13 cm long and 6 cm wide of activated silicic acid (Merck). The column was eluted with chloroform (400 ml), chloroform–ether (1:1) (600 ml), ether (400 ml), and ether–acetone (1:1) (400 ml). The chloroform–ether fraction contained the largest amount of material (2.7 g) which had the component V of R_f 0.54. This fraction was rechromatographed on 70 g of silicic acid (Mallinkrodt) with ethyl acetate as the elution solvent and 25-ml fractions were collected. Fractions 4–6 contained the desired substance. They were combined, the solvent was evaporated, and the product was crystallized to give another 0.60 g of V, total yield 22%.

A small sample of V was deacylated with methanolic sodium methoxide in the usual manner. The product obtained was identical in every respect with I.

Registry No.—I, 13673-75-1; II, 13673-76-2; IV, 13673-77-3; V, 13673-78-4.

Pseudo-Halogens. IX.[1] Reaction of Iodine Isocyanate with Dienes and Acetylenes

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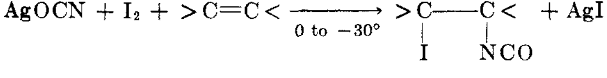
The reaction of iodine isocyanate (INCO) with monoolefinic compounds has received considerable attention in our laboratory[4] and elsewhere.[5] The addition products are useful intermediates in the preparation of carbamates, aziridines, ureas, 2-oxazolidones, and β-iodoamines.

Strikingly absent from the literature, however, are detailed reports on the reaction of INCO with dienes, acetylenes, and allenes. The recently published paper of Hassner, Lorber, and Heathcock,[5c] in which brief mention was made of the reaction of INCO with di- and triolefins and acetylenes, prompts us to report our results with conjugated and nonconjugated aliphatic and alicyclic dienes, acetylenes, and methylallene. Our work has dealt mainly with the relationship between the structure of dienes or acetylenes and moles of INCO consumed, although we have also studied experimental techniques and product isolation.

Typically, INCO additions (eq 1) are conducted in a stirred heterogeneous system containing the monounsaturated compound, iodine, and silver cyanate in ether at low temperatures (0 to −30°). INCO is consumed as it is generated (*in situ* method). In the initial studies with acetylenes, the *in situ* method was found to be unsatisfactory; diiodo compounds formed preferentially thus removing both the acetylene and iodine from the reaction system and also contaminated the desired addition products. In all of the work to be described in this Note, therefore, preformed solutions of INCO of known concentration were prepared in tetrahydrofuran (THF) at −30 to −50° by our published procedure[4b] and these solutions were employed for the addition reactions. Such solutions were not entirely free of iodine, however, as about 5% of it could not be converted to INCO. This probably caused some complications and may account, in part, for the difficulty experienced in obtaining analytically pure derivatives (see Experimental Section). The stoichiometric quantity of INCO was used, that is, 2 moles for each mole of diene, methylallene, or acetylenic compound.



$$\mathrm{AgOCN} + \mathrm{I_2} + {>}\mathrm{C{=}C}{<} \xrightarrow[0\ \text{to}\ -30^\circ]{\mathrm{Et_2O}} {>}\underset{\mathrm{I}}{\mathrm{C}}\!-\!\!-\!\underset{\mathrm{NCO}}{\mathrm{C}}{<} + \mathrm{AgI} \quad (1)$$

Disappearance of INCO was followed iodometrically[4b] and in all cases attempts were made to isolate and characterize the primary reaction products or convert them to carbamates, ureas, or amine hydrochlorides by reaction with methanol, ammonia, or 17% hydrochloric acid, respectively, at or below room temperature. Except in the few cases described in the Experimental Section, well-characterized products with correct elemental analyses could not be obtained, although infrared and nuclear magnetic resonance spectra suggested that INCO addition had occurred in a predictable way. Products obtained were usually high in iodine content suggesting that iodine addition was the main competing reaction.

Addition of INCO to Aliphatic Dienes with Isolated Double Bonds.—Dienes with at least one $-CH_2-$ group between the double bonds are included in this category. Table I summarizes the results. The most noteworthy feature is the high rate even at −28 to −45°. In every case, over 90% of the INCO was consumed between the time the diene was added to the stirred INCO solution in THF and removal of the first analytical sample (15 min or less). The times listed in the table are those at which INCO consumption had ceased for all practical purposes. The high reaction rate precluded a detailed kinetic study.

TABLE I
ADDITION OF INCO TO ALIPHATIC DIENES WITH ISOLATED DOUBLE BONDS[a]

Diene	Reacn temp, °C	Reacn time, min	Moles of INCO consumed per mole of diene
1,4-Pentadiene	−35	15	1.74
1,5-Hexadiene	−28	45	1.82
2,5-Dimethyl-1,5-hexadiene	−45	15	1.60
1,7-Octadiene	−45	30	1.80
4-Vinylcyclohexene	−38	60	1.58

[a] 0.1 mole of INCO/0.05 mole of diene in THF.

As anticipated, all the listed dienes had the stoichiometry of approximately 2 moles of INCO reacting with 1 mole of diene. An excess of INCO was not employed in any of the experiments. The adducts obtained after evaporation of the THF had the expected characteristic band of organic isocyanates in the infrared spectrum (~2280 cm^{-1}). On treatment of the adducts with methanol at room temperature, the band disappeared and was replaced by bands at 3310 (>NH), 1720 (>C=O), and 1550 (amide-II) cm^{-1}, typical of carbamates.

In only one case, from 2,5-dimethyl-1,5-hexadiene,

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[1] Pseudo-Halogens. VIII: T. A. Foglia and D. Swern, *J. Org. Chem.*, **32**, 75 (1967).

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[4] (a) C. G. Gebelein and D. Swern, *Chem. Ind.* (London), 1462, 1965. (b) S. Rosen and D. Swern, *Anal. Chem.*, **38**, 1392 (1966). (c) C. G. Gebelein, Ph.D. Thesis, and S. Rosen, M.A. Thesis, Temple University, February 1967.

[5] (a) L. Birckenbach and M. Linhard, *Ber.*, **63**, 2544 (1930); *ibid.*, **64**, 961, 1076 (1931). (b) G. Drefahl and K. Ponsold, *Chem. Ber.*, **93**, 519 (1960). G. Drefahl, K. Ponsold, and G. Köllner, *J. Prakt. Chem.*, **23**, 136 (1964). (c) A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967), and references contained therein to earlier work of this group.

could a crystalline iodocarbamate, mp 188–189° (60% yield), be isolated.

Addition of INCO to Aliphatic Conjugated Dienes.—Table II summarizes the results. Both dienes reacted rapidly at −35 to −40° and consumed exactly 1 mole of INCO within 15 min; no further consumption was noted for an additional 30 min. The iodoisocyanate adducts (oils) showed an infrared band at 2290 cm^{-1} which disappeared when the adducts were treated with methanol, to be replaced by the expected carbamate bands at 3310, 1720, and 1540 cm^{-1}. The primary addition reaction goes in the 1,4 manner; infrared spectra of the adducts show no evidence of a terminal double bond or of a cyclopropane ring that might have formed by π-participation of the remaining double bond with the intermediate, initially formed iodonium-(carbonium) ion.

TABLE II
ADDITION OF INCO TO ALIPHATIC CONJUGATED DIENES[a]

Diene	Reacn temp, °C	Reacn time, min	Moles of INCO consumed per mole of diene
2,3-Dimethyl-1,3-butadiene	−40	15	0.98
2,4-Hexadiene	−35	15	1.00

[a] 0.1 mole of INCO/0.05 mole of diene in THF.

Crystalline derivatives were not obtained on treating the adducts with methanol, ammonia, or 17% hydrochloric acid.

Addition of INCO to Methylallene.—Only one pure allene was available for study. Methylallene consumed exactly 1 mole of INCO in 50 to 60 min at −40°, a rate lower than that for conjugated dienes. No further consumption of INCO was noted for an additional 2 hr. The adduct showed a strong band at 2290 cm^{-1}. It was not studied further.

Addition of INCO to Alicyclic Dienes.—Table III summarizes the results. With the exception of 1,3-cyclooctadiene, alicyclic dienes also reacted extremely rapidly; over 90% reaction occurred in less than 15 min at −35 to −50°. 1,3-Cyclooctadiene, a conjugated diene, consumed only 1 mole of INCO, as expected, but the reaction was considerably slower than that with 1,3-cyclohexadiene or the conjugated aliphatic dienes listed in Table II, all of which also consumed exactly 1 mole of INCO. The iodoisocyanate adducts from 1,3-cyclooctadiene and 1,3-cyclohexadiene were pale yellow oils that had the characteristic infrared spectra of organic isocyanates, but they could not be converted to crystalline derivatives.

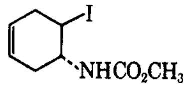
TABLE III
ADDITION OF INCO TO ALICYCLIC DIENES[a]

Diene	Reacn temp, °C	Reacn time, min	Moles of INCO consumed per mole of diene
1,3-Cyclohexadiene	−47	15	1.00
1,4-Cyclohexadiene	−45	15	1.00
1,3-Cyclooctadiene	−47	2.2 hr[b]	0.99
1,5-Cyclooctadiene	−50	30	1.77
Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)	−34	15	1.00

[a] 0.1 mole of INCO/0.05 mole of diene in THF. [b] 50% consumption of INCO in 15 min; 65% consumption in 30 min.

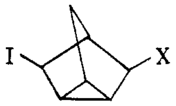
1,5-Cyclooctadiene (isolated double bonds) reacted with almost 2 moles of INCO at a normal rate. The carbamate derivative was a liquid with the expected infrared spectrum; it was not studied further.

Surprisingly, 1,4-cyclohexadiene consumed only 1 mole of INCO. Since 1,4-pentadiene consumed almost 2 moles of INCO (Table I) it was expected that 1,4-cyclohexadiene would behave similarly. The addition product, a pale-yellow oil with an infrared spectrum characteristic of an organic isocyanate (λ_{max} 2290 cm^{-1}) could be converted to a crystalline iodocarbamate I, mp 100–101°, on treatment with methanol. On the basis of its elemental analysis and infrared and nmr spectra, its structure is shown below as the 1,2-addition product, a structure previously proposed by Hassner and co-workers.[5c]



I

Norbornadiene also consumed only 1 mole of INCO. The initial adduct (λ_{max} 2290 cm^{-1}) was converted to the carbamate by reaction with methanol at room temperature. The carbamate was a noncrystallizable, colorless oil. The nmr and infrared spectra of the iodoisocyanate and corresponding carbamate suggested the tricyclene structure II (λ_{max} 820 cm^{-1}).



II (X = NCO or $NHCO_2CH_3$)

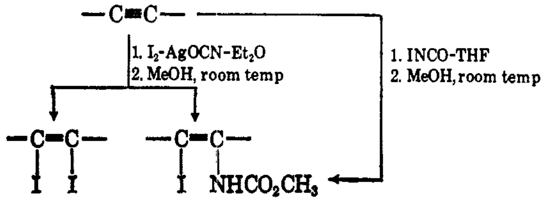
Addition of INCO to Acetylenes.—Table IV summarizes the results. With the exception of stearolic acid, the other acetylenes consumed exactly 1 mole of INCO at −30° in a rapid reaction. The resulting vinylic iodoisocyanates were oils with characteristic absorption at 2290 cm^{-1}. The failure of stearolic acid to react with INCO is not understood. Its olefinic analog, oleic acid, reacts rapidly and completely.

TABLE IV
ADDITION OF INCO TO ACETYLENES[a]

Acetylene	Moles of INCO consumed per mole of acetylene
Phenylacetylene	1
Tolan	1
4-Octyne	1
2-Octyne	1
Stearolic acid	~0

[a] 0.1 mole of INCO/0.05 mole of acetylene in THF at −30°.

With INCO generated *in situ* from iodine and silver cyanate in diethyl ether, acetylenes yield mixtures of vinylic diiodides and iodoisocyanates in the range of 3:1 to 10:1. After conversion of the iodoisocyanates to carbamates, the mixtures could be separated moderately well by chromatography on alumina. The less polar diiodides were eluted with petroleum ether, whereas the iodocarbamates required diethyl ether. When preformed INCO in THF was used, however, vinylic iodoisocyanates (isolated as the carbamates) were the major products (in about 20–40% yields). The only crystalline vinylic iodocarbamate obtained



in analytical purity was from 4-octyne. The product, methyl N-(2-iodo-1-propyl-1-pentenyl)carbamate, mp 72–73°, was obtained in 20% yield.

Experimental Section

Materials Used.—The dienes, acetylenes, and methylallene were the purest grades that could be purchased; they were >98% pure as shown by glpc using the appropriate column packings. Stearolic acid was prepared from oleic acid by bromination and dehydrohalogenation.[6] Iodine was the triply sublimed grade. Silver cyanate was prepared from silver nitrate and potassium cyanate.[4b] Solvents were the purest grades; they were carefully dried just before use.

Instrumentation.—An F & M 500 gas chromatograph or Varian Aerograph was employed to check the purity of starting materials. Infrared spectra were obtained with a Perkin-Elmer Infracord. Nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

Addition Procedures. A. Preformed Solutions of INCO.—To a stirred suspension of silver cyanate (20 g; 0.133 mole) in THF (400 ml) between −30 and −50°, iodine (25.4 g; 0.1 mole) was added in one portion. The mixture was stirred for 90 min after which time the color of the solution had changed from brown to orange. Titration of an aliquot of this solution[4b] indicated approximately 95% conversion of iodine to INCO. The diene, allene, or acetylene (0.05 mole) was then added in one portion. In all cases, a temperature rise was observed. The rate of consumption of INCO was followed by frequent titration. Results of these experiments are summarized in Tables I–IV.

In those cases in which only 1 mole of INCO was consumed per mole of unsaturated compound, the excess INCO was destroyed by adding an additional quantity (0.05 mole) of the unsaturated compound. In this way the problem of impurities arising from decomposition of excess INCO during the work-up at room temperature was avoided.

The reaction solution was filtered and the filter cake of inorganic salts was washed with THF. The combined filtrate and washings were evaporated in a rotary vacuum evaporator (bath temperature not above 40°). The residual iodoisocyanate was then stirred with methanol for 30–60 min, depending on structure of adduct, until the isocyanate function (λ_{max} 2280–2290 cm^{-1}) had been converted to the carbamate (λ_{max} 3310, 1720, and 1550 cm^{-1}). The methanol solution was poured into water and the aqueous system was extracted several times with ether. The ether extracts were washed with water and dried over anhydrous magnesium sulfate, and the ether was evaporated. The crude carbamate was recrystallized from acetone or methanol or purified by chromatography on alumina (Fischer, neutral grade), and elution with ether.

In only three cases were crystalline iodocarbamates of reasonably good purity obtained. 2,5-Dimethyl-1,5-hexadiene consumed 2 moles of INCO and yielded a white crystalline solid diiododicarbamate, mp 188–189° (60% yield).

Anal. Calcd for $C_{12}H_{22}O_4N_2I_2$: C, 28.15; H, 4.33; N, 5.47. Found: C, 29.07; H, 4.44; N, 5.23.

(Difficulty was experienced in obtaining concordant iodine analyses.)

1,4-Cyclohexadiene consumed 1 mole of INCO and yielded a white crystalline solid monoiodocarbamate (I), mp 100–101° (lit.[5c] 93–95°).

Anal. Calcd for $C_8H_{12}O_2NI$: C, 34.38; H, 4.47; N, 4.96; I, 44.98. Found: C, 34.68; H, 4.25; N, 4.40; I, 43.46.

4-Octyne consumed 1 mole of INCO. The adduct was converted to methyl N-(2-iodo-1-propyl-1-pentenyl)carbamate, a white solid, mp 72–73°, isolated in about 20% yield after chromatography of the crude iodocarbamate on alumina followed by elution first with petroleum ether to remove contaminating diiodides, and then with diethyl ether.

Anal. Calcd for $C_{10}H_{18}O_2NI$: C, 38.59; H, 5.83; N, 4.50; I, 40.78. Found: C, 39.15; H, 5.63; N, 4.71; I, 40.65.

B. *In Situ* Generated INCO.—To a vigorously stirred slurry of silver cyanate (20 g; 0.133 mole) in dry ether (300 ml) at −20°, there was added in rapid succession iodine (25.4 g; 0.10 mole) and then the unsaturated compound (0.05 mole). Stirring was continued until the brown color of the solution had changed to canary yellow. This required several hours to overnight at −20°. The remainder of the procedure was the same as in A above.

Procedure B was examined only with acetylenes. Diiodides were major products with 1-,2- and 4-octyne and phenylacetylene, the only compounds studied by this method. They could be separated from the expected addition products by tedious chromatography over alumina. Since the addition reaction by this procedure was not only slow but yielded diiodo adducts mainly, it was abandoned and not used with any of the other unsaturated compounds.

Registry No.—Iodine isocyanate, 3607-48-5; 1,4-pentadiene, 591-93-5; 1,5-hexadiene, 592-42-7; 2,5-dimethyl-1,5-hexadiene, 627-58-7; 1,7-octadiene, 3710-30-3; 4-vinylcyclohexane, 100-40-3; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2,4-hexadiene, 592-46-1; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; bicyclo[2.2.1]-hepta-2.5-diene, 121-46-0; phenylacetylene, 536-74-3; tolan, 501-65-5; 4-octyne, 1942-45-6; 2-octyne, 2809-67-8; stearolic acid, 506-24-1; diiododicarbamate, 13815-78-6; methyl N(2-iodo-1-propyl-1-pentenyl)carbamade, 13815-79-7.

Acknowledgment.—The authors acknowledge with thanks support of this investigation by U.S. Public Health Service Research Grants No. CA-07803 and CA-07174 from the National Cancer Institute.

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[6] N. A. Khan, F. E. Deatherage, and J. B. Brown, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 851.

Toluene Chlorination in Mixtures of Tetramethylene Sulfone and Acetonitrile or Nitromethane

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It has been reported previously[1] that the rates of chlorination of aromatic substances in acetonitrile–nitromethane mixtures increase appreciably as the nitromethane content of the solvent is increased. The rates of addition of chlorine to an unsaturated substance in such media are much less sensitive to the change in solvent composition. Both the substitution and addition reactions are presumed to proceed by way of polar activated complexes of the type SX^+X^- where S is the organic reactant and X_2 is the halogen. In explaining the differences in sensitivity to solvent composition in these two processes, it has been suggested that an electrophilic or acceptorlike solvating agent, in this case nitromethane, contributes more substantially to stabilization of the activated complex for the substitution reaction than does acetonitrile.

Presumably the charge in the electropositive portion of the polar activated complex for the aromatic sub-

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[1] R. M. Keefer and L. J. Andrews. *J. Am. Chem. Soc.*, **84**, 3335 (1962).