Coleman and Bell Chromatoquality acetonitrile were measured using the single photon counting technique.[40] Excitation was by an N_2 spark lamp filtered through a Corning 7-54 glass filter, while a Jarrel-Ash 0.25-m monochromator was used to isolate the acetone fluorescence. Details of the single photon-counting apparatus used are given elsewhere.[41]

Acknowledgment. The authors wish to thank Dr. Louis Brus and Terrence Tao for making the acetone fluorescence lifetime determinations.

(40) For a discussion of this technique see J. B. Birks and I. H. Munro, *Progr. Reaction Kinetics*, 4, 239 (1967).

(41) T. Tao, *Biopolymers*, in press.

Electronic *vs.* Steric Effects in the Addition of Iodine Isocyanate to Olefins[1]

Alfred Hassner, Richard P. Hoblitt, Clayton Heathcock, James E. Kropp, and Milton Lorber

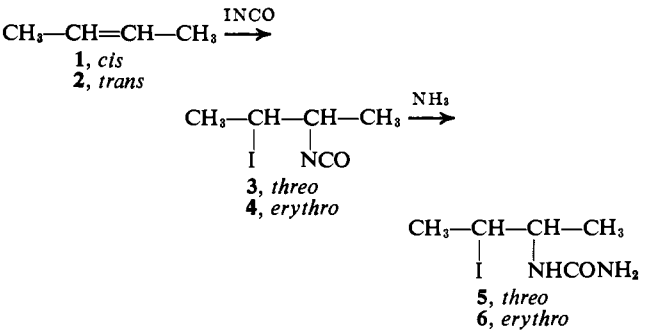
Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado. *Received July 22, 1969*

Abstract: The reaction of INCO with a number of olefins has been studied with a view toward elucidating electronic and steric influences in the addition. The stereospecific addition of INCO to *cis*- and *trans*-2-butene and β-deuteriostyrene is consistent with the intermediacy of a three-membered iodonium ion. A definite dependency on steric factors is evidenced by the I-*t*-Bu regiospecificity in the INCO addition to *t*-butylethylene. The structure proof in these systems was facilitated by our finding that hydrogenolysis of the iodo function in iodo carbamates is possible. Except in diaxial iodo carbamates for which zinc treatment leads to olefin by elimination, this method serves for the introduction of a carbamate function starting with olefins. Although no methyl migration or neighboring hydroxyl participation was observed during INCO addition, examples of skeleton rearrangement have been found.

The addition of the pseudohalogens iodine isocyanate (INCO) and iodine azide to unsaturated systems as been extensively studied in our laboratory in recent years.[2,3] The reactions of INCO have proved of preparative value leading to the stereospecific synthesis of *trans*-N-(2-iodoalkyl) carbamates,[3] aziridines,[4] oxazolidones,[3] *cis*- and *trans*-2-amino alcohols,[3] 1,2-diamines,[5] and azepines.[6] It has been demonstrated that these additions in cyclic olefins generally occur in a stereospecific manner and that the two functional groups are introduced *trans* to each other and diaxially in fused cyclohexanes. These results have been explained by the formation of a three-membered ring iodonium ion intermediate which was opened from the backside by isocyanate (or azide) ion.

Stereoselectivity in INCO Additions

Consistent with these interpretations are our current findings that the open chain *cis*- and *trans*-2-butenes give cleanly and in almost quantitative yield *threo*- and *erythro*-iodo isocyanate adducts, respectively. This was apparent from the distinctive ir and nmr spectra of iodo isocyanates **3** and **4**.



The major difference in the nmr spectra of these diastereomers is the relative shielding of the proton geminal to isocyanate in **3** relative to **4**. This average shielding is attributable to the anisotropic effect of the iodine atom in preferred conformation **3a** (I *anti* to H) *vs.* **4a** (I *gauche* to H). *erythro* isomer **4** is assigned the *gauche* conformation **4a** rather than an *anti* conformation as previously described,[1c] because of the low H–H coupling (J = 3.5 Hz) characteristic of *gauche* protons. The isocyanates **3** and **4** were converted with ammonia to solid urea derivatives **5** and **6**.

It has been shown that addition of INCO to disubstituted terminal olefins proceeds in an I–H regiospecific[7] manner leading to tertiary isocyanates.[3] While monoalkyl olefins, such as 1-hexene, lead to a mixture of regioisomeric adducts, unsymmetrical arenes give exclusively the *NCO–phenyl* regiospecific adduct, suggesting involvement of a benzyl carbonium ion **8**. If such an ion were free to rotate (**8a** ⇆ **8b**) *trans* addition would not be observed. To test this possibility and to

(1) (a) Stereochemistry. XLV. For paper XLIV see A. Hassner and F. Boerwinkle, *Tetrahedron Lett.*, 3309 (1969); (b) presented in part before the Gordon Research Conference on Organic Reactions and Processes, New Hampton, N. H., July 1965; (c) a preliminary report of part of this study has appeared in *Tetrahedron Lett.*, 1125 (1964).

(2) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 89, 2077 (1967).

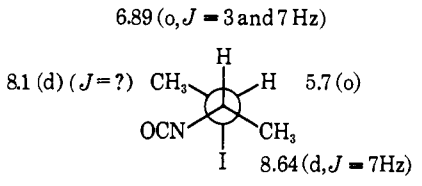
(3) A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, 32, 540 (1967), and references cited.

(4) A. Hassner and C. Heathcock, *Tetrahedron*, 1037 (1964).

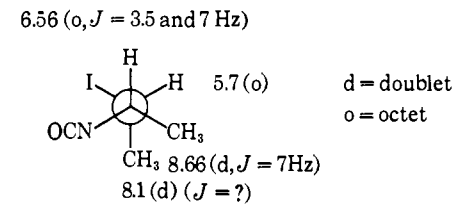
(5) G. Swift and D. Swern, *J. Org. Chem.*, 32, 511 (1967).

(6) L. A. Paquette and D. E. Khula, *Tetrahedron Lett.*, 4517 (1967).

(7) Regio is used to describe directive effects in bond making or breaking; A. Hassner, *J. Org. Chem.*, 33, 2684 (1968).

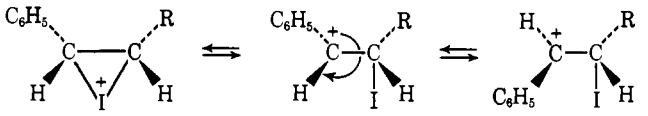


3a, *threo*



4a, *erythro*

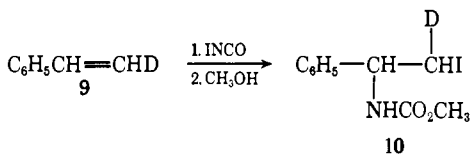
minimize steric inhibition to free rotation in carbonium ion **8** during INCO addition, β-deuteriostyrene was chosen as a substrate.

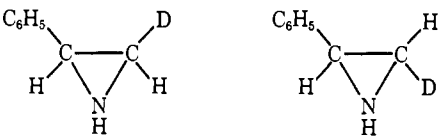


7 **8a** **8b**

The olefin, prepared by deuteration of phenylacetylene followed by hydrogenation with a Lindlar catalyst, proved to be a mixture of 71% *cis*- and 29% *trans*-β-deuteriostyrene (**9**) as established by nmr spectra. The *cis* isomer showed β-proton absorption centered at τ 4.74 as a doublet (J = 11 Hz) while the corresponding proton in the *trans* isomer absorbed at τ 4.23 with a coupling constant of 18 Hz.

INCO was added to this stereoisomeric mixture (**9**) at 25° and the adduct was directly converted to the iodocarbamate in 93% over-all yield. Ring closure of **10** with base gave in 98% yield a mixture of *cis*- and *trans*-3-deuterio-2-phenylaziridine (**11a** and **11b**) and



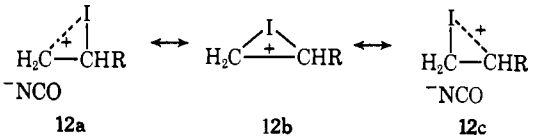


11a **11b**

acetophenone (14%). Integration of the nmr spectrum of the phenylaziridine, after exchange of the N-hydrogen with deuterium oxide, indicated the isomer distribution to be 71% *cis* (**11a**) and 29% *trans* (**11b**). Since ring closure of diastereomeric 2-halo amines to aziridines is known to proceed stereospecifically *trans*,[8] it follows that INCO addition had taken place in the same manner and equilibration of **7** to a freely rotating carbonium ion **8** is excluded.

Since in weakly dissociating solvents tight ion pairs are likely to play an important role, the addition can be interpreted as proceeding *via* an ion pair intermediate[9]

(8) A. Weissberger and H. Bach, *Ber.*, **64**, 1095 (1931).



12a **12b** **12c**

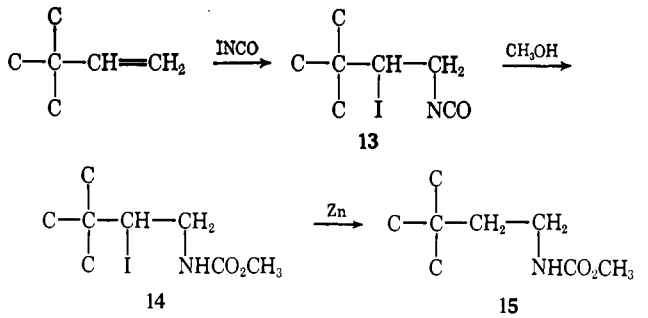
for which structure **12c** is a major contributor when R is able to stabilize a positive center (*i.e.*, in arenes and geminally disubstituted olefins). This means that the transition state for attack of NCO^- at the benzylic carbon is lower than at the terminal carbon in **12**, due to the ability of the phenyl group to stabilize an incipient positive charge.

Regioselectivity[7]

The addition of INCO to styrene is not only stereospecific (*trans*) but also regiospecific (*NCO–phenyl*). One can visualize cases in which the nature of the R group in **12b** would influence the regiochemistry of INCO additions in a different sense. In fact, 1-hexene reacts with INCO to give a 70:30 mixture of secondary–primary isocyanate. Although this contrasts the IN_3 addition to 1-hexene which gives exclusively the secondary azide,[2] it should be kept in mind that IN_3 additions are carried out in CH_3CN whereas INCO is added in ether. Our results show some similarity with the opening of episulfonium ion intermediates. Thus in the addition of RSCl to monosubstituted olefins phenyl substituents cause electronically controlled opening of the three-membered ring at the benzylic position, whereas alkyl substituents show an opposite regioselectivity which is sensitive to the size of the alkyl group.[10]

The problem of determining the ratio of regioisomeric INCO adducts was resolved by the finding that hydrogenolysis of the iodo function in β-iodo carbamates can be accomplished smoothly with zinc (see below). The resulting carbamates, unlike the iodo carbamates, were separable by glpc and/or identifiable by nmr.

t-Butylethylene reacted with INCO readily to yield (3,3-dimethyl-2-iodo)butyl isocyanate (**13**) as the exclusive product. The nmr spectrum of **13** showed the iodo methine proton absorption at τ 5.88 (triplet, J = 6 Hz) and the isocyanato methylene protons at τ 6.43 (doublet, J = 6 Hz). The iodo isocyanate was readily converted to the corresponding iodocarbamate **14** whose nmr spectrum (in DMSO) showed the iodomethine proton at τ 5.82 (quartet, J = 3 and 10 Hz), and the carbamate methylene protons at τ 6.7 (sextet). Treatment of **14** with zinc in acetic acid gave rise to carbamate **15** in



13 **14** **15**

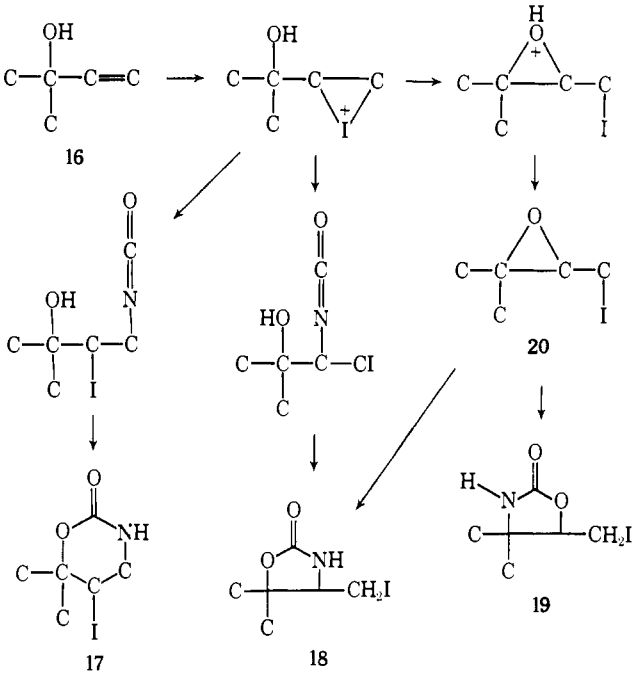
(9) INCO addition in ether as well as ICl additions are presumably first order in pseudohalogen and first order in olefin and exhibit behavior typical of ionic electrophilic additions: C. Gebelein and D. Swern, *Chem. Ind.*, 1462 (1965).

(10) W. H. Mueller and P. E. Butler, *ibid.*, **90**, 2075 (1968).

which the carbamate methylene protons appeared as a multiplet at τ 6.80 and the other methylene group at τ 8.6.

These results are noteworthy in light of the fact that the addition of hydrogen chloride to *t*-butylethylene gave 60–65% of the rearranged chloride, 2-chloro-2,3-dimethylbutane.[11a] On the other hand, Newman and Puterbaugh[11b] have shown that the addition of bromine in methanol to *t*-butylethylene produced unrearranged dibromide and 2-bromo-1-methoxy-3,3-dimethylbutane. IN_3 as well as RSCl additions showed similar sterically influenced regiospecificity.[2,10]

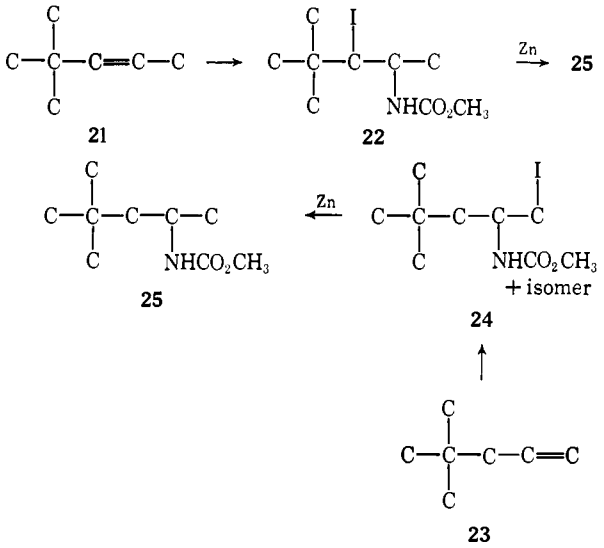
A related system, 3-hydroxy-3-methylbutene **16**, also adds INCO readily to yield the product **17** resulting from NCO–H regiospecific addition with no detectable epoxide (**20**) formation.



The infrared spectrum of the product shows a typical carbamate spectrum with the carbonyl absorption at 1690 cm^{-1} consistent with **17** but inconsistent with **18** or **19**, since oxazolidones absorb at 1740 cm^{-1}.[3] The nmr spectrum of **17** has signals at τ 5.78 (quartet) integrating for one proton and at τ 6.30 (complex quintet) integrating for two protons. In both five-membered ring carbamates the methine proton should appear as a broadened triplet while the methylene protons appear as a doublet. In the six-membered ring carbamate the methine proton would be expected to be a quartet and the methylene proton a broadened quartet of an ABX system.

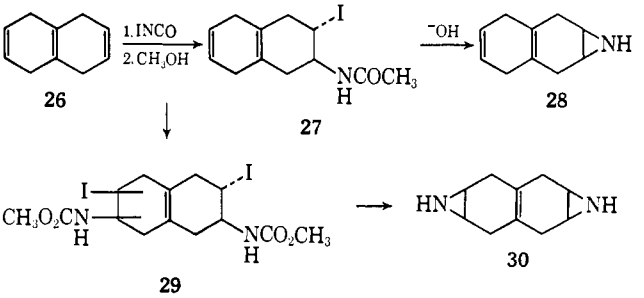
These results show clearly that the addition of iodine isocyanate can be influenced greatly by steric factors and that no free carbonium ion is formed in these systems which would lead to skeletal rearrangements or hydroxy participation.

Another interesting system where steric *vs.* electronic effects can be tested involves *t*-butylmethylethylene (**21**) and neopentylethylene (**23**). INCO addition to **21** gave exclusively **22**, again indicating the steric influence of the



t-butyl group. When INCO was added to 3-methyl-1-butene a mixture of products resulted which points out the considerably smaller size of the isopropyl group. When the *t*-butyl group was further removed as in **23**, no steric effect was observed, the major product being **24**. Zinc reduction of **22** or **24** afforded the same carbamate **25**.

Further evidence of the importance of steric as opposed to electronic factors in INCO additions comes from the reaction of isotetralin **26**. The less substituted double bond in **26** reacted preferentially leading to



27 and thence to **28**. If only inductive influences were operating, INCO would have been expected to add to the more highly substituted olefinic linkage as is the case in NOCl addition to **26**.[12] Integration of the vinyl protons (two) in the nmr spectrum of the product makes the assignment of **27** unambiguous. A diaddition product **29** was also obtained and converted to the diaziridine **30**.

Rearrangements

Since the addition of iodine isocyanate has all the markings of an electrophilic addition it was of interest to investigate the reaction of INCO with olefins which are known to undergo rearrangements upon the addition of electrophilic reagents.

The addition to norbornene, α-pinene, and norbornadiene yielded complex mixtures as shown by glpc and nmr and no pure products could be obtained. 5-Methylenenorbornene-2 (**31**) reacted extremely rapidly. Conversion of the adduct to a carbamate and zinc reduction gave an oil of which the major component was separable by preparative glpc and identified as **33**.

(11) (a) G. G. Ecke, N. C. Cook, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 72, 1511 (1950); (b) W. H. Puterbaugh and M. S. Newman, *ibid.*, 79, 3469 (1957).

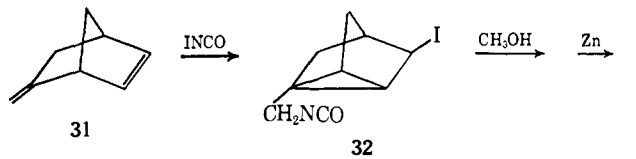
(12) E. Vogel, M. Bishup, W. Pretzes, and W. A. Boll, *Angew. Chem.*, 76, 785 (1964).

Table I. Hydrogenolysis of Iodo Carbamates to Carbamates

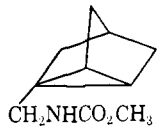
Olefin[a]	Zinc hydrogenolysis products[b]	Reaction time,[c] hr	Yield,[d] %
Styrene	C_6H_5—CH(A)—CH_3	18	80[f]
1-Hexene	*n*-Bu-CH_2CH_2-A 30%; *n*-Bu-CH(A)-CH_3 70%	5	50[e]
1-Phenylpropene	C_6H_5—CH(A)—CH_2CH_3	18	90[f]
2,5-Dimethyl-3-hexene	*i*-Pr-CH_2—CH(A)-*i*Pr	18	85
3,3-Dimethyl-1-butene	*t*-Bu-CH_2—CH_2-A (**15**)	5	95
4,4-Dimethyl-1-pentene (**23**)	*t*-Bu-CH_2—CH(A)—CH_3 80%; *t*-Bu-$CH_2CH_2CH_2$-A 20% (A **25**)	5	33
4,4-Dimethyl-2-pentene (**21**)	*t*-Bu-CH_2—CH(A)—CH_3 100% (A **25**)	5	68
Cyclohexene	Cyclohexyl-A	18	85
Methylenecyclohexane (**39**)	**42** 55%; **43** 45%	2	70
5-Methylene-2-norbornene (**31**)	**33**	15 min	*ca.* 50

[a] From which iodocarbamate was derived by INCO addition followed by treatment with methanol. [b] A = $NHCO_2CH_3$. [c] For Zn reduction. [d] Total yield of products based on iodocarbamate unless shown under *e*. [e] Total yield based on olefin. [f] Identified by nmr only.

Crude **32** showed two downfield absorptions at τ 6.1 and 6.3 which integrated for one and two protons, respectively, while olefinic protons were absent.

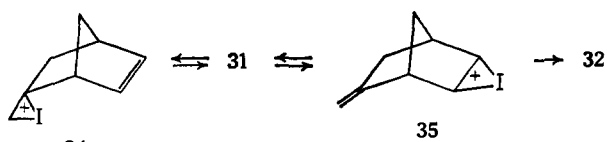


31 32



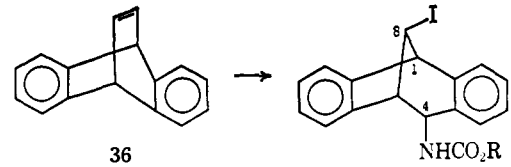
33

The assignment of structure **33** is based on its nmr spectrum in which olefinic protons were absent, methylene protons appeared as a broad singlet at τ 6.6, sharpening on addition of D_2O, and the cyclopropane protons absorbed at τ 8.95. The major mode of INCO addition to **31** is noteworthy in view of the reported[13] preferential protonation of the exocyclic double bond in **31**, still leading to nortricyclyl derivatives. The reaction may involve the formation of both iodonium ions **34** and **35** in equilibrium with **31**, with preferential formation of **32** from **35**.



34 35

Another system that is known to rearrange[14] when treated with ionic electrophilic reagents is ethenoanthracene **36**.



36

37a, R = CH_3
37b, R = *t*-Bu

INCO added fairly readily to this system and work-up of the resulting iodo isocyanate with methanol and lithium methoxide yielded **37a** as a stable white solid. Its nmr spectrum is consistent with the rearranged skeleton and is interpreted as follows.[14] The doublet at τ 5.96 is due to H-1 which is coupled with H-8 (J = 4 Hz). Hydrogen-5 appears as a distinct shoulder of the methoxide singlet at τ 6.4 but should be a quartet split by H-4 and H-8. Hydrogens-4 and -8 are superimposed on one another at τ 5.2; H-4 appearing as a doublet and H-8 as a superimposed triplet, J = 4.3 Hz in each case.

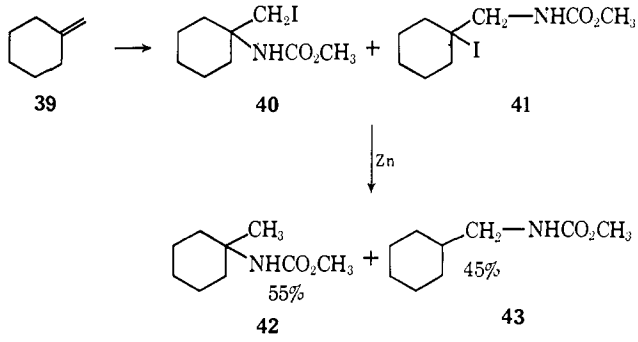
Zinc Reduction of β-Iodo Carbamates

Since the addition of INCO to olefins allows the introduction of carbamate and iodo functions, hydrogenolysis of the latter would provide a regioselective synthesis of carbamates. For instance the zinc reduction of **14** to **15** proceeded in 95% yield. A few examples are provided in Table I to indicate the generality of this reduction. The diaxial N-carbomethoxy-2β-amine-3α-iodocholestane, presumably for stereoelectronic reasons, gave olefin as the only detectable prod-

(13) P. von Schleyer and R. E. O'Connor, Abstracts, 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1958, p 39 P.

(14) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, 30, 1956 (1965).

uct on zinc reduction. The diequatorial methyl *trans*-N-(2-iodocyclohexyl)carbamate (**38**) as well as the acyclic iodocarbamates led in good yield to hydrogenolysis of the iodo function. The method is particularly valuable in establishing the regioselectivity of INCO additions. Thus, methylenecyclohexane (**39**) which was believed[3] to add INCO regiospecifically to afford **40** was shown by the nmr spectrum of the crude zinc reduction product (**42** + **43**) to lead to a mixture in which **40** predominates but is not the sole product.



39 40 41 42 43

Experimental Section[15]

threo-**3-Iodo-2-butyl Isocyanate (3).** *cis*-2-Butene (23 g), was added to a slurry containing 50 g of silver cyanate in 300 ml of ether at −15°. The mixture was stirred vigorously while 60 g of iodine was added. Stirring was continued for 2.5 hr while the ice bath melted. The flask was warmed to 20° and after stirring for an additional hour, the slurry was filtered through a layer of filter-cel. Concentration of the solution under reduced pressure gave a mobile brown liquid which was distilled, mostly at 57–59° (1.5 mm). Nmr analysis of the various distillation cuts, including the forerun (4.85 g, bp 54–64° (2.5 mm)) indicated that the distillate was completely homogeneous.

The yield of distilled product was 45.75 g (86%): ir (CCl_4) 3760, 2970, 2910, 2865, 2370 sh, 2250, 2100, 1442, 1378, 1330, 1308, 1177, 1122, 1105, 1058, 951, and 868 cm^{-1}.

threo-**3-Iodo-2-butylurea (5).** *threo*-3-Iodo-2-butyl isocyanate (**3**, 9.70 g) was dissolved in 50 ml of ether and ammonia was passed in until a solid mass resulted. The precipitate was filtered off and washed with ether. The filtrate was treated with ammonia as before. The procedure was repeated until no more precipitate was formed on ammonia treatment. After drying, the combined white product weighed 9.67 g (92.7%) and melted at 105–107°. A mixture of this material and *erythro*-3-iodo-2-butylurea (**6**, mp 103–104°) melted at 100.5–101.5°.

An analytical sample, mp 103–105°, was obtained by recrystallization from acetone–ether. *Anal.* Calcd for $C_5H_{11}N_2OI$: C, 24.81; H, 4.58; N, 11.58. Found: C, 24.79; H, 4.55; N, 11.74. The infrared spectrum was noticeably different from that of *erythro*-3-iodo-2-butylurea (**6**): ir (KBr) 3390, 3300, 3200, 1649, 1598, 1530, and 1180 cm^{-1}.

erythro-**3-Iodobutyl isocyanate (4)** was obtained from *trans*-2-butene (14 g) as described for **3**. The product was a slightly brown distillate, 26.59 g (83.2%), boiling mostly at 56–58° (1.5 mm): ir (CCl_4) 3640, 2950, 2900, 2860, 2360 sh, 2220, 2090, 1440, 1377, 1340, 1308, 1182 sh, 1166, 1150 sh, 1137, 1105, 1082, 1050, 957, and 864 cm^{-1}.

erythro-**3-Iodo-2-butylurea (6)** was prepared from 12.09 g of *erythro*-3-iodo-2-butyl isocyanate (**4**) in the same manner as described for the *threo* isomer **5**. The yield of **6** was 12.51 g (96.5%), mp 101–103°. An analytical sample, mp 103–104°, was obtained by recrystallization from ether. *Anal.* Calcd for $C_5H_{11}NO_2I$: C, 24.81; H, 4.58; N, 11.58. Found: C, 24.85; H, 4.66; N, 11.45.

The infrared spectrum showed the following characteristics: ir (KBr) 3310, 3300, 3200, 1655, 1595, 1535, and 1273 cm^{-1}.

1-(3,3-Dimethyl-2-iodo)butyl Isocyanate (13). From 3.00 g of 3,3-dimethylbutene there was obtained 7.2 g of an oil (80% yield). This material was dissolved in ether, washed again with sodium bisulfite, filtered through anhydrous magnesium sulfate, evaporated, and then molecularly distilled twice to give an analytical sample of **13**, $n^{24}D$ 1.5200: ir 2273, 1134, and 875 cm^{-1}.

Anal. Calcd for $C_7H_{12}NOI$: C, 33.22; H, 4.78; I, 50.14. Found: C, 33.62; H, 4.73; I, 50.53.

Methyl N-(3,3-Dimethyl-2-iodo)butylcarbamate (14). 1-(3,3-Dimethyl-2-iodo)butyl isocyanate, 7.2 g, was treated with methanol to give 5.9 g (74%) of **14**. An analytical sample, mp 55.5–57°, was recrystallized from ether: ir 3333, 1690, 1504, and 1265 cm^{-1}.

Anal. Calcd for $C_8H_{16}NO_2I$: C, 34.15; H, 5.62; I, 44.20. Found: C, 33.60; 33.49; H, 5.50; 5.67; I, 44.28.

Perhydro-6,6-dimethyl-5-iodo-2-ketooxazine (17). From 3.00 g (34.8 mmol) of 2-methyl-3-buten-2-ol (**16**), 69.6 mmol of silver cyanate, and 34.8 mmol of iodine, upon refluxing for 20 hr and work-up there was obtained 4.84 g of a liquid–solid mixture. Trituration with a small amount of ether gave **17**, mp 128–132°. Recrystallization from methanol gave an analytical sample, mp 130.5–132°: ir 3235, 3013, and 1690 cm^{-1}; nmr signals at τ 5.78, (q, 1, J = 6 and 8.5 Hz), 6.30 (complex quintet that collapses to a broad doublet on D_2O treatment, 2), 8.42 (s, 6).

Anal. Calcd for $C_6H_{10}NO_2I$: C, 28.25; H, 3.95; I, 49.76. Found: C, 28.38; H, 3.96; I, 49.94.

Phenylacetylene-d_1. A solution of 21.45 g of phenylacetylene in 30 ml of dry ether was added to a solution of C_2H_5MgBr prepared from 7 g of Mg and 32 g of ethyl bromide. After 4 hr of reflux 10 ml of deuterium oxide (99.81 g-atom % deuterium) was added and the mixture was filtered through a layer of filter-cel. Another 4 ml of D_2O was added to the filtrate. Filtration and distillation under reduced pressure yielded 15.3 g of a clear liquid (71%), bp 50–53° (7 mm); nmr analysis showed 93 ± 3% deuterium in the acetylenic position.

β-Deuteriostyrene (9). Phenylacetylene-d_1 (10.22 g) in 100 ml of pentane was hydrogenated with 1.5 g of Lindlar's catalyst[14] at 22.8 psi. After 18 min, 1.1 mol of hydrogen had been absorbed. Work-up and distillation yielded 7.5 g (73%) of product boiling at 50–52° (7 mm).

Nmr analysis showed that the material had the following composition: β-deuterioethylbenzene, 22.8%; *trans*-β-deuteriostyrene, 22.2%; *cis*-β-deuteriostyrene, 54.5%. The ratio of *cis*–*trans* deuteriostyrene was 71:29. Vpc analysis showed 23% ethylbenzene and 77% styrene.

Methyl (2-Iodo-2-deuterio-1-phenylethyl)carbamate (10). The same procedure was used on the deuterated styrene as was used for the undeuterated analog:[4] yield, 93%; mp 85–86°; nmr analysis showed 90 ± 3% deuterium on C-2.

***cis*- and *trans*-2-Phenyl-3-deuterioaziridine (11a and 11b).** Iodo carbamate **10** was converted to the aziridine by treatment with potassium hydroxide as described for the undeuterated compound.[4] The nmr spectrum of the product, 98% yield, after exchange of NH with deuterium from D_2O and distillation indicated a composition of 14% acetophenone and 86% aziridines **11a** and **11b** in a ratio of 71:29. The proton at C-3 absorbs as a doublet at τ 8.05, J = 6 Hz for the *cis* isomer **11a** and at 8.51, J = 3 Hz for the *trans* isomer **11b**.

The general procedure for formation of iodocarbamates from olefins was followed as described.[3]

Methyl N-(3-iodo-4,4-dimethyl-2-pentyl)carbamate (22) was prepared from 4,4-dimethyl-2-pentene (**21**): yield, 65%; mp 65–67° (from methanol); ir 3300, 1705, and 1535 cm^{-1}.

Anal. Calcd for $C_9H_{18}NO_2I$: C, 36.13; H, 6.06. Found: C, 36.35; H, 6.25.

Methyl N-(1-iodo-4,4-dimethyl-2-pentyl)carbamate (24) was prepared from 4,4-dimethyl-1-pentene (**23**): yield 55%, mp 83–85° (from pentane); ir 3300, 3000, 1705, and 1510 cm^{-1}.

Anal. Calcd for $C_9H_8NO_2I$: C, 36.13; H, 6.06. Found: C, 35.89; H, 5.91.

Methyl N-(2-iodo-1-phenylethyl)carbamate was prepared from styrene: yield 72%; mp 102–104° (from methanol); ir 3350, 3100, 1700, and 1542 cm^{-1}.

(15) All melting points are uncorrected and were determined on a Fischer-Johns melting block. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were determined on a Perkin-Elmer Model 457 grating infrared spectrometer; solids in KBr pellets and liquids as neat films on NaCl plates. Proton magnetic resonance spectra were obtained on a Varian Associates Model A-60A spectrometer in deuteriochloroform or dimethyl sulfoxide-d_6; tetramethylsilane (τ = 10 ppm) was used as an internal standard. A Varian Aerograph Model 700 employing a $^3/_8$ in. × 20 ft 30% SE-30 45/60 on Chromosorb W column was used for preparative vapor phase chromatographic separations. Analytical samples of liquid carbamate mixtures were obtained by filtering the crude oils through neutral alumina of activity I. The term *in vacuo* refers to the use of a rotary evaporator.

Anal. Calcd for $C_{10}H_{12}NO_2I$: C, 39.26; H, 4.21. Found: C, 39.15; H, 4.02.

Methyl N-(*syn*-8-iododibenzobicyclo[3.2.1]octadienyl-4-*endo*)-carbamate (37a) was prepared from ethenoanthracene: yield, 85%; mp 151–152° (from methanol); ir 3400, 2900, 1705, 1510, and 1225 cm^{-1}; nmr ($CDCl_3$) τ 6.4 (broad, 1, shoulder), 6.30 (s, 3), 5.9 (d, 1, J = 4 Hz), 5.2 (t, broad, 2, J = 4.5 Hz), 4.1 (NH), 2.9 (m, 10).

Anal. Calcd for $C_{18}H_{16}NO_2I$: C, 53.32; H, 3.97. Found: C, 53.08; H, 4.00.

***t*-Butyl N-(*syn*-8-iododibenzobicyclo[3.2.1]octadienyl-4-*endo*)-carbamate (37b)** was prepared from ethenoanthracene: yield 49%, mp 63–65° (from methanol); ir 3400, 1705, 1505, and 1230 cm^{-1}.

Anal. Calcd for $C_{21}H_{24}NO_2I$: C, 56.47; H, 4.93. Found: C, 56.42; H, 4.91.

Methyl N-(2-iodo-1-phenylpropyl)carbamate was prepared from 1-phenyl-1-propene: yield 64%; mp 103–104° (from methanol); ir 3300, 3100, 1700, and 1525 cm^{-1}; nmr τ 2.65 (s, 5), 4.4 (NH broad), 5.4 (CHI, m, 1), 5.56 (CHN, m, 1), 6.4 (s, 3), 8.25 (d, 3, J = 7 Hz).

Anal. Calcd for $C_{11}H_{14}NO_2I$: C, 41.39; H, 4.42. Found: C, 41.52; H, 4.41.

Methyl N-(4-iodo-2,5-dimethyl-3-hexanyl)carbamate was prepared from diisopropylethylene: yield 62%; mp 130–135° (from methanol); ir 3300, 3100, 1705, and 1525 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}NO_2I$: C, 38.33; H, 6.43. Found: C, 38.24; H, 6.43.

Methyl N-(1-iodo-3-methyl-2-butyl)carbamate was prepared from 3-metyyl-1-butene, 60% yield, mp 138–141° (from methanol); ir 3300, 1700 cm^{-1}; nmr CCH_3 at τ 9 (broad) and O-CH_3 at τ 6.2-(d) indicative of a mixture of isomers.

N-Carbomethoxy-2-methylaminotricyclo[2.2.1.0^{2,6}]heptane (33) was prepared from 5-methylene-2-norbornene in 50% overall yield. Glpc indicated at least five other minor products. Since the crude nmr proved to be so complex as to preclude the determination of the yield *via* this method, the yield given is a mimimum estimate based on glpc data. None of the minor products were isolated due to overlapping retention times. The [2.2.1.0^{2,6}]heptane product **33** melted at 30–32° and was identified on the basis of its nmr spectrum: ir 3330, 2930, 1700, and 1530 cm^{-1}; nmr ($CDCl_3$), τ 5.0 (broad, 1, NH), 6.34 (s, 3, OMe), 6.60 (broad s, 2, CH_2N), 8.0 (broad s, 1, bridgehead H), and 8.95 (s, 2, cyclopropane methine H).

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34. Found: C, 66.42; H, 8.52.

***trans*-2-Iodo-3-(N-carbomethoxy)amino-1,2,3,4,5,8-hexahydronaphthalene (27) (93%) and *trans*-2-iodo-3-(N-carbomethoxy)amino-6,7-iodo-(N-carbomethoxy)amino-1,2,3,4,5,6,7,8-octahydronaphthalene (29) (7%)** (stereochemistry partially unspecified) were prepared in 31% overall yield from 0.05 mol of INCO and 0.05 mol of triene **26** (τ 4.25, s, 7.45, s).[12] The nmr spectrum of the crude isocyanate indicated the presence of allylic protons at τ 7.2–7.6 (m, 4), doubly allylic protons at 6.7 (m, 4), methine protons at 5.8 (m, 2) and vinylic protons at 4.15 (m, 2). The crude carbamate reaction mixture was poured into water containing a trace of sodium sulfite and extracted with ether. The diadduct failed to dissolve and was removed by filtration (600 mg). Its analytical sample was obtained by extraction with boiling 95% ethanol, in which it was insoluble; mp 205–209° (dec); ir 3310, 1690, and 1550 cm^{-1}.

Anal. Calcd for $C_{14}H_{20}N_2O_4I$: C, 31.48; H, 3.77. Found: C, 31.65; H, 3.86.

The ethereal layer was then washed with water and saturated salt solution and dried over anhydrous magnesium sulfate. Removal of solvent *in vacuo* yielded an oil consisting of unreacted starting material and the monoadduct which solidified. This mixture was thoroughly washed with pentane to remove unreacted isotetralin **26** and yielded 4.8 g of a light yellow solid. The analytical sample of the monoadduct was recrystallized three times from ethanol–water; mp 136–136.5°; ir 3310, 1685, and 1540 cm^{-1}; nmr (dimethyl sulfoxide-d_6), τ 4.31 (s, 2, vinylic), 6.42 (s, 3, OMe), 7.51 (broad s, 8, CH_2).

Anal. Calcd for $C_{12}H_{16}NO_2I$: C, 43.26; H, 4.84. Found: C, 43.51; H, 5.13.

2,3:6,7-Diimino-1,2,3,4,5,6,7,8-octahydronaphthalene (30). *trans*-2-Iodo-3-(N-carbomethoxy)amino-1,2,3,4,5,8-hexahydronaphthalene (**27**, 200 mg) was refluxed in 50 ml of 2 N KOH in anhydrous MeOH for 1 hr. The mixture was cooled, diluted with 50 ml of saturated salt solution, and extracted twice with ether. Evaporation of the dried ($MgSO_4$) ether extract left a methanolic solution of the diaziridine. Saturated picric acid was added and yellow crystals (20 mg) formed within a few minutes. The analytical sample of the dipicrate of **30** was obtained by extracting the crude solid with boiling 95% ethanol, in which it was insoluble; the dipicrate decomposes near 180°; ir 3320, 1610, 1530, and 1310 cm^{-1}; nmr (dimethyl sulfoxide-d_6), τ 6.8 (broad s, 4, CHN), 7.5 (broad s, 8, CH_2), no vinylic protons were present; the signals due to picric acid occurred below τ 2.5.

Anal. Calcd for $C_{22}H_{20}N_8O_{12}$: C, 42.50; H, 3.25. Found: C, 42.72; H, 3.33.

11-Aza-$\Delta^{3,8}\Delta^{5,6}$-Tricyclo[8.1.0.0^{3,8}]undecadiene (28). A solution of 1 g of the iodo carbamate **27** and 20 ml of 1.5 N potassium hydroxide in methanol was refluxed for 12 hr and converted to the picrate of **28** and recrystallized from ethanol; yield 55%, mp 166–170°.

Anal. Calcd for $C_{16}H_{16}O_7N_4$: C, 51.06; H, 4.29. Found: C, 50.91; H, 4.38.

Determination of INCO–Adduct Product Ratios. General Procedure for Zinc Reduction. Methyl β-iodoalkylcarbamates were prepared as previously described[3] on a 0.1 or 0.05 molar scale. The crude β-iodocarbamates, obtained by removing the methanol–ether solvent from the reaction mixture *in vacuo*, were dissolved in 1:1 acetic acid–ether (100:100 ml/0.1 mol of starting olefin) and refluxed over powdered zinc (10 g per 0.1 mol of starting olefin) for 5–24 hr. The resulting mixture was extracted with saturated sodium bicarbonate until CO_2 evolution ceased after which time the ethereal layer was washed with saturated salt solution and dried over anhydrous magnesium sulfate. The ether solvent was removed *in vacuo* to yield the methyl carbamates as colorless to faint yellow oils. Whenever possible, a portion of the crude carbamates was separated into the pure components *via* preparative glpc. This facilitated the determination of product ratios by integration of the nmr spectra of the crude carbamate mixtures.

Methyl N-cyclohexylcarbamate after 18 hr of reflux led to 73% yield of methyl N-cyclohexylcarbamate, mp 68–70°, recrystallized twice from MeOH and identical with material prepared from cyclohexyl isocyanate and methanol.

Methyl N-(2,5-dimethyl-3-hexyl)carbamate, from methyl N-(4-iodo-2,5-dimethyl-3-hexyl)carbamate; after 18 hr of reflux with zinc there was obtained methyl N-(2,5-dimethyl-3-hexyl)carbamate, 85%, mp 36–37.5°: ir 3300, 3100, 1703, and 1525 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}NO_2$: C, 64.13; H, 11.30. Found: C, 63.92; H, 11.18.

Methyl N-(3,3-Dimethylbutyl)carbamate (15). Reduction of **14** yielded methyl N-(3,3-dimethylbutyl)carbamate (**15**, 95%) as a viscous high boiling liquid: ir 3330, 1700, and 1505 cm^{-1}; nmr ($CDCl_3$) τ 6.32 (s, 3, OCH_3), 6.85 (m, 2, CH_2–N), 8.70 (m, 2), 9.09 (s, 9).

Anal. Calcd for $C_8H_{17}NO_2$: C, 60.34; H, 10.76. Found: C, 60.27; H, 10.61.

Methyl N-(1-hexane)carbamate (30%) and methyl N-(2-hexane)-carbamate (70%) were prepared from 1-hexene in 50% overall yield. The INCO addition failed to go to completion as evidenced by the incomplete decolorization of the reaction mixture: ir (carbamate mixture) 3315, 2940, 1700, and 1530 cm^{-1}; nmr ($CDCl_3$) for methyl N-(1-hexane)carbamate τ 4.5 (broad, 1, NH), 6.34 (s, 3, OMe), 6.8 (m, 2, CHN); nmr ($CDCl_3$) for methyl N-(2-hexane)-carbamate τ 4.8 (broad, 1, NH), 6.36 (s with shoulder, 4, OMe, CHN).

Anal. (mixture) Calcd for $C_8H_{17}NO_2$: C, 60.34; H, 10.76. Found: C, 60.58; H, 10.63.

Methyl N-(1-methyl-1-cyclohexane)carbamate (42) (55%) and methyl N-(cyclohexylmethane)carbamate (43) (45%) were prepared from methylenecyclohexane. The iodocarbamate was isolated (70%) prior to reduction: ir (carbamate mixture) 3340, 2930, 1710, and 1525 cm^{-1}; nmr ($CDCl_3$) for methyl N-(1-methyl-1-cyclohexane)carbamate τ 6.43 (s, 3, OMe), 8.7 (s, 3, Me); nmr ($CDCl_3$) for methyl N-(cyclohexylmethane)carbamate τ 6.36 (s, 3, OMe).

Anal. Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.00. Found: C, 63.35; H, 9.80.

Methyl N-(4,4-dimethyl-1-pentane)carbamate (20%) and methyl N-(4,4-dimethyl-2-pentane)carbamate (80%) were prepared from 4,4-dimethyl-1-pentene **23** in 33% overall yield. The INCO addition failed to go to completion as evidenced by the failure of the reaction mixture to decolorize: ir (carbamate mixture) 3330, 2950, 1700, and 1530 cm^{-1}; nmr ($CDCl_3$) for methyl N-(4,4-dimethyl-1-pentane)carbamate τ 5.1 (broad, 1, NH), 6.35 (s, 3, OMe), 6.85 (q, J = 6 Hz, 2, CH_2N), 9.13 (s, 9, $C(Me)_3$); nmr for methyl N-(4,4-dimethyl-2-pentane)carbamate τ 5.1 (broad, 1, NH), 6.35 (s, 3, OMe), 6.17 (m, 1, CHN), 9.05 (s, 9, $C(Me)_3$).