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Nitration of 2-Aryl-1,1-dihalocyclopropanes Containing Methyl or Phenyl Group

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Gem-dihalocyclopropanes bearing a phenyl group and an additional group were nitrated by using nitric acid in a sulfuric acid matrix. The products from the nitration of aryl rings are major. The presence of a methyl group on the C(2) position of the cyclopropane ring leads to the isoxazoline from nitration at the C(1)-position instead of that from nitration at the C(2)-position.

INTRODUCTION

The cyclopropane ring possess a pi character and is able to communicate electron density between substituents on the phenyl ring. This nature has been demonstrated by using ^{19}F and ^{13}C NMR spectroscopic techniques.[1] Chemical shifts of hydrogen nuclei on the cyclopropane ring are also found to be influenced by substituents of the phenyl ring.[2] The nitration of phenyldichlorocyclopropane has been studied in the presence of nitric acid and acetic anhydride at -50 °C to give the nitrated products.[3] However, we have found that the cyclopropane ring of 1-aryl-2,2-dichlorocyclopropanes can undergo nucleophilic reaction with nitronium ion resulted in ring opening to produce isoxazoles in the matrix containing sulfuric acid and nitric acid or nitrate.[4] This reaction took place only when the phenyl ring bears the electron-withdrawing group, such as NO_2, F, or CN. According to the literature, isoxazolines are also formed from the nitration of arylcyclopropanes by using dinitrogen tetraoxide, cupric nitrate in acetic anhydride.[5] In this work, we extended the nitration to 2-aryl-1,1-dihalocyclopropanes to study the orientation of electrophilic substitution and the ring opening reaction. Coupling patterns of ^1H NMR absorptions will be useful for the characterization of the isomers of mononitro- and dinitrophenyl products.

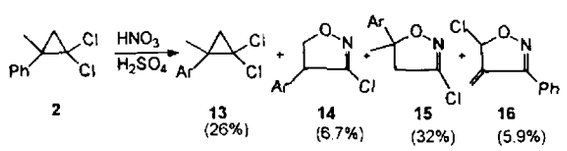
RESULTS AND DISCUSSION

Our previous work indicated that the formation of isoxazoles from nitration of 2-aryl-1,1-dichlorocyclopropanes is strongly dependent upon the nature of the substituent on the phenyl ring.[4] The substituent with electron-donor character enhances the substitution on the phenyl ring and retards the reaction for the formation of the isoxazole. In this work, we attempt to nitrate the cyclopropane bearing the phenyl group and an additional substituent to study their role in nitration at the cyclopropane ring.

Nitration of dihalocyclopropanes (**1-6**) was carried out in a mixture of nitric acid and sulfuric acid at ice-bath temperatures for two hours.[4] After work-up, the pure compounds were isolated by column and/or thin-layer chromatography for characterization and estimation of the yields. The product distributions and their physical properties are listed in the experimental section. The products from the nitration were described according to the elution sequence from the silica gel column. The order of the products from elution also suggests the sequence of polarities of the products. From the results, we can find that the products distribution strongly depended on the nature of the reactant. In general, the products from simple nitration of the phenyl are the major products. An example of the cyclopropane ring opening reaction is illustrated by Equation 1. Compounds containing 2- or 3-methyl group on the cyclopropanes (**2**, **3**) lead to isoxazolines or isoxazoles as ring opening products. The formation of such products depends upon the competitive nucleophilic reaction between the C1-carbon bearing two halogens and C2 or C3 carbon bearing phenyl groups towards the nitronium ion. An additional methyl group on the cyclopropane ring alters the position of the cyclopropane ring attacked by the nitronium ion and the subsequent bond cleavage. The possible reaction mechanisms to yield different isoxazolines (isoxazoles) are illustrated in Scheme I. However, the methyl group at the benzylic position (**2**) might cause steric hinderence to diminish the possibility of a C2 nitronium ion attack. Hence C1 position is able to un-

Dedicated to Professor Hsien-Ju Tien on the occasion of his 65th birthday.

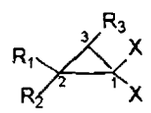
dergo nucleophilic reaction leading to isoxazoline **15** as the major product. Lone pair of chlorine atom orbital can be better overlapped with carbon orbital than that of bromine atom (**2** vs. **3**). This overlapping allows the chlorine atom to donate an electron pair to C1 and to activate the C1 position toward nitronium ion attack. This fact leads to a more than 38% yield of related compounds (i.e. **14**, **15**). The carbon bearing cation as a result of the cyclopropyl ring opening (**A**) forms a five-membered ring (**B**) by the attack of the nitro group oxygen. The coordinated oxygen can be removed to form an oxonium ion (**C**) by the presence of a suitable reducing reagent, such as NO_2 or NO in the reaction matrix. Isoxazoline and isoxazole are formed by the loss of a halogen or a proton. C(2)-Methylcyclopropane leads to nitration at the C(2)-position. The presence of a methyl group in the third carbon seems to encourage the double bond migration to form compound **27** instead of further elimination of hydrogen bromide to form isoxazole.



(1)

Ar: 4-nitrophenyl

Nitration of 1,1-dichloro-2,3-diphenylcyclopropanes gave only nitrated products. Chief among them were 4,4'-dinitrated derivatives from the nitration of both *E*- and *Z*-isomers. The nitro group is known to deactivate the phenyl ring towards the addition of a second nitronium ion. Nevertheless, under ice-bath conditions, our title compounds furnished compounds (**30**, **35**) containing a maximum of four nitro groups.

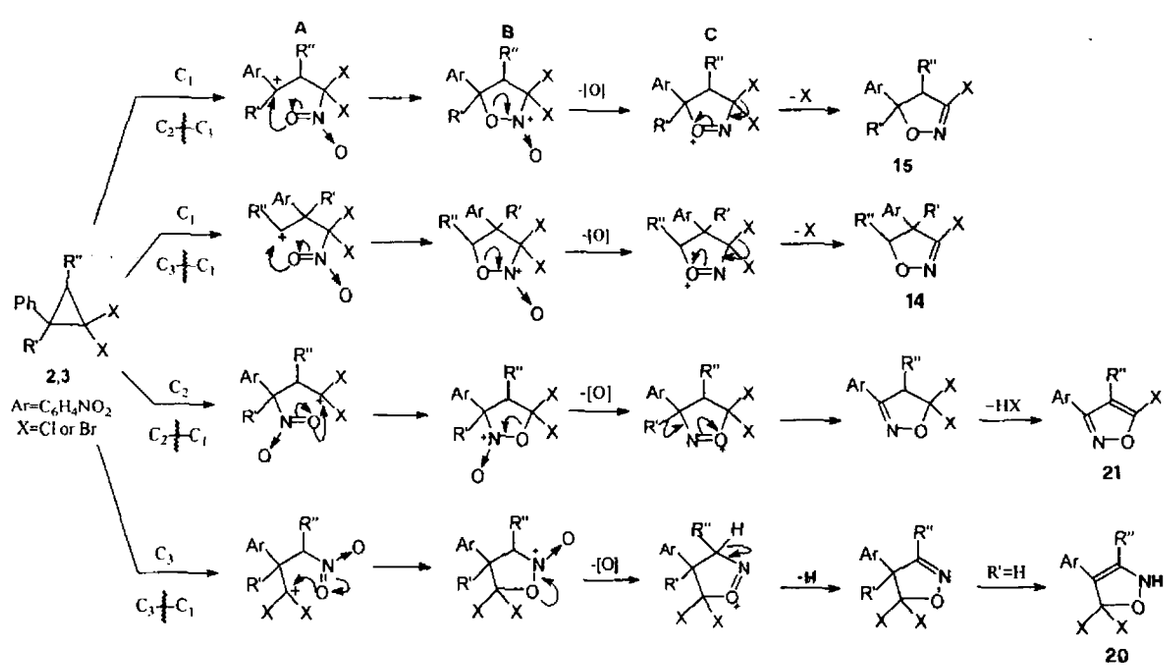


R_1, R_2, R_3, X: $C_6H_5CH_2$, H, H, Cl (**1**); C_6H_5, Me, H, Cl (**2**); C_6H_5, H, Me, Br (**3**); C_6H_5, CH_2Cl, H, Cl (**4**); C_6H_5, H, C_6H_5, Cl (**5**); H, C_6H_5, C_6H_5, Cl (**6**).

CONCLUSION

This series of reactions shows that nitration on the phenyl ring is also feasible other than ring opening process of cyclopropane. During the nitration on the phenyl ring, the nitro group is directed by the cyclopropyl ring to either an *ortho-* or *para-* position. Isoxazoles and isoxazolines, obtained from the nitration of the compounds, contained a methyl group on the cyclopropane ring.

Scheme 1 The possible reaction mechanisms to yield different isoxazoles or isoxazolines



EXPERIMENTAL

M.p.s. were determined on a Yanaco MP-J3 apparatus and are uncorrected. B.p.s. of isolated products from column separation was determined by means of Emrich's method under reduced pressure.[6] ^{1}H NMR spectra were recorded on a Bruker AC-250 instrument with deuteriochloroform as the solvent. Mass spectra were obtained on a JEOL DX-300 double focusing mass spectrometer. Samples were introduced via a direct insertion probe. The ionization energy was 70 eV. The IR spectra were recorded on a Perkin-Elmer 883 spectrometer as KBr pellets or neat. *Gem*-dihalocyclopropanes were prepared by treating styrene with trihalogenomethane in pentane in the presence of KOBu^t in accordence with procedures in the literature.[3b] The yields were isolated from separation by means of either column or thin-layer chromatography.

Typical Procedure for Nitration of *Gem*-dihalogenocyclopropanes

To an ice-cooled 1-benzyl-2,2-dichlorocyclopropane (5.4 mmol) was added slowly a mixture of HNO_3 (0.74 mL, 8.1 mmol) and H_2SO_4 (10 mL). The mixture was stirred under that temperature for an additional 2 h. The reddish brown resultant was poured into ice (50 g) and then extracted with ethyl acetate (100 mL × 3). The combined organic solution was washed with saturated Na_2CO_3 aqueous solution (100 mL × 3) and water (100 mL × 3) and then dried over Na_2SO_4. After filtration and evaporation of the solvent, the products were isolated by means of silica gel column chromatography and/or further purified by preparative thin-layer chromatography (silica gel, 1 mm or 2 mm thickness). The yields, physical properties and the spectroscopic data of products are as follows:

From 1-benzyl-2,2-dichlorocyclopropane (**1**): 1,1-dichloro-2-(4-nitrobenzyl)cyclopropane **7**, bp 103 °C/20 torr, yield 4.6%, light yellow liquid, ^{1}H NMR δ 1.29 (1H, dd, J = 6.9, 7.5 Hz), 1.73 (1H, dd, J = 6.9, 10.4 Hz), 1.83-1.95 (1H, m), 2.92-3.09 (2H, m), 7.46 (2H, J = 8.5 Hz), 8.19 (2H, d, J = 8.5 Hz); IR 1517, 1346 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 210 ([M-35]$^+$, 5), 149 (100); Anal. Calcd. for $C_{10}H_9Cl_2NO_2$: C, 48.81, H, 3.69, N, 5.69; Found: C, 48.90; H, 3.65; N, 5.66. 1,1-dichloro-2-(2-nitrobenzyl)cyclopropane **8**, bp 122 °C/9.5 torr, yield 4.5%, brown liquid, ^{1}H NMR δ 1.30 (1H, dd, J = 7.2, 7.5 Hz), 1.71 (1H, dd, J = 7.2, 10.5 Hz), 1.93-2.06 (1H, m), 3.13-3.29 (2H, m), 7.43 (1H, d, 8.1, 8.3 Hz), 7.55 (1H, d, J = 6.2 Hz), 7.62 (1H, d, J = 6.2, 8.3 Hz), 7.97 (1H, d, J = 8.1 Hz), IR 1527, 1345 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 245 (M$^+$, -), 132 (100); Anal. Calcd. for $C_{10}H_9Cl_2NO_2$: C, 48.81, H, 3.69, N, 5.69; Found: C, 48.99; H, 3.72; N, 5.77. 1,1-dichloro-2-(2,4-dinitrobenzyl)-cyclopropane **9**, 141 °C/5.8 torr; yield 76%, brown liquid, ^{1}H NMR δ 1.35 (1H, dd, J = 7.3, 7.5 Hz), 1.77 (1H, dd, J = 7.3, 10.4 Hz), 1.93-2.06 (1H, m), 3.21 (1H, dd, J = 8.2, 16.5 Hz), 3.38 (1H, dd, J = 5.7, 16.5 Hz), 7.84 (1H, d, J = 8.5 Hz), 8.45 (1H, dd, J = 2.0, 8.5 Hz), 8.76 (1H, d, J = 2.0 Hz); IR 1535, 1352 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 290 (M$^+$, -), 165 (100); Anal. Calcd. for $C_{10}H_8Cl_2N_2O_4$: C, 41.26, H, 2.77, N, 9.62; Found: C, 41.22; H, 2.80; N, 9.69; 1,1-dichloro-2-(2,6-dinitrobenzyl)cyclopropane **10**, bp 125 °C/4.5 torr; yield 8.3%, brown liquid, ^{1}H NMR δ 1.30 (1H, dd, J = 7.3, 7.6 Hz), 1.64 (1H, dd, J = 7.3, 10.4 Hz), 1.82-1.95 (1H, m), 3.01 (1H, dd, J = 8.4, 14.8 Hz), 3.54 (1H, dd, J = 6.1, 14.8 Hz), 7.60 (1H, t, J = 8.1 Hz), 8.00 (2H, d, J = 8.1 Hz); IR 1533, 1353 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 290 (M$^+$, -), 109 (100); Anal. Calcd. for $C_{10}H_8Cl_2N_2O_4$: C, 41.26, H, 2.77, N, 9.62; Found: C, 41.40; H, 2.70; N, 9.54; 1,1-dichloro-2-(2,5-dinitrobenzyl)cyclopropane **11**, yellow liquid, bp 144 °C/1.3 torr; yield 4.2%, ^{1}H NMR δ 1.34 (1H, dd, J = 6.7, 7.0 Hz), 1.80 (1H, dd, J = 6.7, 10.3 Hz), 1.85-1.98 (1H, m), 2.99-3.16 (2H, m), 7.70 (1H, d, J = 8.3 Hz), 7.81 (1H, s), 7.95 (1H, d, J = 8.3 Hz); IR 1535, 1355 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 290 (M$^+$,-), 109 (100); Anal. Calcd. for $C_{10}H_8Cl_2N_2O_4$: C, 41.26, H, 2.77, N, 9.62; Found: C, 41.22; H, 2.80; N, 9.55; 1,1-dichloro-2-(2,3-dinitrobenzyl)cyclopropane **12**, yellow liquid, yield 1.5%, ^{1}H NMR δ 1.32 (1H, dd, J = 7.2, 8.5 Hz), 1.77 (1H, dd, J = 7.2, 10.4 Hz), 1.84-2.00 (1H, m), 2.95 (2H, d, J = 7.6 Hz), 7.72 (1H, t, J = 7.3, 8.1 Hz), 7.90 (1H, d, J = 7.3 Hz), 8.12 (1H, d, J = 8.1 Hz); IR 1540, 1349 cm^{-1} (ν_{NO2}), MS (*m/z*, %) 290 (M$^+$,-), 177 (100); HRMS Anal. Cald. for $C_{10}H_8Cl_2N_2O_4$: 289.9861; Found: 289.9862.

From 1,1-dichloro-2-methyl-2-phenylcyclopropane **2**: 1,1-dichloro-2-methyl-2-(4-nitrophenyl)cyclopropane **13**, yellow liquid, bp 124 °C/0.6 torr; yield 26.0%; ^{1}H NMR δ 1.70 (3H, s), 1.72 (1H, d, J = 7.5 Hz), 2.01 (1H, d, J = 7.5 Hz), 7.48 (2H, d, J = 8.7 Hz), 8.22 (2H, d, J = 8.7 Hz); IR 1523, 1349 cm^{-1} (ν_{NO2}), MS (*m/z*, %) 245 (M$^+$, 6), 210 (100); Anal. Calcd. for $C_{10}H_9Cl_2NO_2$: C, 48.81, H, 3.69, N, 5.69; Found: C, 48.82; H, 3.69; N, 5.73; 3-chloro-4-(4-nitrophenyl)isoxazoline **14**, yellow solid, mp 101.5-102.7 °C; yield 6.7%; ^{1}H NMR δ 3.38 (1H, d, J = 17.2 Hz), 3.81 (1H, d, J = 17.2 Hz), 3.82 (1H, s), 7.63 (2H, d, J = 8.8 Hz), 8.28 (2H, d, J = 8.8 Hz); IR 1532, 1342 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 226 (M$^+$, 100); Anal. Calcd. for $C_9H_7ClN_2O_3$: C, 47.70, H, 3.11, N, 12.36; Found: C, 47.72; H, 3.12; N, 12.42; 3-chloro-5-methyl-5-(4-nitorphenyl)isoxazoline **15**, yellow solid, mp 50.7-51.9 °C; yield 32.3%, ^{1}H NMR δ 1.80 (3H, s), 3.27 (1H, d, J = 17.0 Hz), 3.38 (1H, d, J = 17.0 Hz), 7.58 (2H, d, J = 8.1 Hz), 8.21 (2H, d, J = 8.1 Hz); IR 1530, 1348 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 240 (M$^+$, 31), 225 (100); Anal.

Calcd. for $C_{10}H_9ClN_2O_3$: C, 49.91, H, 3.77, N, 11.64; Found: C, 49.91; H, 3.77; N, 11.72; 5-chloro-4-methylene-3-phenylisoxazoline **16**, yellow solid, mp 87-88 °C, yield 5.9%, ^{1}H NMR δ 4.96 (2H, s), 6.35 (1H, s), 7.51 (5H, s); MS (*m/z*, %) 193 (M^+, 89), 128 (100); Anal. Calcd. for $C_{10}H_8ClNO$: C, 62.03, H, 4.16, N, 7.23; Found: C, 62.03; H, 4.18; N, 7.22.

From 1,1-dibromo-2-methyl-3-phenylcyclopropane **3**: 1,1-dibromo-2-methyl-3-(4-nitrophenyl)cyclopropane **17**, yellow liquid, bp 146 °C/0.8 torr; yield 6.5%, ^{1}H NMR δ 1.49 (3H, d, J = 6.1 Hz), 2.01-2.06 (1H, m), 2.52 (1H, d, J = 8.3 Hz), 7.39 (2H, d, J = 8.4 Hz), 8.19 (2H, d, J = 8.4 Hz); IR 1517, 1348 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 333 (M^+, 2), 129 (100); Anal. Calcd. for $C_{10}H_9Br_2NO_2$: C, 35.85, H, 2.71, N, 4.18; Found: C, 35.89; H, 2.71; N, 4.22; 1,1-dibromo-2-methyl-3-(2-nitrophenyl)cyclopropane **18**, white solid, mp 42.0-43.5 °C, yield 6.1%; ^{1}H NMR δ 1.52 (3H, d, J = 6.2 Hz), 1.92-2.03 (1H, m), 2.89 (1H, d, J = 8.5 Hz), 7.35 (1H, dd, J = 0.8, 7.5 Hz), 7.51 (1H, ddd, J = 0.8, 7.6, 8.0 Hz), 7.63 (1H, ddd, J = 1.1, 7.5, 7.6), 8.11 (1H, dd, J = 1.1, 8.0 Hz), IR 1525, 1349 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 254 ($(M-Br)^+$, 7), 135 (100); Anal. Calcd. for $C_{10}H_9Br_2NO_2$: C, 35.85, H, 2.71, N, 4.18; Found: C, 35.90; H, 2.72; N, 4.19; 1,1-dibromo-3-(2,4-dinitrophenyl)-2-methylcyclopropane **19**, yellow liquid, 200 °C/0.75 torr; yield 51.6%, ^{1}H NMR δ 1.53 (3H, d, J = 6.3 Hz); 2.01-2.12 (1H, m), 2.93 (1H, d, J = 8.5 Hz), 7.59 (1H, d, J = 8.5 Hz), 8.45 (1H, dd, J = 2.0, 8.5 Hz), 8.89 (1H, d, J = 2.0 Hz); IR 1533, 1349 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 378 (M^+, -), 180 (100); Anal. Calcd. for $C_{10}H_8Br_2N_2O_4$: C, 31,61, H, 2.12, N, 7.37; Found: C, 31.60; H, 2.15; N, 7.39; 5,5-dibromo-3-methyl-4-(4-nitrophenyl)-2,5-dihydroisoxazoline **20**, yellow solid, mp 184.5-186.5 °C, yield 7.5%, ^{1}H NMR δ 1.96 (3H, s), 6.32 (1H, s), 7.33 (2H, d, J = 7.5 Hz), 7.52 (2H, d, J = 7.5 Hz), IR 1528, 1350 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 362 (M^+, -), 316 ($[M-46]^+$, 8), 148 (100); Anal. Calcd. for $C_{10}H_8Br_2N_2O_3$: C, 33.00, H, 2.22, N, 7.70; Found: C, 33.09; H, 2.22; N, 7.71; 5-bromo-4-methyl-3-(4-nitrophenyl)-isoxazole **21**, yellow solid, mp 137-138 °C, yield 6.3%; ^{1}H NMR δ 2.17 (3H, s), 7.86 (2H, d, J = 8.7 Hz), 8.35 (2H, d, J = 8.7 Hz), IR 1520, 1350 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 282 (M^+, 9), 203 (100); Anal. Cald. for $C_{10}H_7BrN_2O_3$: C, 42.43, H, 2.49, N, 9.90; Found: C, 42.43; H, 2.51; N, 9.96; nitrobenzoic acid **22**, white solid, mp 239-241 °C. (lit.[7] 242.4 °C); yield 9.1%.

From 1,1-dichloro-2-chloromethyl-3-phenylcyclopropane **4**: 1-chloromethyl-2,2-dichloro-3-(4-nitrophenyl)-cyclopropane **23**, yellow liquid, bp 100 °C/1.0 torr; yield 25.4%, ^{1}H NMR δ 2.44 (1H, dd, J = 7.6, 8.1 Hz), 2.81 (1H, d, J = 8.1 Hz), 3.77-3.93 (2H, m), 7.43 (2H, d, J = 8.7 Hz), 8.18 (2H, d, J = 8.7 Hz), IR 1530, 1355 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 279 (M^+, 5), 239 (100); Anal. Calcd. for $C_{10}H_8Cl_3NO_2$: C, 42.81, H, 2.87, N, 4.99; Found: C, 42.80; H, 2.87; N, 4.99; 1-chloromethyl-2,2-dichloro-3-(2-nitrophenyl)cyclopropane **24**, yellow solid, mp 101.5-102.0 °C, yield 10.6%, ^{1}H NMR δ 2.34 (1H, dd, J = 7.7, 8.1 Hz), 3.21 (1H, d, J = 8.1 Hz), 3.78 (1H, dd, J = 7.7, 11.7 Hz), 3.98 (1H, dd, J = 7.7, 11.7 Hz), 7.42 (1H, dd, J = 0.8, 7.7 Hz), 7.53 (1H, td, J = 7.7, 1.1 Hz), 7.65 (1H, td, J = 7.8, 0.8 Hz), 8.13 (1H, dd, J = 8.0, 1.1 Hz); IR 1545, 1352 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 279 (M^+, -), 244 ($[M-35]^+$, 10), 135 (100); Anal. Calcd. for $C_{10}H_8Cl_3NO_2$: C, 42.81, H, 2.87, N, 4.99; Found: C, 42.80; H, 2.88; N, 5.03; 1-chloromethyl-2,2-dichloro-(2,4-dinitrophenyl)cyclopropane **25**, yellow solid, mp 107-108 °C, yield 55.0%, ^{1}H NMR δ 2.41 (1H, dd, J = 6.9, 7.7 Hz), 3.28 (1H, d, J = 6.9 Hz), 3.75 (1H, dd, J = 7.7, 11.7 Hz), 4.04 (1H, dd, J = 7.7, 11.7 Hz), 7.68 (1H, d, J = 8.4 Hz), 8.49 (1H, dd, J = 2.3, 8.4 Hz), 8.97 (1H, d, J = 2.3 Hz); IR 1532, 1345 cm^{-1} (ν_{NO2}), MS (*m/z*, %) 289 ($[M-35]^+$, 5), 134 (100); Anal. Calcd. for $C_{10}H_7Cl_3N_2O_4$: C, 36.90, H, 2.17, N, 8.61; Found: C, 36.90; H, 2.18; N, 8.60.

From 1,1-dichloro-*Z*-2,3-diphenylcyclopropane **5**: 1,1-dichloro-*Z*-2-(4-nitrophenyl)-3-phenylcyclopropane **26**, yellow solid, mp 118-120 °C, yield 29.2%, ^{1}H NMR δ 3.35 (1H, d, J = 11.6 Hz), 3.46 (1H, d, J = 11.6 Hz), 7.02-7.06 (2H, m), 7.14 (2H, d, J = 8.7 Hz), 7.25-7.31 (3H, m), 8.08 (2H, d, J = 8.7 Hz); IR 1519, 1349 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 307 (M^+, 11), 191 (100); Anal. Calcd. for $C_{15}H_{11}Cl_2NO_2$: C, 58.47, H, 3.60, N, 4.55; Found: C, 58.47; H, 3.60; N, 4.55; 1,1-dichloro-*Z*-2,3-di(4-nitrophenyl)cyclopropane **27**, yellow solid, mp 108-109 °C, yield 4.5%; ^{1}H NMR δ 3.35 (2H, s), 7.04 (4H, d, J = 8.7 Hz), 7.98 (4H, d, J = 8.7 Hz); IR 1522, 1350 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 352 (M^+, 6), 271 (100); HRMS Calcd. for $C_{15}H_{10}Cl_2N_2O_4$: 352.0018. Found: 352.0017; 1,1-dichloro-*Z*-2-(2-nitrophenyl)-3-(4-nitrophenyl)-cyclopropane **28**, yellow solid, mp 43-44 °C, yield 7.2%; ^{1}H NMR δ 3.48 (1H, d, J = 11.6 Hz), 3.86 (1H, d, J = 11.6 Hz), 6.93 (2H, d, J = 7.1 Hz), 7.49-7.69 (3H, m), 7.99 (1H, d, J = 7.8 Hz), 8.02 (2H, d, J = 7.1 Hz); IR 1525, 1350 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 352 (M^+, -), 166 (100); Anal. Calcd. for $C_{15}H_{10}Cl_2N_2O_4$: C, 51.01, H, 2.85, N, 7.93; Found: C, 51.00; H, 2.90; N, 7.93; 1,1-dichloro-*Z*-2-(4-nitrophenyl)-3-(2,4-dinitrophenyl)cyclopropane **29**, yellow solid, mp 69-70 °C, yield 28.4%; ^{1}H NMR δ 3.44 (1H, d, J = 11.6 Hz), 3.74 (1H, d, J = 11.6 Hz), 6.82 (2H, d, J = 8.8 Hz), 7.56 (1H, d, J = 8.6 Hz), 8.33 (1H, dd, J = 2.4, 8.6 Hz), 8.68 (1H, d, J = 2.4 Hz), 8.92 (2H, d, J = 8.8 Hz); IR 1523, 1351 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 397 (M^+, -), 211 (100); Anal. Calcd. for $C_{15}H_9Cl_2N_3O_6$: C, 45.25, H, 2.28, N, 10.55; Found: C, 45.29; H, 2.28; N, 10.54; 1,1-dichloro-*Z*-2,3-bis(2,4-dinitrophenyl)cyclopropane **30**, yellow solid, mp 218-219 °C,

yield 8.5%; ^{1}H NMR δ 3.85 (2H, s), 7.79 (2H, d, J = 8.5 Hz), 8.56 (1H, dd, J = 2.3, 8.5 Hz), 9.06 (2H, d, J = 2.3 Hz); IR 1536, 1338 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 442 (M^+, -) 371 (39), 211 (100); Anal. Calcd. for $C_{15}H_8Cl_2N_4O_8$: C, 40.65, H, 1.82, N, 12.64; Found: C, 40.65; H, 1.80; N, 12.66.

From 1,1-dichloro-*E*-2,3-diphenylcyclopropane **6**: 1,1-dichloro-2,3-di(4-nitrophenyl)-cyclopropane **31**, yellow solid, mp 173-174 °C, yield 4.9%, ^{1}H NMR δ 3.39 (2H, s), 7.58 (4H, d, J = 8.6 Hz), 8.29 (4H, d, J = 8.6 Hz); IR 1526, 1346 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 352 (M^+, 4), 166 (100); Anal. Calcd. for $C_{15}H_{10}Cl_2N_2O_4$: C, 51.01, H, 2.85, N, 7.93; Found: C, 51.03; H, 2.90; N, 7.93; 1,1-dichloro-*E*-2-(2-nitrophenyl)-3-(4-nitrophenyl)cyclopropane **32**, yellow solid, mp 127-129 °C, yield 34.1%; ^{1}H NMR δ 3.27 (1H, d, J = 8.9 Hz), 3.82 (1H, d, J = 8.9 Hz), 7.49 (1H, d, J = 7.6 Hz), 7.59 (2H, d, J = 7.8 Hz), 7.61 (1H, dd, J = 7.3, 7.6 Hz), 7.70 (1H, dd, J = 7.3, 8.2 Hz), 8.22 (1H, d, J = 8.2 Hz), 8.31 (2H, d, J = 7.8 Hz); IR 1521, 1349 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 352 (M^+, -) 317 (8), 166 (100); Anal. Calcd. for $C_{15}H_{10}Cl_2N_2O_4$: C, 51.01, H, 2.85, N, 7.93; Found: C, 51.00; H, 2.87; N, 7.95; 1,1-dichloro-E-2-(2,4-dinitrophenyl)-3-(4-nitrophenyl)-cyclopropane **33**, yellow, mp 178-180 °C, yield 11.6%, ^{1}H NMR δ 3.33 (1H, d, J = 9.0 Hz), 3.85 (1H, d, J = 9.0 Hz), 7.58 (2H, d, J = 8.6 Hz), 7.73 (1H, d, J = 8.4 Hz), 8.29 (2H, d, J = 8.6 Hz), 8.51 (1H, dd, J = 2.3, 8.4 Hz), 9.02 (1H, d, J = 2.3 Hz); IR 1531, 1349 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 397 (M^+, -) 344 (7), 211 (100); Anal. Calcd. for $C_{15}H_9Cl_2N_3O_6$: C, 45.25, H, 2.28, N, 10.55; Found: C, 45.27; H, 2.29; N, 10.54; 1,1-dichloro-*E*-2-(2,4-dinitrophenyl)-3-(2-nitrophenyl)-cyclopropane **34**, yellow solid, mp 151.0-152.5 °C; yield 8.8%, ^{1}H NMR δ 3.75 (1H, d, J = 9.4 Hz), 3.83 (1H, d, J = 9.4 Hz), 7.51 (1H, d, J = 7.7 Hz), 7.61 (1H, dd, J = 7.0, 7.7 Hz), 7.71 (1H, d, J = 7.0 Hz), 7.76 (1H, t, J = 7.7 Hz), 8.23 (1H, d, J = 7.7 Hz), 8.53 (1H, dd, J = 2.2, 8.5 Hz), 9.03 (1H, d, J = 2.2 Hz); IR 1533, 1350 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 397 (M^+, -) 326 (9), 166 (100); Anal. Calcd. for $C_{15}H_9Cl_2N_3O_6$: C, 45.25, H, 2.28, N, 10.55; Found: C, 45.27; H, 2.21; N, 10.62; 1,1-dichloro-E-2,3-bis(2,4-dinitrophenyl)cyclopropane **35**, yellow solid, mp 215-216 °C, yield 7.6%; ^{1}H NMR δ 3.84 (2H, s), 7.78 (2H, d, J = 8.5 Hz), 8.56 (2H, dd, J = 2.3, 8.5 Hz), 9.05 (2H, d, J = 2.3 Hz); IR 1536, 1342 cm^{-1} (ν_{NO2}); MS (*m/z*, %) 371 (M^+, 37), 211 (100); Anal. Calcd. for $C_{15}H_8Cl_2N_4O_8$: C, 40.65, H, 1.82, N, 12.64; Found: C, 40.64; H, 1.82; N, 12.66.

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Dihalogenocyclopropanes; Nitration; Isoxazoles: Ring-opening process; Steric hinderence; Substituent effect.

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