15.55. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 1855 (broad; pyridine carboxylic acid), 1701 (C=O), 1525 (nitro), 1359 (nitro), 1285 (N-oxide), 1610 (aromatic C=C), 1590 (aromatic C=C), 1459 (aromatic C=C), 1176 (CH in plane or skeletal), 1089 (CH in plane or skeletal), 1027 (CH in plane or skeletal), 937 (CH in plane or skeletal), 813 (CH out of plane), 743 (CH out of plane), 710 (CH out of plane).

5-Nitronicotinonitrile 1-Oxide (XV)—To a solution of XIV (3 g.), dissolved in CHCl_3 (150 ml.) was added dropwise CHCl_3 solution (60 ml.) of *p*-nitrobenzoyl chloride (4.65 g.) with stirring at $-5 \sim -7^\circ$ for 5 min. followed by adding finely powdered AgNO_3 (6 g.) at a time. The reaction mixture was stirred for 1 hr. at $-5 \sim -7^\circ$, 2 hr. at room temperature, 2.5 hr. at $40 \sim 50^\circ$ and 2 hr. at 55° respectively. After the mixture was allowed to stand overnight, AgCl precipitated was collected by filtration and washed with CHCl_3 . Combined solution of the filtrate and washed CHCl_3 was concentrated to 4/5 volume and allowed to stand overnight. Yellow crystals separated was recrystallized from acetone to give XV as yellow needles, m.p. 205° (decomp.). Yield: 36.5%. Anal. Calcd. for $\text{C}_6\text{H}_3\text{O}_3\text{N}_2$: C, 43.64; H, 1.83; N, 25.45. Found: C, 43.73; H, 1.78; N, 24.76. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 2240 (CN), 1543 (nitro), 1365 (nitro), 1270 (N-oxide), 1631 (aromatic C=C), 1571 (aromatic C=C), 1455 (aromatic C=C), 1150 (CH in plane or skeletal), 1032 (CH in plane or skeletal), 1015 (CH in plane or skeletal), 945 (CH in plane or skeletal), 1015 (aromatic C=C), 935 (aromatic C=C), 815 (CH out of plane), 724 (CH out of plane).

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Summary

As a part of studies on the Janovsky reaction of nitropyridines, 3-substituted-5-nitropyridines such as 2-hydrazino-5-nitronicotinonitrile (I), 5-nitronicotinonitrile (II), 5-nitronicotinic acid (III), ethyl 5-nitronicotinate (VIII), 5-nitronicotinamide (IX), and 3-amino-5-nitropyridine (XI) were prepared. Some of their N-oxides such as ethyl 5-nitronicotinate 1-oxide (VII), 5-nitronicotinic acid 1-oxide (XII) and 5-nitronicotinonitrile 1-oxide (XV) were also prepared.

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17. Issei Iwai, Kazuo Tomita, and Junya Ide: Studies on Acetylenic Compounds. XL. The Addition Reaction of Nitrosyl Chloride and Nitryl Chloride to Acetylenic Compounds.*¹

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The reaction of nitrosyl chloride or nitryl chloride with olefinic compounds has been investigated extensively, and the reaction of nitrosyl chloride with olefins has especially been a useful method for the structural determination of terpenes.¹⁾ However, there have been only a few reports²⁻⁵⁾ on the addition of these reagents to acetylenic compounds, and such investigations have not been systematic.

The present investigation was carried out to obtain information concerning with the direction and mode of addition of nitrosyl chloride or nitryl chloride to the carbon-carbon triple bond.

*¹ Part XXXIX: This Bulletin, 12, 1446 (1964).

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1) O. Wallach: "Terpene und Camphor," 2nd Ed., Viet and Co., Leipzig, 1914, pp. 69-75; L. J. Beckham, W. A. Fessler, M. A. Kise: Chem. Rev., 48, 319 (1951).

2) R. Perrot, R. Berger; Compt rend., 235, 185 (1952).

3) W. Steinkopf, M. Kuhnel: Ber., 75B, 1323 (1942).

4) J. P. Freeman, W. D. Emmons: J. Am. Chem. Soc., 79, 1712 (1957).

5) H. H. Schlubach, A. Braun: Ann., 627, 28 (1959).

Furthermore, we wish to clarify the differences in reactivity between nitrosyl chloride and nitril chloride towards a triple bond. With this intention, nitrosyl chloride or nitril chloride were reacted with phenylacetylene, phenylmethylacetylene, diphenylacetylene, 3-phenyl-2-propyn-1-ol acetate, phenylpropionic acid and ethyl phenylpropiolate to obtain corresponding nitrochloroölefins (II).

Chart 1.

Addition of Nitrosyl Chloride to Acetylenic Compounds

It has been found that many olefins from nitrosochlorides with nitrosyl chloride, but some do not. From the results of extensive investigations, Tilden and Forster⁶⁾ have concluded that the proximity of a nitro or carboxyl group to an ethylene carbon seems to hinder the addition of nitrosyl chloride. Moreover, Thorne⁷⁾ has concluded that nitrosochlorides are more readily formed by olefins containing groups which reduce the reactivity of the double bond towards nucleophilic reagents and increase it towards electrophilic reagents.

Perrot and Berger²⁾ have reported addition of nitrosyl chloride to phenylacetylene and substituted ethynylbenzene, where the addition products are identified as the α -chloro- β -nitrostyrenes, but their configurations have not been proved. These reactions were carried out in sealed tubes without solvent at room temperature. In present work, the reagents were subjected to the following general conditions; acetylenic compound was added quickly to a cold solution of a relative non-polar solvent such as carbon tetrachloride, chloroform or methylene chloride containing about three to five equivalents of nitrosyl chloride, and the reaction mixture was kept at -10° for several days. The reaction was rather complicated, and produced not only chloronitroölefins but many other products which would not be expected from the normal addition reaction. As the separation of the various products from the reaction mixture of phenylacetylene (Ia) was relatively easier than that from other acetylenes, most of the work was carried out with this compound. The following five components were isolated from the reaction mixture of nitrosyl chloride and phenylacetylene; crystalline nitrochlorostyrene (A), liquid nitrochlorostyrene (B), chloroketone (C), benzoic acid (D), and a mixture of chlorinated styrenes (E). Both of the nitrochlorostyrenes (A and B) had the same empirical formula $\text{C}_8\text{H}_6\text{ClO}_2\text{N}$, both were hydrolyzed with alkali to afford the same ω -nitroacetophenone (III) and the infrared spectra of A and B were very similar (Fig. 2). Therefore, it was concluded that these two compounds should be *cis*- and *trans*- α -chloro- β -nitrostyrene. The chloroketone (C) was identical to the 2,2-dichloroacetophenone (IV) obtained by the chlorination of acetophenone.⁸⁾ A mixture of chlorinated styrenes were not further investigated because of the difficulties involved in their separation.

Reaction of nitrosyl chloride and phenylmethylacetylene (Ib) resulted principally in formation of chloronitropropenylbenzene (IIb), the direction of addition of nitrosyl chloride to Ib was identical to that of phenylacetylene. The structure of IIb was identified

6) W. A. Tilden, M. O. Forster: J. Chem. Soc., 65, 324 (1894).

7) N. Thorne: *Ibid.*, 1956, 4271.

8) J. G. Aston, *et al.*: Org. Syntheses, 23, 48.

as 1-chloro-2-nitro-1-phenyl-1-propene upon being converted into DL-1-phenyl-2-propylamine (V)⁹ by catalytic hydrogenation. Benzoylation of the amine (V) was yielded N-(α -methylphenethylbenzamide (VI) which was identical to an authentic sample prepared by the independent route^{9,10} shown in the Chart 3.

Addition of nitrosyl chloride to 3-phenyl-2-propyn-1-ol acetate (Id) in carbon tetrachloride gave 2-nitro-3-chloro-3-phenyl-2-propen-1-ol acetate (IIId) in excellent yield. The identification of IIId was established upon being converted into DL-2-amino-3-phenyl-1-propanol (VII) by reduction with lithium aluminum hydride, and N-dichloroacetyl derivative of VII was identical to DL-2-N-dichloroacetamido-3-phenyl-1-propanol (VIII) prepared from DL-phenylalanine by a known method.¹⁰

9) R. T. Gilsdorf, F. F. Nord : J. Am. Chem. Soc., **74**, 1837 (1957).

10) S. Yamada, K. Koga, H. Matsuo : This Bulletin, **11**, 1140 (1963); P. Karrer, P. Portman, *et al.* : Helv. Chim. Acta, **31**, 1617 (1948); J. H. Hunt, D. McHal : J. Chem. Soc., **1957**, 2073; M. C. Rebstock, *et al.* : J. Am. Chem. Soc., **73**, 3666 (1951); A. Dornow, G. Winter : Ber., **84**, 307 (1951).

The addition of nitrosyl chloride to phenylpropionic acid (Ie) in methylene chloride gave α -nitro- β -chlorocinnamic acid (IIe) in low yield. The structure of IIe was established by conversion into DL-phenylalanine after catalytic hydrogenation. Moreover, when IIe was treated with morpholine, α -morpholino- β -nitrostyrene (X) was obtained by substitution accompanied with decarboxylation. This styrene derivative was identical to an authentic sample produced from α -chloro- β -nitrostyrene (IIa) and morpholine.

The addition of nitrosyl chloride to ethyl phenylpropiolate (If) furnished ethyl nitrochlorocinnamate (IIf) which was converted into morpholino-derivative (X) by treatment with morpholine. Attempts to saponify the morpholino ester with alkali resulted in hydrolysis of the enamine and decarboxylation to afford 2-nitroacetophenone (III). From these facts, the structure of the ethyl α -nitro- β -chlorocinnamate (IIf) was established.

The direction of addition of nitrosyl chloride to phenylpropionic acid and ethyl phenylpropiolate were same as in the case of phenylacetylene, namely, the chloro atom was attached to the α -position with respect to the phenyl group and nitro group to the β -position.

Chart 5.

Diphenylacetylene (Ic) was also examined in this reaction and furnished a crystalline isomer of α -nitro- β -chlorostilbene (IIc) which was characterized by elementary analyses and infrared spectrum. This compound (IIc) was also converted into α -nitro- β -morpholinostilbene.

In the addition of nitrosyl chloride there are remarkable differences between olefinic compounds and acetylenic compounds: the former give nitrosochlorides, whereas the latter give further oxidized nitrochlorides. Moreover, olefinic compounds containing carboxy group adjacent to the ethylenic carbon atoms, namely cinnamic acid or ethyl cinnamate, affords no addition products,⁷⁾ but the acetylenic analogues such as phenylpropionic acid and ethyl phenylpropiolate give the corresponding addition products.

Addition of Nitryl Chloride to Acetylenic Compounds

The addition of nitryl chloride to unsaturated systems is considered to proceed in different way than nitrosyl chloride. Nitrosyl chloride reacts with styrene to give 1-chloro-1-phenyl-2-nitrosoethane in 30% yield,⁷⁾ while nitryl chloride gives 1-phenyl-1,2-dichloroethane in 70~80% yield accompanied by β -nitrostyrene which is obtained by dehydrohalogenation of 1-chloro-1-phenyl-2-nitroethane on distillation.¹¹⁾

Addition of nitryl chloride to a carbon-carbon triple bond has been investigated mainly with phenylacetylene. Steinkopf and Kuhnel³⁾ have reported the formation of 1-nitro-1-phenyl-2-chloroethylene (α -nitro- β -chlorostyrene) by the reaction of nitryl chloride with phenylacetylene in ether. On the contrary, Freeman and Emmons⁴⁾ have reported that the reaction of nitryl chloride with phenylacetylene furnished α -chloro- β -nitrostyrene under the similar reaction conditions. Recently, Schlubach and Braum⁵⁾ have reported the addition of nitryl chloride to some other acetylenic compounds such as 3-hexyne, 5-decyne and 1-phenyl-1-hexyne.

We investigated the addition reaction of nitryl chloride with phenylacetylene under various reaction conditions in order to clarify whether α -nitro- β -chlorostyrene or α -chloro- β -nitrostyrene was obtained. When a chilled ethereal solution of nitryl chloride was added to phenylacetylene at -20° , a solid isomer (A) of α -chloro- β -nitrostyrene was obtained in low yield (about 10%), and even application of inverse addition technique had no effect on the yield of the chloronitrostyrene. The reaction also occurred in absence of solvent or in carbon tetrachloride at 0° , and no significant differences were observed in the yield of α -chloro- β -nitrostyrene (5~10%). But in all cases, we could isolate no compound suggestive of Steinkopf's α -nitro- β -chlorostyrene.³⁾

When nitryl chloride was introduced into dried ethyl ether at about 10° , the solution turned reddish in color. The solution was reacted with phenylacetylene giving yellow needles in better yield (40~50%) which was identical to solid isomer (A) of α -chloro- β -nitrostyrene obtained from nitrosyl chloride and phenylacetylene. Other products (D) were also obtained which were identified as 2,2-dichloroacetophenone (C), benzoic acid and a mixture of chlorinated styrenes (E). These four components were same as the compounds obtained from the reaction of nitrosyl chloride with phenylacetylene except the liquid isomer (B) of α -chloro- β -nitrostyrene. However, isomer (B) is probably present in the reaction mixture, for a fraction showing characteristic absorption bands corresponding to the liquid isomer B was obtained by silica-gel chromatography. Similar results were obtained in isopropyl ether or normal butyl ether under the same reaction conditions.

The yields of the solid isomer of α -chloro- β -nitrostyrene are subject to the temperature at which nitryl chloride is introduced into ether, which may suggest that nitryl chloride, introduced into ether at about 10° , does not simply dissolve in ether. Free nitryl chloride may not occur itself but may be present in form of some reaction complex*³ nitryl chloride of nitryl chloride and ether, which then reacted with phenylacetylene.

This reaction was extended to other acetylenes employed in the reaction with nitrosyl chloride under the same reaction conditions as in the case of phenylacetylene. These results are summarized in Table I. In general, the corresponding chloronitro-olefins were also obtained accompanying considerable amounts of chloro-olefins and the

*³ No physical nor chemical investigations were undertaken for the property of the reaction-complex, however, the reaction-complex would be one composed of nitrosyl chloride and ether-peroxide. This proposal would be supported by the following facts; (1) the components of reaction products with phenylacetylene were similar to that of the reaction with nitrosyl chloride, (2) ether absorbed nitryl chloride at high temperature taking on a red-orange color like that of nitrosyl chloride but at low temperature the color of the solution was pale yellow which turned to red-orange and evolved heat on standing at room temperature. The resulting reddish solution did not regenerate the original pale yellow by cooling.

11) D. R. Goddard: J. Chem. Soc., 1958, 1955.

Starting materials R	Reagents	Solvents	Products		
			R	Yield (%)	m.p. or b.p. (°C/mm. Hg)
H (Ia)	NOCl	CCl ₄	H (<i>trans</i> -IIa)	33.5	55~56
"	NO ₂ Cl	—	H (<i>cis</i> -IIa)	2.5	105~110 (2)
"	"	CCl ₄	H (<i>trans</i> -IIa)	10.0	55~56
"	"	CH ₂ Cl ₂	"	15.1	55~56
"	"	(C ₂ H ₅) ₂ O ^{a)}	"	7.6	55~56
"	"	" ^{b)}	"	9.0	55~56
"	"	" ^{c)}	"	17.5	55~56
"	"	i-Pr ₂ O ^{c)}	"	46.6	55~56
"	"	Bu ₂ O ^{c)}	"	43.8	55~56
"	"	Bu ₂ O ^{c)}	"	48.9	55~56
CH ₃ (Ib)	NOCl	CCl ₄	CH ₃ (IIb)	40.7	93~96 (3)
"	NO ₂ Cl	(C ₂ H ₅) ₂ O ^{c)}	"	35.2	93~95 (3)
C ₆ H ₅ (Ic)	NOCl	CCl ₄	C ₆ H ₅ (IIc)	16.6	144~144.5
"	NO ₂ Cl	(C ₂ H ₅) ₂ O ^{c)}	"	3.4	144~144.5
CH ₂ OCOCH ₃ (Id)	NOCl	CCl ₄	CH ₂ OCOCH ₃ (IIId)	86.1	107~168 (0.08)
CH ₂ OCOCH ₃ (II)	NO ₂ Cl	(C ₂ H ₅) ₂ O ^{c)}	"	22.2	85~56 (0.03)
COOH (Ie)	NOCl	CCl ₄	COOH (IIe)	17.2	144~145
"	"	CH ₂ Cl ₂	"	11.5	144~145
"	NO ₂ Cl	(C ₂ H ₅) ₂ O ^{c)}	"	ca. 1.0	144~145
COOC ₂ H ₅ (If)	NOCl	CCl ₄	COOC ₂ H ₅ (IIIf)	35.4	103~105 (0.03)
"	NO ₂ Cl	(C ₂ H ₅) ₂ O ^{c)}	"	1.8	103~105 (00.5)

a) To the ether absorbed nitryl chloride at -20° was added ethereal solution of phenylacetylene.

b) Inverse addition of (a).

c) General procedure for addition of nitryl chloride to phenylacetylene derivatives described in experimental part.

yields of chloronitroolefins were lower than in the case of the reaction with nitrosyl chloride. Reaction of nitryl chloride with diphenylacetylene (Ic) in ether at about 10° afforded α -nitro- β -chlorostilbene (IIc), *cis*- α,β -dinitrostilbene (XI),¹²⁾ *trans*- α,β -dichlorostilbene (XII) and *cis*- α,β -dichlorostilbene (XIII) which was isolated as molecular complex with 2 moles of diphenylacetylene.¹³⁾ Identification of these structures was confirmed by melting points, elemental and spectral analysis.

Determination of Configuration of α -Chloro- β -nitrostyrenes (*trans*-IIa, *cis*-IIb)

The structure of α -chloro- β -nitrostyrene should exhibit geometric isomerism. Although one of the isomers of α -chloro- β -nitrostyrenes has been already obtained as crystals, its configuration has been still open to question and the other isomer has not yet been obtained as a pure compound. In this work the two isomers of α -chloro- β -nitrostyrenes (solid one, A and liquid one, B) were isolated in pure state from the reaction mixture of nitrosyl chloride and phenylacetylene. It was definitely proved in the foregoing description and by the following reactions that both compounds were actually the geometric isomers. Reaction of either compounds with aniline, morpholine and potassium thiocyanate afforded the same anilino-, morpholino- and thiocyano-derivatives, respectively. After the liquid one (B) was stored at room temperature for several months, some yellow crystals deposited, which were identical with the solid isomer (A).

12) J. Schmidt: Ber., 34, 619 (1901); H. Wieland, E. Blumick: Ann., 424, 100 (1921); E. Bergmann: J. Chem. Soc., 1936, 402; K.N. Campbell Jr., B.K. Campbell, et al.: J. Am. Chem. Soc., 75, 2400 (1953).

13) H. Staudinger: Ber., 49, 1971 (1916); Y. Ogata, H. Nakamura: J. Org. Chem., 21, 1170 (1956).

Chart 6.

Stereochemistry of the α -chloro- β -nitrostyrenes was established by physical methods. The dipole moments of these isomers were measured in an attempt to determine their configuration and values of 2.7 and 4.8 debeys for the crystals (A) and liquid isomer (B) were found. Comparing these moments with that of the model compounds, *p*-nitrochlorobenzene (2.78 D)¹⁴ and *o*-nitrochlorobenzene (4.59 D),¹⁴ the moments of the crystal (A) and the liquid isomer (B) were approximate with that of *p*-nitrochlorobenzene and *o*-nitrochlorobenzene, respectively. This facts indicate that the former (A) should have *trans*- and the latter (B) *cis*-configuration.*⁴

Chart 7.¹⁵⁾

Ultraviolet absorption spectra of both isomers were examined and data was presented in Table II and Fig. 1. The α -chloro- β -nitrostyrene molecule having *cis*-configuration*⁴ is almost planar and, therefore, resonance between the nitro group and the styrene moiety is at maximum. In the *trans* isomer, such a coplanar arrangement would be extremely crowded, and a scale model indicates that benzene ring and nitro group must be oriented at a considerable angle out of the plane of the ethylenic double bond in order to avoid excessive Van der Waals repulsions. Consequently the *trans* isomer*⁴ has less resonance energy and is less stable than the *cis**⁴ isomer. Absorption bands of the liquid isomer (B) were similar to those of β -nitrostyrene^{16,17} but those of

TABLE II. Physical Data of *trans*- and *cis*- α -Chloro- β -nitrostyrene (*trans*-IIa and *cis*-IIa)

Compound	m.p. or b.p. (°C/mm. Hg.)	IR (cm ⁻¹)			UV m μ (log ϵ)	Dipole moment (D)
		$\nu_{as \text{ NO}_2}$	$\nu_{s \text{ NO}_2}$	$\nu_{\text{C}=\text{C}}$		
<i>trans</i> -IIa	55~56	1534	1342	1622	277 (3.678) 233 (4.003)	2.7
<i>cis</i> -IIa	105~110/5	1520	1342	1604	287 (4.066) 226.5 (3.911)	4.8

*⁴ In this case, *trans* means that the nitro and chloro groups are on the opposite side and *cis* means they are on the same side.

14) L. G. Groves, S. Sugden: J. Chem. Soc., 1937, 1782.

15) V. N. Vasol'eva, V. V. Perekalin, V. G. Vasil'ev: Dok. Akad. Nauk. S. S. S. R., 141, 620 (1961).

16) E. A. Braude, E. R. H. Jones, G. G. Rose: J. Chem. Soc., 1947, 1104.

17) G. A. Shrekheimer, S. S. Novikov, V. I. Slovetskii: Izvest. Akad. Nauk. S. S. S. R. Otdel. Khim. Nauk, 1961, 182, C. A., 55, 18559e (1961). They have reported that β -nitrostyrene (m.p. 57°) has *trans*-configuration, and which is converted into *cis*-isomer by means of irradiation of ultraviolet light.

the solid isomer (A) were not. The position of the long wave length band of B 10 m μ higher than that of the corresponding band of A, moreover the second absorption band around 220~230 m μ is more intense in A than in B.

In infrared spectra the solid isomer (A) showed higher C=C stretching and nitro asymmetric stretching frequencies than those of the liquid isomer (B) as shown in Table II and Fig. 2. The solid isomer (A) had a strong nitro asymmetric stretching band at the same position (1534 cm⁻¹) as *trans*-3-nitro-4-chloro-3-hexene³⁾ (1533 cm⁻¹) but the liquid isomer (B) had a band at the almost same position (1520 cm⁻¹) as β -nitrostyrene (1517 cm⁻¹). When the phenyl- and nitro-groups of α -chloro- β -nitrostyrene are on the same side, it is difficult to preserve coplanarity. This difficulty gives rise to decrease contributions of resonance from XV,¹⁸⁾ resulting in an increase of nitro asymmetric stretching frequency. These spectral analyses also supported the conclusion that the solid isomer (A) of α -chloro- β -nitrostyrenes should be assigned to the *trans*-configuration*⁴ while the liquid isomer (B) should be *cis*.*⁴

Fig. 1. Ultraviolet Absorption Spectra of : (in Cyclohexane)

----- *trans*- α -Chloro- β -nitrostyrene
 ————— *cis*- α -Chloro- β -nitrostyrene

Infrared Absorption Spectra of *cis*- α -Chloro- β -nitrostyrene (in liquid film)

Infrared Absorption Spectra of *trans*- α -Chloro- β -nitrostyrene (in liquid film)

Fig. 2.

Experimental*⁵

General Procedure for Addition of Nitrosyl Chloride to Phenylacetylene Derivatives—A solution of acetylene derivative (1.0 mol.) in suitable solvent such as CCl₄, CHCl₃, CH₂Cl₂ was added to cold solution of NOCl¹⁹⁾ (3 to 5 mol.) dissolved in the same solvent as described above with dry ice-acetone chilling at -40° to -60° with mechanical stirring. The reaction mixture was continuously stirred for 2 to 3 hr. and then allowed to stand for several days at -10° or at room temperature with occasionally shaking. The solvent was evaporated under reduced pressure and the residue was purified either by recrystallization, *vacuo* distillation or silica gel chromatography.

*⁵ All melting points are uncorrected.

- 18) R. D. Kross, V. A. Fassel: J. Am. Chem. Soc., 78, 4225 (1956). They have reported that the contribution of resonance forms XIV and XV has influence upon nitro asymmetric stretching frequency of nitrobenzene derivatives, that is, the larger the contribution of resonance form XV, the lower the frequency.

- 19) Inorg. Syntheses IV, pp. 48~52 (1953).

General Procedure for Addition of Nitryl Chloride to Phenylacetylene Derivatives—Freshly distilled nitryl chloride gas²⁰⁾ (1.0 mol.) was introduced into abs. ether controlling the temperature from 5° to 10° under cooling with ice water. After absorption, the ethereal solution was additionally stirred for 1 hr. To the resulting orange colored ethereal solution was added the solution of phenylacetylene derivative (0.75 mol.) dissolved in abs. ether below 12° under cooling. The reaction mixture was stirred for about 10 hr. at 0° or at room temperature. Evaporation of solvent and excess of nitryl chloride gave a residue, which was purified either by distillation, recrystallization or silica gel chromatography.

α -Chloro- β -nitrostyrene (*trans*-IIa) and (*cis*-IIa) from Nitrosyl Chloride—A solution of phenylacetylene (30 g., 0.294 mol.) in 50 ml. of CCl₄ was added to a solution of NOCl (40 g., 0.61 mol.) in 50 ml. of CCl₄ at -45° with dry ice-acetone bath. After completing the addition, the reaction mixture was left at -10° for 4 days and then the temperature was gradually raised to room temperature overnight. The solvent was removed under reduced pressure and the residue (ca. 53 g.) was distilled to give 46.5 g. of an oil, b.p.₄ 90~116°, which was partially solidified on scratching in ice-salt bath. The solid was filtered off and recrystallized from petr. ether (b.p. 40~60°) to give 16 g. of yellow needles (*trans*-IIa), m.p. 55~56°. *Anal.* Calcd. for C₈H₆O₂NCl: C, 52.33; H, 3.29; N, 7.63; Cl, 19.31. Found: C, 52.04; H, 3.21; N, 7.69; Cl, 18.97. UV: $\lambda_{\max}$ 277 m μ (log ϵ 3.678) (in cyclohexane). Dipole moment (in benzene) at 25°: 2.7 D. The filtrate (30.6 g.) was chromatographed on silica gel (320 g.). Elution with hexane gave the following substances successively; (1) 12.4 g. of haloderivatives which was not further investigated. (2) 2.4 g. of *trans*-IIa, (4) 3.2 g. of *cis*-IIa, b.p.₂ 105~110° (bath temp.). *Anal.* Calcd. for C₈H₆O₂NCl: C, 52.33; H, 3.29; N, 7.63. Found: C, 52.52; H, 3.38; N, 8.05. UV: $\lambda_{\max}$ 267 m μ (log ϵ 4.066) (in cyclohexane). Dipole moment (in benzene): 4.8 D. (3) 10.0 g. of dichloroacetophenone which was identified with the authentic sample.⁸⁾

α -Chloro- β -nitrostyrene (*trans*-IIa) from Nitryl Chloride—To a stirred solution of nitryl chloride (100 g., 1.22 mol.) in 500 ml. of abs. ether which was prepared, by the same method as the general procedure described above, was added dropwise phenylacetylene (85 g. 0.835 mol.) without solvent maintaining a temperature of 0° under ice-water cooling. After completing addition the reaction mixture was further stirred below 5° for 5 hr. and then at room temperature for 35 hr. The evaporation of solvent gave semi solid on cooling in ice-salt bath, which afforded 71 g. of pale yellow crystals after filtration (46.6% yield). Recrystallisation from C₂H₅OH gave yellow needles, m.p. 55~56°. *Anal.* Calcd. for C₈H₆O₂NCl: C, 52.33; H, 3.29; N, 7.63; Cl, 19.31. Found: C, 52.30; H, 3.01; N, 7.75; Cl, 19.59.

1-Chloro-1-phenyl-2-nitro-1-propene (IIb) from Nitrosyl Chloride—To a stirred solution of nitrosyl chlorid (65.5 g., 0.1 mol.) in 100 ml. of CCl₄ prepared as in the general procedure, was added 41.4 g. (0.357 mol.) of 1-phenyl-1-propyne in 50 ml. of CCl₄ maintaining the temperature below -40°. After completing the addition, the reaction mixture was stirred for an additional 12 hr. The temperature was gradually raised to room temperature during the reaction. After evaporation of the solvent, the residue was taken up with ether and the ethereal solution was washed with satd. NaHCO₃, water, dried over Na₂SO₄ and ether evaporated. Vacuum distillation of the residue gave a pale yellow oil (17.5 g.), b.p.₃ 94~96°. *Anal.* Calcd. for C₉H₈O₂NCl: C, 54.69; H, 4.08; N, 7.08. Found: C, 54.52; H, 3.98; N, 7.11.

1-Chloro-1-phenyl-2-nitro-1-propene (IIb) from Nitryl Chloride—To a stirred solution of nitryl chloride (30 g., 0.368 mol.) in 120 ml. of abs. ether which prepared according to the general procedure described above, was added dropwise 1-phenyl-1-propyne (32.8 g., 0.282 mol.) in 50 ml. of abs. ether maintaining temperature below 12° by ice-water cooling. After finishing the addition, the reaction mixture was stirred for an additional 10 hr. under ice cooling. The evaporation of solvent gave an oily residue which was taken up with ether. The ethereal solution was successively washed with satd. NaHCO₃ solution, H₂O, dried over Na₂SO₄ and ether was evaporated. Vacuum distillation of the residue gave 12 g. of a crude oily substance, b.p.₃ 97~114°, which was purified by redistillation to afford 10 g. of an oil, b.p.₃ 95~96°. *Anal.* Calcd. for C₉H₈O₂NCl: C, 54.69; H, 3.98; N, 7.08. Found: C, 54.98; H, 4.01; N, 6.88.

α -Chloro- β -nitro-stilbene (IIc) from Nitrosyl Chloride—To a stirred solution of nitrosyl chloride (13 g., 0.19 mol.) in 20 ml. of CCl₄ was added diphenylacetylene (6 g., 0.0336 mol.) in 35 ml. of CCl₄ under chilling with dry ice-acetone at -40°. The reaction mixture was left for a week at room temperature. The solvent was evaporated and the residue was dissolved in hot hexane. The cooled solution yielded 1.45 g. of pale yellow needles, m.p. 137~140°. Recrystallization of the crude substance from 99% ethanol gave a pure compound (IIc), m.p. 144~144.5°. *Anal.* Calcd. for C₁₄H₁₀O₂NCl: C, 64.74; H, 3.88; N, 5.39. Found: C, 64.70; H, 3.91; N, 5.13. From the mother liquor 3 g. of starting material was recovered and 0.3 g. of a chloronitro-compound of bright pale yellow needles, m.p. 134~135° (from hexane), which should have the structure such as from spectral data. *Anal.* Calcd. for C₁₄H₈-

O₄NCl: C, 58.04; H, 2.78; N, 4.83; Cl, 12.24. Found: C, 58.03; H, 2.78; N, 4.53; Cl, 12.28.

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α -Chloro- β -nitrostilbene (IIc), *cis*- α,β -Dichlorostilbene (XIII), *trans*- α,β -Dichlorostilbene (XII) and *cis*- α,β -Dinitrostilbene (XI) from Nitryl Chloride—To a solution of nitryl chloride (12 g., 0.147 mol.) in 60 ml. of abs. ether which was obtained by the same method as general procedure was added diphenyl acetylene (20 g., 0.112 mol.) in 80 ml. of abs. ether. During the addition heat evolution was observed and the temperature rose from 4° to 12°. The reaction mixture was further stirred for 15 hr. Evaporation of solvent and excess of nitryl chloride gave a semi solid substance (28 g.), which was purified by silica gel chromatography. Elution with benzene-hexane (1:4) gave the following four substances; (1) 5.2 g. of colorless plates (XII), m.p. 142~143°, which was recrystallized from 99% ethanol. *Anal.* Calcd. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.04; Cl, 28.46. Found: C, 67.34; H, 4.19; Cl, 28.50. (2) 3.4 g. of colorless needles (XIII), which was a molecular compound consisting of 2 equivalents of diphenyl acetylene and 1 of *cis*- α,β -dichlorostilbene. Recrystallization from 99% of ethanol gave colorless needles, m.p. 67~68°. *Anal.* Calcd. for $C_{42}H_{30}Cl_2$: C, 74.56; H, 4.47; Cl, 20.96. Found: C, 74.38; H, 4.68; Cl, 21.37. (3) 0.929 g. of pale yellow needles (IIc), m.p. 144~144.5, recrystallized from 99% ethanol. *Anal.* Calcd. for $C_{14}H_{10}O_2NCl$: C, 64.74; H, 3.96; N, 5.39. Found: C, 64.44; H, 3.96; N, 5.51. (4) 1.817 g. of XI, m.p. 107~108° recrystallized from hexane. *Anal.* Calcd. for $C_{10}H_{14}O_4N_2$: C, 62.22; H, 3.73; N, 10.37. Found: C, 61.94; H, 3.91; N, 10.29.

2-Nitro-3-chloro-3-phenyl-2-propen-1-ol Acetate (IId) from Nitrosyl Chloride—A solution of 3-phenyl-2-propyn-1-ol acetate (23.5 g., 0.135 mol.) in 15 ml. of CCl_4 was added to nitrosyl chloride (31 g., 0.474 mol.) dissolved in 40 ml. of CCl_4 at once at -10°, and left for a week at this temperature and then for another week at room temperature. The solvent was removed under reduced pressure and the vacuum distillation of the residue afforded 26.5 g. of a pale yellow liquid, b.p._{0.3} 131~133°. *Anal.* Calcd. for $C_{11}H_{10}O_4NCl$: C, 51.67; H, 3.94; N, 5.48; Cl, 13.86. Found: C, 51.72; H, 3.91; 5.41; Cl, 13.94.

2-Nitro-3-chloro-3-phenyl-2-propen-1-ol Acetate (IId) from Nitryl Chloride—To a stirred solution of nitryl chloride (30 g., 0.368 mol.) in 120 ml. of abs. ether prepared as described in general procedure was added dropwise 3-phenyl-2-propyn-1-ol acetate (49.3 g., 0.283 mol.) under ice-water cooling. Heat evolution was observed and temperature increased from 0° to 12° during addition. After completing the addition, the reaction mixture was stirred for 8 hr. under cooling with ice-water. The solvent and excess of nitryl chloride was removed. The residue was dissolved in 200 ml. of ether and washed successively with satd. $NaHCO_3$, H_2O , dried over Na_2SO_4 and ether was evaporated. Vacuum distillation of the residue gave a crude oil, b.p._{0.3} 121~133°, which was redistilled to give 15 g. of a pale yellow liquid, b.p._{0.03} 85~86°. *Anal.* Calcd. for $C_{11}H_{10}O_4NCl$: C, 51.67; H, 3.94; N, 5.48; Cl, 13.86. Found: C, 51.39; H, 3.85; N, 5.74; Cl, 13.21.

α -Nitro- β -chlorocinnamic Acid (IIa) from Nitrosyl Chloride—To a solution of phenylpropionic acid (7.5 g., 0.048 mol.) in 13 ml. of CCl_4 was added $NOCl$ (10 g., 0.105 mol.) in 10 ml. of CCl_4 at once at -8° and then allowed to stand for 10 days at room temperature. The solvent and excess of $NOCl$ were removed under reduced pressure to afford a solid which was washed with small amount of petr. ether and recrystallized from benzene to give 2 g. of pale yellow needles, m.p. 144~145°. *Anal.* Calcd. for $C_9H_6O_4NCl$: C, 47.49; H, 2.66; N, 6.16; Cl, 15.58. Found: C, 47.50; H, 2.86; N, 6.19; Cl, 15.64.

α -Nitro- β -chlorocinnamic Acid (IIe) and *cis*- α,β -Dichlorocinnamic Acid (XVI) from Nitryl Chloride—The nitryl chloride gas (13 g., 0.16 mol.) was absorbed into 80 ml. of abs. ether with stirring under ice-water cooling. The temperature was controlled with the range of 5 to 8° during the absorption. After absorption, the solution was additionally stirred for 30 min. To this stirred solution was added dropwise the solution of phenylpropionic acid (17.2 g., 0.117 mol.) dissolved in 80 ml. of abs. ether at 5~8° under ice-water cooling. After addition, the reaction mixture was stirred for 10 hr. at room temperature. The solvent was removed and the residue (31 g.) was dissolved in 100 ml. of ether and washed with H_2O and extracted with cold satd. $NaHCO_3$ solution three times. The alkaline solution was washed with ether and acidified with 10% HCl solution under ice-cooling, and extracted with ether and washed with H_2O three times and dried over Na_2SO_4 . The solvent was evaporated leaving semicrystalline mass which was recrystallized from benzene to give 11.3 g. of XVI, m.p. 120~121°, *Anal.* Calcd. for $C_9H_6O_2Cl_2$: C, 49.79; H, 2.78; Cl, 32.68. Found: C, 49.96; H, 2.83; Cl, 33.03.

From mother liquors 1.1 g. of IIe was obtained by silica gel chromatography on elution of hexane. Recrystallization of IIe from benzene gave pale yellow needles, m.p. 144~145°.

Ethyl α -Nitro- β -chlorocinnamate (IIf) from Nitrosyl Chloride—Nitrosyl chloride gas (57 g., 0.873 mol.) was introduced into the solution of ethyl phenylpropionate⁵⁾ (27 g., 0.155 mol.) in 25 ml. of CCl_4 under cooling with dry ice acetone-bath at -40°. The reaction mixture was left for 10 days at room temperature. The solvent and excess of nitrosyl chloride was removed and then the obtained residue (39 g.) was submitted to vacuum distillation to give a pale yellow liquid (15.5 g.), b.p._{0.3} 114~116°. *Anal.* Calcd. for $C_{11}H_{10}O_4NCl$: C, 51.67; H, 3.94; N, 5.48; Cl, 13.86. Found: C, 51.23; H, 4.12; N, 5.55; Cl, 13.40.

Ethyl α -Nitro- β -chlorocinnamate (IIf) from Nitryl Chloride—Ethyl phenylpropionate (17.4 g., 0.1 mol.) dissolved in 20 ml. of abs. ether was added dropwise to a solution of nitryl chloride (11 g., 0.135 mol.) in 80 ml. of abs. ether prepared by the general procedure described above under ice-water cooling. The temperature was kept below 10° during the addition. After addition, the reaction mixture was stirred for 10 hr. at room temperature. The vacuum distillation of residue (ca. 15 g.) obtained after removing

solvent, gave a pale yellow oil, b.p._{0.3} 114~116° (3.8 g.). *Anal.* Calcd. for $C_{11}H_{10}O_4NCl$: C, 51.67; H, 3.94; N, 5.48; Cl, 13.86. Found: C, 51.93; H, 3.62; N, 5.39; Cl, 13.08.

α -Morpholino- β -nitrostyrene (IX) from IIe—To α -nitro- β -chlorocinnamic acid (620 mg.) in abs. ethanol (20 ml.) was added morpholine (880 mg.) with stirring under ice-water cooling. Heat evolution was observed. After twenty minutes yellow crystals appeared, which were filtered off to give pale yellow crystals (610 mg.). Recrystallization from 99% ethanol gave pale yellow prisms, m.p. 167~168°. *Anal.* Calcd. for $C_{12}H_{14}O_3N_2$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.40; H, 6.17; N, 12.13.

α -Morpholino- β -nitrostyrene (IX) from *trans* α -Chloro- β -nitrostyrene (IIa-A) or *cis* α -Chloro- β -nitrostyrene (IIa-B)—To compound (IIa-A) (2.0 g.) in benzene (20 ml.) was added morpholine (2.0 g.) with stirring under ice cooling. After heat evolution was observed, crystals separated which were filtered off and washed with ether. The combined filtrates were concentrated under reduced pressure to give crystalline residue (2.1 g.). Recrystallization from 99% ethanol gave pale yellow prisms, m.p. 167~168°. *Anal.* Calcd. for $C_{12}H_{14}O_3N_2$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.56; H, 6.04; N, 11.92. From compound (IIa-B) (1.0 g.) and morpholine (1.0 g.), 0.8 g. of IX was afforded by the same procedure described above.

Ethyl α -Nitro- β -morpholinocinnamate (X)—To ethyl α -nitro- β -chlorocinnamate (IIc) (2.063 g.) in 10 ml. of ethanol was added morpholine (1.41 g.) under ice-water cooling. Crystals appeared with heat evolution and were filtered off. Recrystallization from methanol afforded 958 mg. of yellow prisms, m.p. 183~184°. *Anal.* Calcd. for $C_{15}H_{18}O_5N_2$: C, 58.81; H, 5.92; N, 9.15. Found: C, 58.77; H, 6.10; N, 9.27.

2-Nitroacetophenone (III) from Ethyl α -Nitro- β -morpholinocinnamate (IIc)—A suspension of α -nitro- β -morpholinocinnamate (X) (200 mg.) in 25 ml. of 5% KOH-ethanol was stirred at room temperature. After the suspension became clear, crystals appeared again and stirring was continued for 90 min. The stirred reaction mixture was acidified with 10% HCl under ice water cooling accompanied with evolution of CO_2 and extracted with benzene. The combined benzene solutions were washed with water, dried over Na_2SO_4 and benzene was evaporated to give solid. Recrystallization from benzene-hexane afforded colorless needles (65 mg.), m.p. 105~106°. *Anal.* Calcd. for $C_8H_7O_3N$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.25; H, 4.40; N, 8.55.

ω -Nitroacetophenone (III) from α -Morpholino- β -nitrostyrene (IX)—A solution of α -morpholino- β -nitrostyrene (IX) (632 mg.) in 10 ml. of 90% ethanol, 10 ml. of benzene and 5 drops of conc. HCl was stirred under cooling with ice-water for 2 hr., 2 more drops of conc. HCl was added and stirred for an additional 2 hr. The reaction mixture poured into water, extracted with benzene, washed with H_2O until neutral to litmus and dried over Na_2SO_4 . The evaporation of benzene afforded solid which was recrystallized from hexane-benzene (6:1) to give colorless needles, m.p. 105~106°.

DL-N-Dichloroacetyl-3-phenylalaninol (VIII) from 2-Nitro-3-chloro-3-phenyl-2-propen-1-ol Acetate (IIc) via DL-3-Phenylalaninol (VII)—VIII was prepared according to the P. Karrer, *et al.*'s¹⁰ method with some modification as follows: To a suspension of $LiAlH_4$ (4.45 g., 0.12 mol.) in 150 ml. of abs. ether was added dropwise a solution of 2-nitro-3-chloro-3-phenyl-2-propen-1-ol acetate (8.4 g., 0.03 mol.) keeping the temperature from 3 to 5°. After completing the addition, the reaction mixture was refluxed for 7 hr. and 10 ml. of $CH_3COOC_2H_5$ was added under ice-water cooling. The reaction mixture was decomposed with 10% solution of potassium sodium tartarate (20 g.). The organic layer was separated and aqueous layer was extracted with ether. The combined ethereal solutions were washed with satd. NaCl solution and dried over Na_2SO_4 . Evaporation of ether afforded a gummy substance, which was acidified with 10% HCl solution and extracted with ether to remove unreduced substances. The acidic solution was made alkaline with 10% of NaOH solution under cooling and extracted with ether. The ethereal solution was washed with satd. NaCl solution and dried over anhyd. Na_2SO_4 . Evaporation of ether gave a semisolid (VII) (1.5 g.) which was not purified. A solution of this substance (1.1 g., 0.0073 mol.) and methyl dichloroacetate (2 g., 0.014 mol.) in 5 ml. of ethanol was refluxed for 2 hr. Evaporation of solvent and excess of methyl dichloroacetate *in vacuo* gave a gummy substance which purified by silica gel chromatography. Elution with benzene-ether (7:2) gave crystalline, DL-N-dichloroacetyl-3-phenylalaninol (VIII) (700 mg.), which was recrystallized from methanol- H_2O (1:10) giving colorless needles, m.p. 106~107°. *Anal.* Calcd. for $C_{11}H_{13}O_2NCl_2$: C, 50.39; H, 4.99; N, 5.34; Cl, 27.05. Found: C, 50.13; H, 4.72; N, 5.70; Cl, 26.74.

DL-Phenylalanine Ethyl Ester (XVII)—This compound was prepared according to Brenner's method with some modification as follows: To a stirred suspension of DL-phenylalanine (15 g., 0.091 mol.) in 400 ml. of abs. ethanol was added dropwise freshly distilled $SOCl_2$ (16.25 g., 0.1365 mol.) keeping the temperature from 5 to 8° with ice-water, the reaction mixture was refluxed for 3.5 hr. and then allowed to stand at room temperature for 8 hr. Ethanol was removed under reduced pressure to give a colorless gummy substance which was dissolved in H_2O . The solution was made alkaline with satd. K_2CO_3 solution and extracted with ether. The ethereal solution was washed with H_2O and dried over anhyd. Na_2SO_4 . The evaporation of solvent left an oil (17 g.) which was distilled *in vacuo* to give XV as a colorless liquid (12 g.), b.p.₄ 117~118°. *Anal.* Calcd. for $C_{11}H_{15}O_2N$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.02; H, 7.86; N, 7.33.

DL-3-Phenylalaninol (VII) via Hydrochloride of XVII—This compound was prepared according to the method of S. Yamada.¹⁰⁾ A solution of hydrochloride of DL-3-phenylalanine ethyl ester (6.0 g., 0.026 mol.) in 50 ml. of abs. ethanol was added to the stirred, ice-cold suspension of NaBH₄ (6.0 g., 0.158 mol.) in 150 ml. of abs. ethanol. After addition, the reaction mixture was refluxed for 25 hr. Evaporation of ethanol under reduced pressure gave a residue, which was dissolved in H₂O and extracted with CH₃COOC₂H₅. The CH₃COOC₂H₅ solution was shaken with satd. NaCl solution, dried over Na₂SO₄ and evaporation of solvent afford 3.04 g. of colorless crystals m.p. 64~65°. *Anal.* Calcd. for C₉H₁₃ON: C, 71.49; H, 8.67; N, 9.26. Found: C, 71.11; H, 8.57. N, 9.48.

N-(α -Methylphenethyl)benzamide (VI) from 1-Chloro-1-phenyl-2-nitro-1-propene (IIb) via 1-Phenyl-2-propylamine (V)—A mixture of 1-chloro-1-phenyl-2-nitro-1-propene (2.0 g.), 400 mg. of PtO₂ and 50 ml. of ethanol was hydrogenated at atmospheric pressure and 1330 ml. uptake of H₂ was observed (99.5% of calcd. amount at 26°) for 7 hr. After removal of catalyst, removal of solvent gave a residue which dissolved in water and shaken with ether. The aqueous layer was made alkaline with 10% of NaOH solution, extracted with ether, washed with satd. NaCl solution, and dried over Na₂SO₄. Evaporation of ether afforded a liquid (920 mg.). To the stirred suspension of this liquid (920 mg.) in 10% of NaOH solution (18 ml.) was added benzoyl chloride (2.0 g.) under cooling. The reaction mixture was stirred for 30 min. to afford a solid, which was filtered off and recrystallized from benzene-hexane giving colorless needles, m.p. 129~130°. *Anal.* Calcd. for C₁₆H₁₇ON: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.34; H, 7.25; N, 5.95.

N-(α -Methylphenethyl)benzamide (VI) from 1-Phenyl-2-nitro-1-propene via 1-Phenyl-2-propylamine (V)—A mixture of 1-phenyl-2-nitro-1-propene (2.0 g.), 400 mg. of PtO₂ and 50 ml. of ethanol was hydrogenated with agitation at atmospheric pressure and 990 ml. uptake of H₂ was observed (92.5% of calcd. amount at 26°) for 10 hr. After removal of catalyst, evaporation of solvent gave a residue which was acidified with 10% of cold HCl solution and the aqueous solution was washed with ether. The aqueous layer was made alkaline with cold 10% NaOH solution, extracted with ether, washed with satd. NaCl solution and dried over Na₂SO₄. Removal of ether gave a liquid (450 mg.). To the stirred, cold suspension of this liquid (450 mg.) in 10% of NaOH solution was added 1.0 g. of benzoyl chloride and stirred for 30 min. A gummy substance separated which was recrystallized from benzene-hexane to afford colorless needles, m.p. 129~130°.

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Summary

The addition reaction of nitryl chloride and nitrosyl chloride with phenyl acetylene (Ia), phenylmethylacetylene (Ib), diphenylacetylene (Ic), 3-phenyl-2-propyn-1-ol alcohol acetate (Id), phenylpropionic acid (Ie), and ethyl phenylpropiolate (If) was carried out under various conditions which afforded the corresponding chloro-nitroolefins: α -chloro- β -nitrostyrene (*trans* IIa and *cis* IIa), 1-chloro-1-phenyl-2-nitro-1-propene-1 (IIb), α -chloro- β -nitrostyrene (IIc), 2-nitro-3-chloro-3-phenyl-2-propen-1-ol acetate (IIId), α -nitro- β -chlorocinnamic acid (IIe), and ethyl α -nitro- β -chlorocinnamate (IIIf) respectively. The geometrical relationship of the isomers of α -chloro- β -nitrostyrene were determined by dipole moments and infrared and ultraviolet spectra.

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