H**$_2C_6H_4$), 7.09 m (2H, 3-H, 5-H), 7.39 m (2H, 2-H, 6-H). Mass spectrum, *m*/*z* (I_{rel}, %): 171 (9.7) $[M]^+$, 125 (35.5), 123 (34.2), 109 (50.1), 97 (27.6), 95 (100), 78 (20.2), 75 (27.1), 57 (3.7).

Compound **LIII**. ^{1}H NMR spectrum, δ, ppm: 2.09 s (3H, CH_3), 5.03 m (2H, C**H**$_2C_6H_4$), 7.01 m (2H, 3-H, 5-H), 7.33 m (2H, 2-H, 6-H). Mass spectrum, *m*/*z* (I_{rel}, %): 168 (37.1) $[M]^+$, 126 (79.8), 109 (100), 108 (65.8), 97 (17.7), 83 (16.1), 75 (8.1), 57 (6.4), 43 (29.8).

Compound **L**. Colorless crystalline substance, mp 165–166°C. ^{1}H NMR spectrum, δ, ppm: 4.09 m (2H, CH_2); 7.46 m (3H), 7.76 m (2H), and 8.18 m (2H) (H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 249 (100) $[M]^+$, 232 (9.2), 202 (53.2), 201 (75.8), 183 (41.9), 170 (6.4), 149 (9.7), 125 (35.5), 109 (48.4), 95 (8.4), 83 (16.5), 73 (6.4), 57 (14.2).

Nitration of 1-allyl-4-cyclopropylbenzene (LV). The nitration of 3.16 g (0.02 mol) of compound **LV** according to the standard procedure gave 3.43 g of a mixture of products; by column chromatography on aluminum oxide we isolated 1.13 g (35.7%) of initial compound **LV** and 2.23 g (81%, calculated on the reacted **LV**) of a mixture of 3- and 2-nitro-1-allyl-4-cyclopropylbenzenes **LVIII** and **LIX** at a ratio of 1:6 (according to the GC–MS and ^{1}H NMR data).

Compound **LVIII**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.62 m (2H), 1.02 m (2H), and 2.39 m (1H)

(cyclopropane); 3.41 d (2H, C**H**$_2$C$_6$H$_3$, J = 6.4); 5.14 m (2H, CH=C**H**$_2$); 5.85 m (1H, C**H**=CH$_2$); 7.06 d (1H, 5-H, J_o = 7.8); 7.27 d.d (1H, 6-H, J_o = 7.8, J_m = 2.0); 7.59 d (1H, 2-H, J_m = 2.0). Mass spectrum, m/z (I_{rel}, %): 203 (1.5) $[M]^+$, 186 (1.9), 175 (37.5), 141 (7.7), 130 (53.8), 115 (100), 104 (37.1), 91 (39.4), 77 (31.7), 63 (19.2), 51 (18.7), 39 (29.8).

Compound **LIX**. ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.75 m (2H), 1.06 m (2H), and 2.01 m (1H) (cyclopropane); 3.62 d (2H, C**H**$_2$C$_6$H$_3$, J = 6.4); 5.16 m (2H, CH=C**H**$_2$); 5.92 m (1H, C**H**=CH$_2$); 7.03 d (1H, 6-H, J_o = 8.2); 7.93 d.d (1H, 5-H, J_o = 8.2, J_m = 2.2); 7.98 d (1H, 3-H, J_m = 2.2). Mass spectrum, m/z (I_{rel}, %): 203 (2.6) $[M]^+$, 188 (5.2), 175 (16.7), 157 (8.3), 142 (39.1), 141 (41.1), 129 (38.4), 128 (100), 115 (71.8), 102 (10.3), 91 (12.2), 77 (18.6), 65 (10.2), 63 (17.2), 51 (15.4). Found (mixture **LVIII**/**LIX**), %: C 80.05; H 6.51; N 6.98. $C_{12}H_{13}NO_2$. Calculated, %: C 70.92; H 6.45; N 6.89.

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