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The Cycloaddition Reaction of Isonitrile to Ketenimine Formed by the Reaction of Isonitrile with Carbene*

Naruyoshi Obata, Haruo Mizuno, Takeo Koitabashi, and Takeo Takizawa
Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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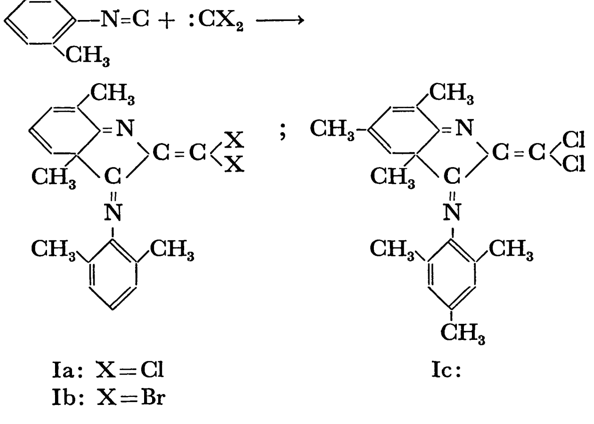
The reaction of several 2-, 4-, and/or 6-methyl-substituted phenylisonitrile with dihalocarbene and diphenylcarbene has been studied. The reaction of methyl-substituted phenylisonitrile with dihalocarbene gave indolenine or indoloquinoline derivatives *via* ketenimine intermediate which might be produced by α-addition of carbene to isonitrile. In contrast, the reaction of 2,6-dimethylphenylisonitrile with diphenylcarbene presumably formed by photolysis of diphenyldiazomethane gave *N*-(2,6-dimethylphenyl)diphenylketenimine, and further caused a cycloaddition reaction with isonitrile to yield indonimine derivatives. The structure of these products are discussed on the basis of the spectral data and chemical reactions. The mechanistic pathway of these reactions and the effect of methyl substituent in the cyclization stage are also discussed.

The reactivity of both carbene and isonitrile has been well recognized as divalent carbon.[1,2] It is expected that the reaction of electrophilic carbene with nucleophilic isonitrile gives the ketenimine derivatives in analogy with the superficial dimerization of carbene.[1,3] Halleux[4] discovered that the reaction of cyclohexylisonitrile with dichlorocarbene generated by $CHCl_3$–*t*-BuOK method[5] led to *N*-cyclohexyldichloroacetamidate. He showed that ketenimine was an intermediate in this reaction. The reactions of cyclohexyl- or *t*-butylisonitrile with diphenylcarbene to form ketenimine derivatives were also reported.[6]

The reactions of aromatic isonitrile with dihalocarbene or diphenylcarbene are of great interest not only with respect to the cycloaddition reaction of isonitrile to aromatic ring** of aryl-substituted ketenimine intermediate but also in connection with the mechanism of the oligomerization of phenylisonitrile to give indigodianil.[7] The reaction of phenylisonitrile with or without methyl substituent(s) at *ortho*-position with dihalocarbene and diphenylcarbene were investigated.

Results and Discussion

Reaction of Arylisonitrile with Dihalocarbene. The reaction of 2,6-dimethylphenylisonitrile with 2 mol equivalent of CHX_3–*t*-BuOK was carried out at 0 °C. After work-up in the usual way, indolenine derivative (Ia) (mp 135 °C, 40%) or (Ib) (mp 122 °C, 27%) was obtained. A similar result was also obtained in the reaction of 2,4,6-triphenylmethylisonitrile with dichlorocarbene giving (Ic) (mp 148 °C, 20%). No acetamidate derivatives reported by Halleux[4] was isolated in these reactions. Elemental analysis and molecular weight determination indicated that compounds Ia—Ic consisted of two molecules of isonitrile and one molecule of dihalocarbene. In the IR region, each of them showed characteristic four peaks at 1500—1700 cm^{-1} which were due to the C=C or C=N stretching. In the NMR spectrum, Ia and Ib showed multiplets at τ 3.05 (3H) and 3.5—4.7 (3H) and three sharp singlets at τ 7.85 (6H), 8.1 (3H) and 8.8 (3H). The signals at τ 3.05 and 3.5—4.7 showed that both aromatic protons and diene protons[9] were present in this compound. Three signals at high field might be attributed to the aromatic methyl protons, unsaturated methyl protons and saturated methyl protons. Consequently, it is most likely that an aromatic ring of two 2,6-dimethylphenylisonitrile was transformed into a cyclohexadiene ring. This was further evidenced by the NMR spectrum of compound Ic which showed three broad singlets at τ 3.15 (2H), 3.78 (1H) and 4.65 (1H) due to aromatic protons and uncoupled protons.



Ia: X=Cl
Ib: X=Br

Ic:

Scheme 1.

The structure of I was confirmed by the following reaction. Compound Ib was hydrolysed by dilute hydrochloric acid to give only polymer but silica gel-catalyzed hydrolysis gave amide (IIb) (mp 143 °C) in an appreciable yield. Elemental analysis and molecular weight determination indicated that compound IIb has a composition of one molecule each of Ib and H_2O. The characteristic peaks at 1640 ($\nu_{C=N}$), 1720 ($\nu_{C=O}$) and 3400 cm^{-1} (ν_{N-H}) in the IR spectrum of IIb suggested the presence of amide group. The NMR spectrum exhibited a complex multiplet at τ 3.0 (6H) and broad singlets at τ 1.43 (1H), 4.13

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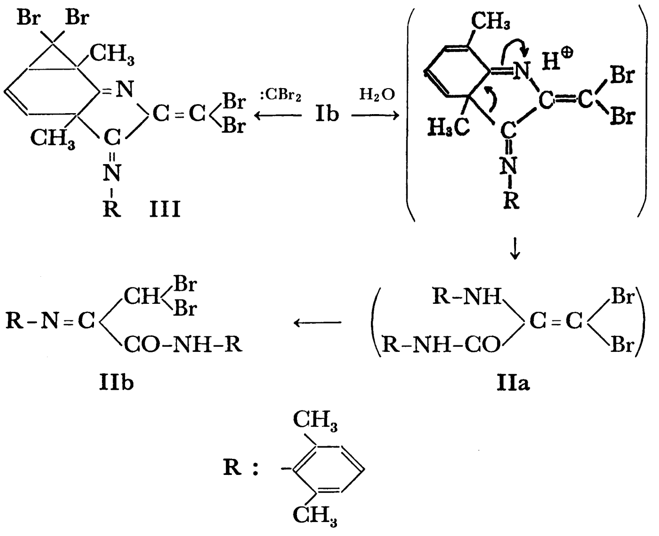
* A part of this work has been published. T. Takizawa, N. Obata, Y. Suzuki and T. Yanagida, *Tetrahedron Lett.*, **1969**, 3407, M. Muramatsu, N. Obata, and T. Takizawa, *Tetrahedron Lett.*, **1973**, 2133. It was also presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967 and at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

** It was reported that the reaction of aromatic imine with *t*-butylisonitrile in the presence of boron trifluoride resulted in the formation of indole and azetidine derivatives.[8]

(1H), 7.7 (6H) and 7.88 (6H). The signals at τ 3.0 7.7 and 7.88 indicated the presence of two 2,6-dimethylphenyl group. The signal at τ 1.43 was assigned to the N–H proton of the amide group because of the disappearance of the signal by the addition of deuterium oxide. The signal at τ 4.13 was attributed to dibromomethin proton.[10] Thus the structure of the amide IIb is not enamine form (IIa) but imine form as shown in Scheme 2. Hydrolysis of Ib might take a route of the ring opening initiated by a protonation and resulting in regeneration of aromatic ring.

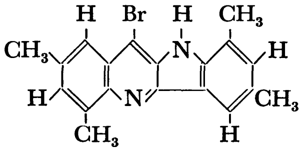


Scheme 2.

If the Seyferth method,[11] decomposition of phenyl(tribromomethyl)mercury, is employed for the generation of dibromocarbene, it might be expected to trap the intermediate giving compound I because of high reactivity of this carbene to multiple bond.[12]

Thus the reflux of the mixture of phenyl(tribromomethyl)mercury and 2 mol equivalent of 2,6-dimethylphenylisonitrile in benzene for 2 hr under nitrogen stream resulted in the formation of Ib (35%), IIb (22%), III (mp 193—195 °C following decomposition, 1.2%) and polymer.*** The identity of the structures Ib and IIb with that obtained above was established by mixing mp. Compound III was found to be the 1 : 1 adduct of Ib and dibromocarbene from elemental analysis and molecular weight determination. In fact the reaction of Ib with phenyl(tribromomethyl)-mercury in benzene gave III in an appreciable yield. In the IR region, III exhibited a characteristic absorption at 1020 cm^{-1} which was due to the cyclopropane skeleton.[13] On comparison of the NMR spectrum of III with that of Ib, it was found that III exhibited an extra multiplet at τ 4.40 (2H), but no multiplet at τ 3.7 (1H) observed in Ib. These spectral data indicated that III was produced by the addition of carbene to methyl substituted double bond[1,14] of cyclohexa-(1,3)-diene Ib. Thus the structure of III is formulated as shown in Scheme 2. Compound IIb might be formed in the hydrolysis of Ib at work-up stage by silica gel chromatography, since IIb could not be obtained on rapid treatment of reaction mixture with silica gel chromatography. The reaction of phenyl(tribromomethyl)mercury with large excess isonitrile gave only Ib in good yield under the conditions without hydrolysis. On the other hand, the reaction of isonitrile with large excess phenyl(tribromomethyl)mercury gave III, carbene addition product to Ib, in good yield.

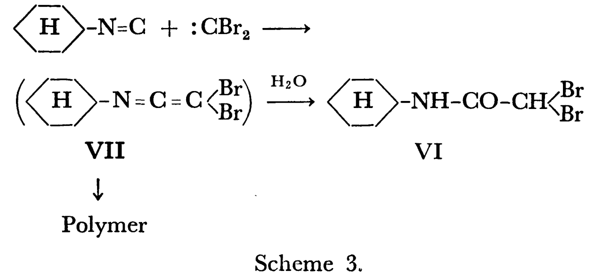
The reaction of 2,4-dimethylphenylisonitrile with dibromocarbene was carried out in the same way in order to investigate the effect of methyl substituent at *ortho* positions in this cycloaddition reaction. In contrast to the reaction mentioned above, a large quantity of polymer and a small amount of indoloquinoline derivative (IV) (mp 194—195 °C, 4%) were obtained. Compound IV was found to have the composition of HBr-elimination from 2 : 1 adduct of isonitrile and dibromocarbene on the basis of elemental analysis and the mass spectrum.



IV

In the IR region, IV exhibited characteristic absorption at 3240 cm^{-1} due to N–H stretching frequency. The UV absorption spectrum of IV showed characteristic maxima at 282 (log ε: 4.83), 350 (4.22), and 385 nm (3.67), which were similar to those of indolo (3′ : 2′—2 : 3)quinoline reported by Clemo and Felton.[15] This shows that compound IV has an indoloquinoline chromophore. The NMR spectrum exhibited five broad singlets at τ 2.05 (1H), 2.4 (1H), and 3.0 (1H) and four sharp singlets at τ 7.0 (3H), 7.45 (3H), 7.55 (3H) and 7.6 (3H). The singlet at τ 2.6 was assigned to N–H protone because of its broadness and the disappearance of the signal by addition of deuterium oxide. In fact, compound IV gave *N*-acetyl derivative (V) (mp 200—202 °C) in the reaction of IV with acetic anhydride. The other four broad signals at low field and four sharp singlets at high field were attributed to uncoupled aromatic protons and four methyl protons in a different atomosphere, respectively. Considering these spectral evidences, it was concluded that the structure of IV should be indoloquinoline derivative as shown in the figure.

The reaction of 4-methylphenylisonitrile, no substituent at *ortho* position, with dibromocarbene in the same condition as above resulted only in the formation of polymer. A similar result was obtained in the



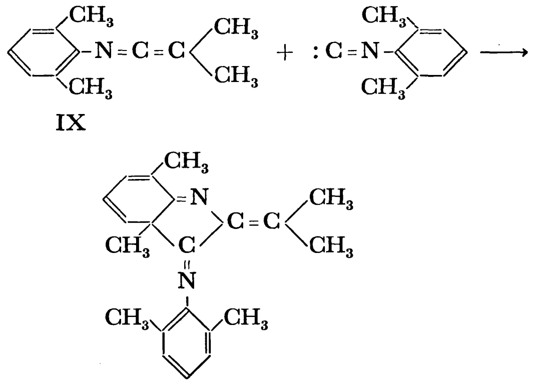
Scheme 3.

*** All polymers obtained in the reaction of arylisonitrile with dihalocarbene showed a similar absorption in the IR spectrum.

reaction of cyclohexylisonitrile with dibromocarbene, and a trace amount of *N*-cyclohexyldibromoacetamide (VI) (mp 142 °C) was isolated. Compound VI might be produced in the reaction of intermediate *N*-cyclohexyldibromoketenimine (VII) with H_2O which was present as an impurity.

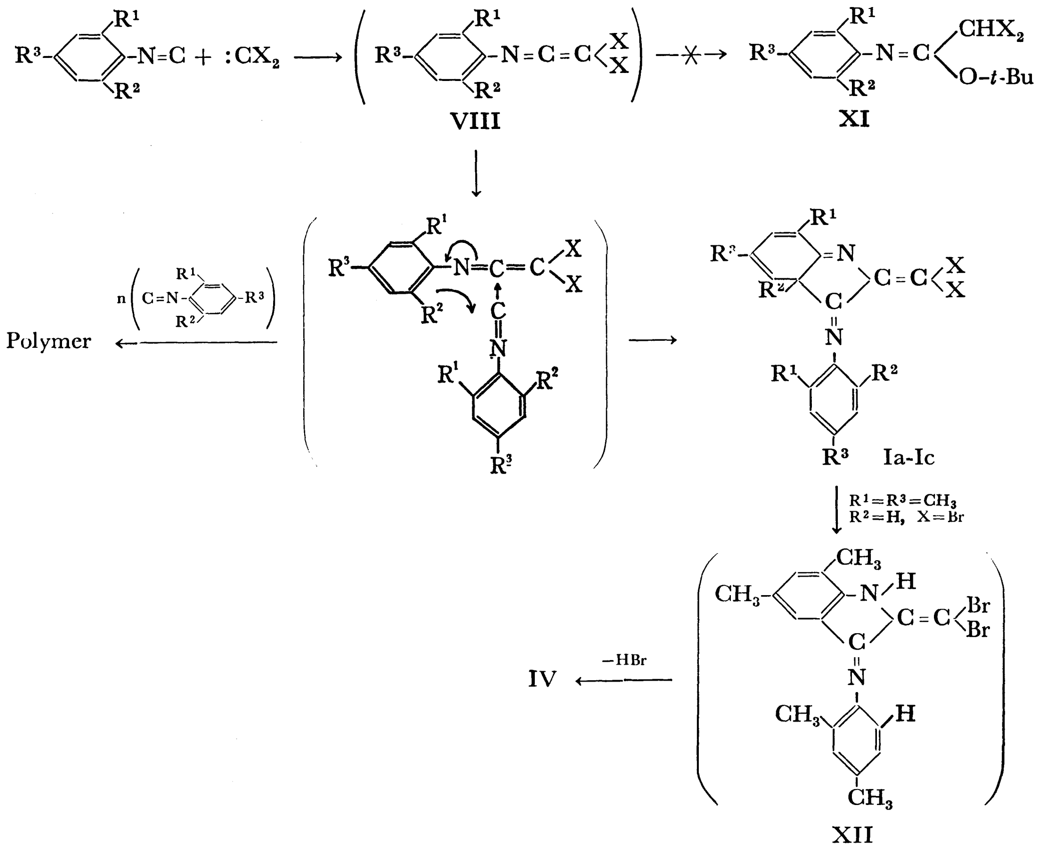
When this reaction was carried out by the $CHCl_3$–*t*-BuOK method for generation of carbene, *N*-cyclohexyldibromoacetamidate was isolated as a result of the addition of *t*-BuOH or *t*-BuOK to VII[4]. The formation of polymer, main product in these cases, might also be taking a route of cationic polymerization initiated by the attack of isonitrile to ketenimine VII. This indicates that the reaction of aromatic isonitrile with dihalocarbene generated by either the CHX_3–*t*-BuOK method or the Seyferth method to give the cycloaddition products I and IV and/or polymer might proceed *via* *N*-aryldihaloketenimine intermediate VIII. In fact the reflux of *N*-(2,6-xylyl)dimethylketenimine (IX) prepared by a modification of the Stevens method[16] with 2,6-dimethylphenylisonitrile resulted in the formation of indolenine derivative (X) (mp 103 °C, 26%). The properties and spectra of compound X were essentially similar to those of I.

Thus it is clear that ketenimine VIII is the real intermediate in these cycloaddition reactions. The most reasonable mechanistic pathway of the reaction of arylisonitrile with dihalocarbene might be illustrated by the following scheme (Scheme 5).



Scheme 4.

Indolenine Ia—Ic could be formed by 1,4-cycloaddition reaction of isonitrile to the ketenimine intermediate VIII formed by the α-addition of carbene or carbenoid[†] to isonitrile. The fact that the reaction of 2,6-dimethylphenylisonitrile with dihalocarbene generated by CHX_3–*t*-BuOK method gave no *N*-2,6-dimethylphenyldihaloacetamidate (XI) but indolenine derivatives I, might be due to the steric requirement of attacking species, *t*-butoxy anion and 2,6-dimethylphenylisonitrile to ketenimine VIII in the cyclization stage. It was considered that for the formation of IV primary cycloaddition products such as I caused



Scheme 5.

[†] We believe that a ketenimine intermediate is formed by the reaction of isonitrile with carbene which is produced by the decomposition of Ph–Hg–CBr_3 and basic α-elimination from haloform, although other mechanisms cannot be excluded completely.

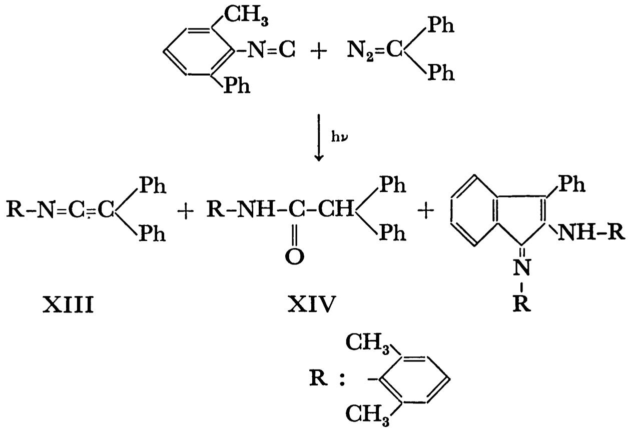
the prototropy to give indole derivative (XII), from which hydrogen bromide might be eliminated by phenyl(tribromomethyl)mercury or phenylmercuric bromide, decomposition product of carbene precursor.[17] The formation of polymer might also be taking a route of cationic polymerization initiated by the nucleophilic attack of isonitrile to ketenimine VIII, since the order of reactivity of the cationic polymerization of isonitrile,[18] *i.e.*, cyclohexyl-≧4-methylphenyl->2,4-dimethylphenyl->2,6-dimethylphenylisonitrile, was identical with that of the formation of polymer in these reactions. This reactivity of isonitrile must be controlled by the steric effect of methyl substituent at *ortho* positions.

Photolysis of Diphenyldiazomethane in the Presence of 2,6-*Dimethylphenylisonitrile.** For further investigation of the cycloaddition reaction of isonitrile with phenyl-substituted ketenimine at cumulated carbon, diphenyldiazomethane as a precursor of diphenylcarbene[1,2,7] was subjected to photolysis in the presence of 2,6-dimethylphenylisonitrile.

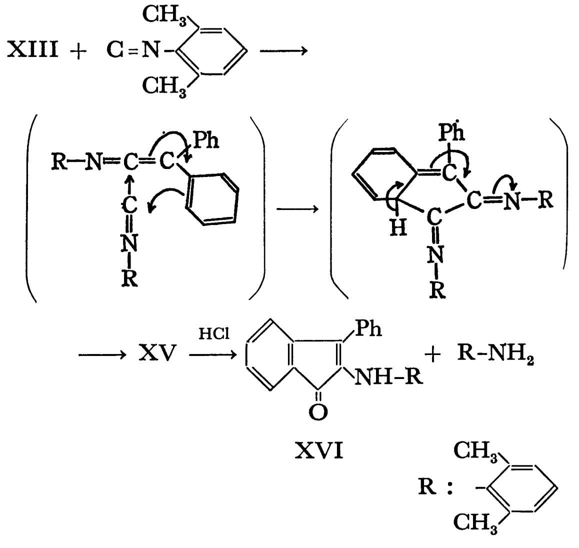
The *n*-hexane solution of diphenyldiazomethane and a molar equivalent of 2,6-dimethylphenylisonitrile was irradiated with a 500 W high pressure mercury lamp for 4 hr. IR absorption spectrum of the reaction mixture showed a new peak at 2020 cm^{-1} besides the peaks due to isonitrile and diazo compound. Subsequent removal of solvent at room temperature and rapid separation by means of alumina chromatography gave *N*-(2,6-xylyl)-diphenylketenimine (XIII) (mp 60—61 °C, 1%), *N*-(2,6-xylyl)-diphenylacetamide (XIV) (mp 210—211 °C, 24%) and a very small amount of 1-(2,6-dimethylphenylimino)-2-(2,6-dimethylanilino)-3-phenylindene (XV) (mp 197—198 °C). The structures of XIII and XIV were established by comparison with authentic samples prepared by a modification of the Stevens method.[16] The infrared and NMR spectra of XIII and XIV were consistent with the assigned structures. Ketenimine XIII was easily hydrolyzed by dilute hydrochloric acid or alumina to produce amide XIV in a quantitative yield. Consequently, the amide XIV corresponding to XIII was formed by hydration of ketenimine XIII on an alumina column.

The results indicate that ketenimine was formed in at least 25% yield in the photochemical reaction. We believe that the formation takes the route of photolysis of diphenyldiazomethane to produce diphenylcarbene and electrophilic attack of this carbene to isonitrile, although other mechanisms for the formation of ketenimine cannot be excluded completely.[6]

The reflex of benzene solution of equimolar mixture of ketenimine XIII and 2,6-dimethylphenylisonitrile resulted in the formation of XV in 73% yield. In the IR region, XV exhibited characteristic absorption bands at 3300, 1655 and 1620 cm^{-1} which might be attributed to N–H group, C=N or C=C double bond, respectively. The UV absorption spectrum of XV showed a characteristic peak at 272 nm (log ε: 4.61). The NMR spectra exhibited a multiplet at τ 3.0—4.0 (16H) and a singlet at τ 7.85 (12H). The structure of XV was further confirmed by the following reaction. Compound XV was hydrolyzed by dilute hydrochloric acid in THF to give 2-(2,6-dimethylanilino)-3-phenylindone (XVI) (mp 133—134 °C) and 2,6-xylydine in good yield. The structure of XVI was established by elemental analysis, molecular weight determination and a comparison of spectral data, IR and UV, with those of known 2,3-diphenylindone.[19] Thus the structure of XV was established as shown in Scheme 6. Its formation indicated that the cycloaddition of isonitrile to ketenimine did not occur in the 2,6-dimethylphenyl ring but in phenyl ring of ketenimine preferentially in the fashion of 1,4-cycloaddition, as shown in the following scheme (Scheme 7).



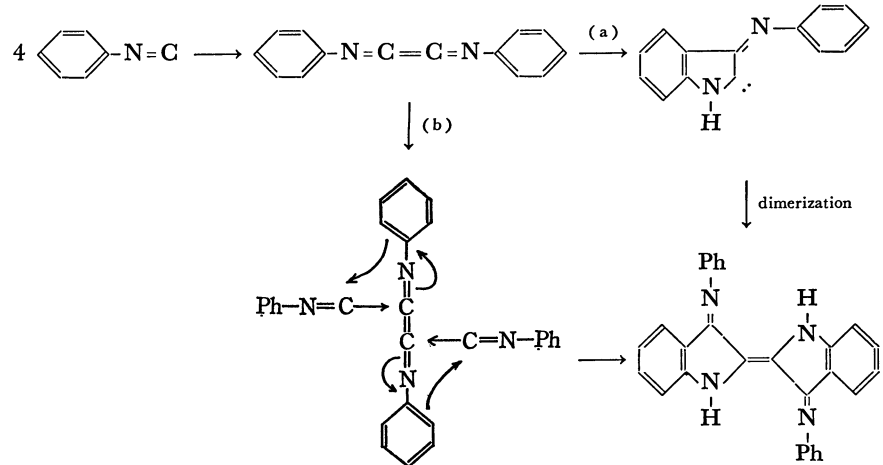
Scheme 6.



Scheme 7.

This reaction as well as that of 2,4-dimethylphenylisonitrile with dibromocarbene to give IV, *i.e.*, the cycloaddition of isonitrile to non-substituted phenyl ring, seems to show that the methyl substitution at *ortho* position did not favour the cycloaddition reaction of isonitrile to phenyl ring of ketenimine.

Also, all these cycloaddition reactions of isonitrile to ketenimine easily produced by the reaction of isonitrile with carbene seem to suggest the mechanism of the formation of indigodianil (XVII) in the oligomerization of phenylisonitrile. Grundmann[7] proposed the following mechanism for this oligomerization, the



XVII

Scheme 8.

dimerization of isonitrile and intramolecular cyclization of the dimer to give carbene followed by its dimerization (path a). But the reactions we investigated so far suggest another possible mechanism, *i.e.*, dimerization and intermolecular double cycloaddition of isonitrile to cumulate double bond (path b).

In conclusion, the reaction of several methyl-substituted phenylisonitrile with dihalocarbene gave indolenine or indoloquinoline derivatives and/or polymer *via* ketenimine intermediate. This was evidenced by the reaction of *N*-(2,6-xylyl)dimethylketenimine with 2,6-dimethylphenylisonitrile to give indolenine such as I. This intermediate ketenimin was isolated only in the photolysis of diphenyldiazomethane in the presence of isonitrile, the formation of which might be taking a route of dimerization of divalent carbon, presumably diphenylcarbene and isonitrile. In the reaction of isonitrile with tri-aryl-substituted ketenimine, two possibilities to form indole and indene derivatives as the result of the cycloaddition of isonitrile to phenyl ring of ketenimine were indicated. Although the electronic effect of methyl group in these reactions does not seem to be an important factor, the steric effect of methyl substituent is supposed to play a more important role on both the direction of the cycloaddition of isonitrile to ketenimine and the reactivity of isonitrile, *i.e.*, the reactivity of cationic polymerization of isonitrile.

Experimental[††]

Starting Materials. Isonitrile was prepared by the I. Ugi procedure[20]. Phenyl(tribromomethyl)mercury was prepared by the Seyferth method[11].

Reaction of 2,6-Dimethylphenylisonitrile (A) with $CHCl_3$–t-BuOK, Indolenine Derivative (Ia). 2.4 g (0.02 mol) of chloroform was added, with cooling for 30 min, to a stirred suspension of 1.3 g (0.01 mol) of 2,6-dimethylphenylisonitrile and t-BuOK (0.02 mol) in 20 ml of peteroleum ether. The reaction mixture was poured into ice-water, extracted with petroleum ether, washed with water and dried, giving yellow solid. Recrystallization from ether gave 0.7 g (40%) of Ia, mp 135.5 °C. The structure of Ia was established by the following data.

Found: C, 65.80; H, 5.27; N, 8.01; Cl, 20.87%; mol. wt, 329. Calcd for $C_{19}H_{18}N_2Cl_2$; C, 66.08; H, 5.22; N, 8.11; Cl, 20.58%; mol. wt, 345. IR(KBr): 1680, 1630, 1595 cm^{-1} ($\nu_{C=C}$ or $\nu_{C=N}$). UV $\lambda_{\max}^{\mathrm{EtOH}}$: 305 (log ε: 3.99); 350 nm (4.14). NMR(CDCl$_3$): τ 3.05 (m, 3H), 3.5—4.7 (m, 3H), 7.85 (s, 6H), 8.1 (s, 3H), 8.8 (s, 3H).

(B) with $CHBr_3$–t-BuOK, Indolenine Derivative (Ib). A similar reaction was carried out between 0.01 mol of 2,6-demethylphenylisonitrile and 0.02 mol of $CHBr_3$–*t*-BuOK, in petroleum ether. After a similar work-up, 0.58 g (27%) yellow crystals of Ib, mp 122 °C was obtained, after recrystallization from ether–petroleum ether (1 : 1).

Found: C, 52.31; H, 4.28; N, 6.21; Br, 36.38%; mol. wt, 438. Calcd for $C_{19}H_{18}N_2Br_2$: C, 52.56; H, 4.71; N, 6.45; Br, 36.12%; mol. wt, 434. IR (KBr): 1680, 1630, 1590, 1505 cm^{-1} ($\nu_{C=C}$ or $\nu_{C=N}$). UV $\lambda_{\max}^{\mathrm{EtOH}}$: 230 (log ε: 4.30), 310 (3.86), 352 nm (4.04).

Reaction of 2,4,6-Trimethyphenylisonitrile with $CHCl_3$–t-BuOK, Indolenine derivative (Ic). A similar reaction was carried out between 1.45 g (0.01 mol) of 2,4,6-trimethylphenylisonitrile and 0.02 mol of $CHCl_3$–*t*-BuOK. The reaction mixture was poured into ice-water and extracted with ether. The extracts were washed with water and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed on a column of silica gel. Elution with hexane-benzene (3 : 2) gave yellow solid. Recrystallization of this material from ether gave 0.3 g (20%) of indolenine derivative (Ic), mp 148 °C.

Found: C, 67.41; H, 5.78; N, 7.85; Cl, 18.37%; Calcd for $C_{21}H_{22}N_2Cl_2$: C, 67.56; H, 5.94; N, 7.51; Cl, 18.72%. IR (KBr): 1680, 1615, 1600, 1520 cm^{-1} ($\nu_{C=C}$ or $\nu_{C=N}$). UV $\lambda_{\max}^{\mathrm{EtOH}}$: 230 (log ε: 4.48), 290 (4.05), 305 (3.02), 360 nm (4.12). NMR(CDCl$_3$): τ 3.15 (broad s, 2H), 3.78 (broad s, 1H), 4.65 (broad s, 1H), 7.7 (s, 3H), 7.88 (s, 6H), 8.1 (s, 3H), 8.32 (s, 3H), 8.82 (s, 3H).

Hydrolysis of Ib. A solution of 100 mg (2.3 mmol) of Ib and 1 g of silica gel in 30 ml aqueous methanol was refluxed for 24 hr and allowed to stand for several days at room temperature. After silica gel chromatography, 16 mg

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[††] All melting points were uncorrected. IR spectra were determined using a Nihonbunko DS 402 G infrared spectrophotometer. UV spectra were recorded with a Carry 11 recording spectrophotometer. NMR spectra were obtained with a Varian A-60 spectrometer, using tetramethylsilane as an internal standard. The molecular weight was determined by use of a Hitachi 105 vapor pressure osmometer.

(15%) of amide IIb was obtained. The structure of IIb was established by the following data.

Found: C, 50.68; H, 4.65; N, 6.35; Br, 35.44%; mol. wt, 443. Calcd for $C_{19}H_{20}ON_2Br_2$: C, 50.44; H, 4.42; N, 6.19; Br, 35.39; mol. wt, 443. IR (KBr): 3400 (ν_{N-H}), 1720 ($\nu_{C=O}$), 1640 cm^{-1} ($\nu_{C=N}$). UV λ_{max}^{EtOH}: 255 nm (log ε: 3.49). NMR($CDCl_3$): τ 1.43 (broad s, 1H), 3.0 (m, 6H), 4.13 (s, 1H), 7.7 (s, 6H), 7.88 (s, 6H).

Reaction of 2,6-Dimethylphenylisonitrile with Phenyl(tribromomethyl)mercury. A solution of 2.49 g (0.019 mol) of 2,6-dimethylphenylisonitrile and 5.03 g (9.5 mmol) of phenyl(tribromomethyl)mercury in 30 ml dry benzene was refluxed for 2 hr under nitrogen stream. The reaction mixture was cooled and filtered. The residue was washed with benzene and combined, and the combined benzene solution was evaporated. The residue was chromatographed on a column of silica gel. From the eluent with hexane, 1.15 g (35%) of Ib (from hexane) and 0.034 g (1.2%) of III were obtained mp 193—195 °C (from hexane). III gave the following analytical and spectral data. Found: C, 39.80; H, 2.86; N, 4.77; Br, 51.64%; mol. wt, 582. Calcd for $C_{20}H_{18}N_2Br_4$: C, 39.60; H, 2.97; N, 4.62; Br, 52.81%; mol. wt, 606. IR (KBr): 1680 ($\nu_{C=N}$), 1618 ($\nu_{C=C}$), 1020 cm^{-1} ($\nu_{cyclopropane}$). UV λ_{max}^{EtOH}: 230 (log ε: 4.13), 290 nm (4.20). NMR($CDCl_3$): τ 3.05 (m, 3H) 4.4 (m, 2H), 7.85 (s, 3H), 8.05 (s, 3H), 8.4 (s, 1H), 8.75 (s, 3H).

From the eluent with benzene over 4 days, 0.92 g (22%) of IIb, mp 143 °C (from hexane) was obtained. However, IIb could not be obtained by rapid treatment with silica gel chromatography (one or two days).

When the reaction was carried out with the reverse mol ratio of 5 mmol of 2,6-dimethylphenylisonitrile to 10 mmol of phenyl(tribromomethyl)mercury, III was obtained in 10% yield. On the contrary, when 5 moles excess isonitrile to phenyl(tribromomethyl)mercury was used, the yield of Ib rose to 65% and IIb and III could not be obtained.

Reaction of Ib with Phenyl(tribromomethyl)mercury. A solution of 0.43 g (1 mmol) of Ib and 0.53 g (1 mmol) of phenyl(tribromomethyl)mercury in 30 ml dry benzene was refluxed for 2 hr under nitrogen stream. After the reaction mixture was filtered, the solvent was removed by evaporation and the residue was chromatographed on a column of silica gel. 51 mg (12%) of III and a trace amount of IIb were obtained.

Reaction of 2,4-Dimethylphenylisonitrile with Phenyl(tribromomethyl)*mercury.* A solution of 1.79 g (14 mmol) of 2,4-dimethylphenylisonitrile and 3.62 g (7 mmol) of phenyl(tribromomethyl)mercury in dry benzene 30 ml was refluxed for 2 hr under nitrogen stream. After work-up in the usual way and silica gel chromatography, 40 mg (2%) of IV, mp 194—195 °C (from hexane) and a large amount of polymer were obtained.

When a benzene solution of phenyl(tribromomethyl)mercury was added to a refluxing solution of 2 equivalent isonitrile in benzene, the yield of IV rose to 4%. The structure of IV was established by the following data.

Found: C, 64.48; H, 4.98; N, 8.15; Br, 22.34%; mol. wt, (mass spectrum) 353. Calcd for $C_{19}H_{17}N_2Br$: C, 64.59; H, 4.82; N, 7.93; Br, 22.66%; mol. wt, 353. IR (KBr): 3240 cm^{-1} (ν_{N-H}). UV λ_{max}^{EtOH}: 282 (log ε: 4.83), 350 (4.22), 385 nm (3.67). NMR (CCl_4): τ 2.05 (s, 1H), 2.4 (s, 1H), 2.6 (s, 1H), 3.0 (s, 1H), 7.0 (s, 3H), 7.45 (s, 3H), 7.55 (s, 3H), 7.6.

Reaction of Cyclohexylisonitrile with Phenyl(tribromomethyl)mercury. A similar reaction was carried out between 0.9 g (8.2 mmol) of cyclohexylisonitrile and 2.19 g (4.1 mmol) of phenyl(tribromomethyl)mercury in benzene 20 ml. After silica gel chromatography, 18 mg (0.7%) of *N*-cyclohexyldibromoacetamide VI, mp 142 °C (from ether) and a large amount of polymer were obtained. Compound VI gave the following analytical and spectral data.

Found: C, 32.22; H, 4.46; N, 5.07%. Calcd for $C_8H_{13}NOBr_2$: C, 32.13; H, 4.38; N, 4.69%. IR (KBr): 3310 (ν_{N-H}), 1670 cm^{-1} ($\nu_{C=O}$).

N*-acetyl Indoloquinoline V.* A solution of 25 mg (0.071 mmol) of IV in 1.5 g of acetic anhydride was heated at 80 °C for 1 hr. The reaction mixture was poured into water, extracted with ether and dried ($MgSO_4$). The solvent was removed and recrystallization from ethanol gave 13 mg (47%) of *N*-acetyl indoroquinoline V, mp 200—202 °C.

Found: C, 64.04; H, 4.73; N, 7.98%. Calcd for $C_{21}H_{19}ON_2Br$: C, 63.80; H, 4.81; N, 7.09%.

Photolysis of Diphenyldiazomethane in the Presence of 2,6-dimethylphenylisonitrile. A equimolar mixture of diphenyldiazomethane 0.74 g and 2,6-dimethylphenylisonitrile 0.5 g in *n*-hexane 30 ml was irradiated with a 500 W high pressure mercury arc lamp at 15 °C in a quartz vessel. After photolysis for 4 hr, the solvent was evaporated at room temperature and the residue was subjected to alumina column chromatography. Elution with *n*-hexane gave *N*-(2,6-xylyl)diphenylketenimine (XIII), mp 61—62 °C, in 7 mg (0.7%) yield. The structure was established by the following data and by melting point determination with the authentic sample prepared by a modification of the Stevens method.[16] Compound XIII showed the characteristic infrared absorption at 2020 cm^{-1} ($\nu_{C=C=N}$).

Found: C, 89.15; H, 6.50; N, 4.97%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%. Further elution with benzene gave a trace amount of purple crystalline 1-(2,6-dimethylphenylimino)-2-(2,6-dimethylanilino)-3-phenylindene (XV), mp 197—198 °C, formed by the reaction of XIII with 2,6-dimethylphenylisonitrile.

Finally *N*-(2,6-xylyl)-diphenylacetamide (XIV), mp 210—211 °C, was obtained in 0.25 g (24%) yield from the eluent with methylenedichloride. The structure of amide XIV corresponding to XIII was identified by comparison with the authentic sample prepared by the following method.

Preparation of Ketenimine: (A) N-(2,6-xylyl)dimethylketenimine(IX) was prepared by a modification of the Stevens method[16], bp 93—95 °C/0.5 mmHg. The characteristic infrared absorption was at 2020 cm^{-1} which was due to the heterocumulated double bond. (B) *N*-(2,6-xylyl)-diphenylketenimine (XIII) was also prepared by the same procedure[16]. Ketenimine XIII showed the mp 62° C (from *n*-hexane) and the characteristic infrared absorption band at 2020 cm^{-1} ($\nu_{C=C=N}$).

Reaction of 2,6-Dimethylphenylisonitrile with N*-(2,6-Xylyl) dimethylketenimine (IX). Indolenine Derivative (X).* A solution of 1.73 g (0.013 mol) of 2,6-dimethylphenylisonitrile and 2.29 g (0.013 mol) of *N*-(2,6-xylyl)dimethylketenimine in dry benzene 20 ml was refluxed for 6 hr. The solvent was removed and the residue was chromatographed on a colunm of alumina. Elution with hexane gave 0.34 g (26%) of X, mp 103 °C (from petroleum ether) and recovered isonitrile 1.18 g.

Found: C, 82.96; H, 7.95; N, 9.23%; mol. wt, 300. Calcd for $C_{21}H_{24}N_2$: C, 82.85; H, 7.95; N, 9.20%; mol. wt, 304. IR (KBr): 1665, 1635, 1625, 1595, 1535 cm^{-1}, UV λ_{max}^{EtOH}: 230 (log ε: 4.24), 299 (3.95), 325 nm (3.90). NMR ($CDCl_3$): τ 3.05 (m, 3H), 3.7—4.6 (m, 3H), 7.65 (d, 6H), 7.85 (d, 6H), 8.05 (s, 3H), 8.9 (s, 3H).

Reaction of 2,6-Dimethylisonitrile with N*-(2,6-Xylyl)diphenylketenimine (XIII). Indonimine Derivative (XV).* A solution of 0.66 g (0.005 mol) of 2,6-dimethylphenylisonitrile and

1.50 g (0.005 mol) of *N*-(2,6-xylyl)diphenylketenimine in dry benzene 20 ml was refluxed for 3 hr. After the solvent was removed by evaporation, a precipitated purple solid was obtained. Recrystallization from hexane-methylenechloride resulted in 1.59 g (73%) of indone imine XV, mp 197—198 °C.

Found: C, 86.60; H, 6.69; N, 6.60%; mol. wt, 420. Calcd for $C_{31}H_{28}N_2$: C, 86.88; H, 6.59%; mol. wt, 429. IR (KBr): 3300 (ν_{NH}), 1655 ($\nu_{C=N}$), 1620 cm^{-1} ($\nu_{C=C}$). UV λ_{max}^{EtOH}: 272 nm (log ε: 4.61). NMR(CCl_4): τ 3.0—4.0 (m, 16H), 7.85 (s, 12H).

Hydrolysis of Indonimine XV. A solution of 0.3 g of XV in 0.3% HCl-THF (20 ml) was refluxed for 3 hr. The reaction mixture was extracted by methylenechloride. After removal of the solvent, the residue was subjected to alumina column chromatography. Elution with benzene gave 2-(2,6-dimethylanilino)-3-phenylindone XVI, mp 133—134 °C (*from petroleum ether*).

Found: C, 83.88; H, 6.07; N, 4.90%. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.17; N, 4.47%. IR (KBr): 3340 (ν_{N-H}), 1717 cm^{-1} ($\nu_{C=O}$). UV λ_{max}^{EtOH}: 269 (log ε: 4.36), 320 sh (3.44), 560 nm (2.80). NMR(CCl_4): τ 2.5—4.7 (m, 14H), 7.95 (s, 6H).

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