a rubber stopper and taken out of the drybox. Usually after several hours, the color darkened, but no differences in the nmr spectra were observed. Small amounts of dimsylate solutions were measured by counting the number of drops added (one drop = *ca.* 0.008 ml).

The measurements of the nmr spectra usually were made about 0.5 hr after preparing the sample. In cases where a small amount of base was used (*ca.* five to ten drops, 0.1–0.2 equiv) after 2–3 hr at 30°, the spectra changed considerably. Probably the small amount of dimsylate deteriorated, possibly by penetration of oxygen.

Solutions for Equilibration of Cyclopropyl Phenyl Sulfone (I) and Isopropyl Phenyl Sulfone (II) and Their Respective Anions. Table III records the weights and volumes employed for the nmr spectra of I and II and their respective anions. The solutions were prepared employing the precautions mentioned in the last section. The solution of sodium dimsylate was prepared from 0.1073 g of sodamide (90%) and 5 ml of DMSO (0.5 *M*).

Stereospecific Introduction of Azide Functions into Organic Molecules[1a,b]

Frank W. Fowler,[1c] Alfred Hassner, and Louis A. Levy

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received November 21, 1966*

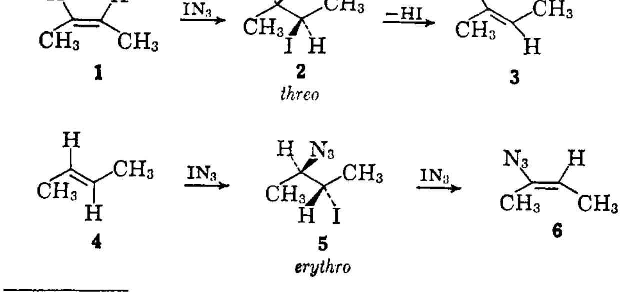
Abstract: Iodine azide prepared *in situ* by the reaction of sodium azide and iodine monochloride in acetonitrile has been shown to add in good yield and in a highly stereospecific manner to a variety of unsaturated systems. Thus, cyclohexene and 2-cholestene produce the *trans* and the *trans*-diaxial adduct, respectively; straight-chain *cis* and *trans* olefins give respectively the *threo* and *erythro* adducts; terminal olefins form adducts where the azido function is at the 2 position; and conjugated olefins such as 1,2-dihydronaphthalene lead to products with the azido function occupying the benzylic position. Tolane and 1,3-cyclooctadiene yield one-to-one adducts; conjugated ketones and esters give adducts where the azido function occupies the β position; and isonitriles give iodotetrazoles. Possible mechanisms for these reactions are discussed.

In our studies on the use of pseudohalogens as a method of stereospecific synthesis of organic nitrogen compounds,[2] we were led to the consideration that α,β-iodo azides may be formed by the addition of the pseudohalogen iodine azide (IN_3). Organic azides are of considerable use in organic synthesis. A new useful synthesis of azides would be of value since the only known general route to aliphatic azides involves nucleophilic displacement of groups such as halides and tosylates. Such reactions often are accompanied by elimination, rearrangement, and introduction of undesirable stereochemistry.

Iodine azide was first synthesized and isolated by Hantsch[3] in 1900 by stirring an aqueous suspension of silver azide in ether with iodine. From this suspension he was able to isolate highly explosive yellow crystals of iodine azide. This method was found unsuitable for the generation of IN_3 as applicable in the synthesis of α,β-iodo azides. Thus, when an olefin was added to the slurry of IN_3 formed as described by Hantsch, only black intractable oils that showed both hydroxyl and azido absorption in the infrared resulted. These findings were not too surprising since it is known that IN_3 slowly decomposes in the presence of water.

We have found that when iodine monochloride is added to a cold stirred slurry of sodium azide in acetonitrile, the dark color of iodine monochloride is replaced with the yellow-orange color of, presumably, IN_3. Although iodine azide has never been isolated from these solutions, its presence can be inferred. If the inorganic salts are filtered and an olefin is added to the clear yellow-orange solution, a high yield of an α,β-iodo azide can be obtained. Since sodium azide is essentially insoluble in acetonitrile, these results are incompatible with azide ion attacking a cation derived from iodine monochloride but are completely consistent with the existence of IN_3 in solution.

We have observed that the addition of IN_3 is highly stereospecific. The iodo azide adducts of *cis*- and *trans*-2-butene possess the *threo*- and *erythro*-2-azido-3-iodobutane structures **2** and **5**, respectively. Although the stereochemistry of these adducts is not obvious directly from their physical data, except that these isomers are formed cleanly and uncontaminated with each other, insight can be gained from a *trans* elimination of hydrogen iodide to form in both cases the vinyl azides.[4] It would be expected that the azido group, because of a magnetic anisotropic effect, would deshield a *cis* hydrogen and cause a downfield shift with respect to a *trans*



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[1] (a) Stereochemistry. XXIII. For paper XXII see A. Hassner, P. Catsoulacos, and E. G. Nash, *Tetrahedron Letters*, 489 (1967). (b) A preliminary report of part of this work has appeared: A. Hassner and L. A. Levy, *J. Am. Chem. Soc.*, **87**, 4203 (1965). (c) National Aeronautics and Space Administration predoctoral fellow.

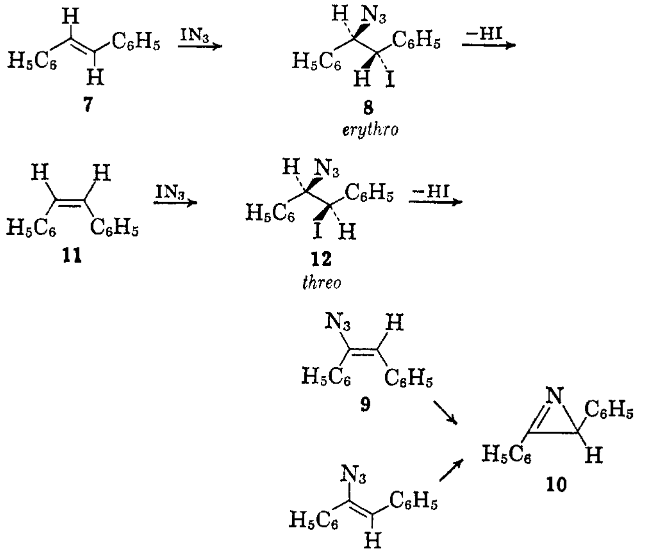
[2] See A. Hassner, M. Lorber, and C. H. Heathcock, *J. Org. Chem.*, **32**, 540 (967), and preceeding papers.

[3] A. Hantsch, *Ber.*, **33**, 524 (1900).

[4] The synthetic utility of α,β-iodo azides in general will be reported in a following paper.

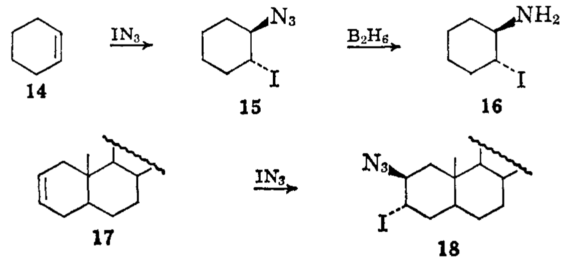
hydrogen. That this is in fact the case is shown by the shift of the vinylic hydrogen of **6** downfield by 0.43 ppm while the corresponding hydrogen in **3** absorbs at τ 5.30. The infrared spectra of all iodo azides show a strong absorption at *ca.* 2100 cm^{-1}, and its position does not change appreciably in the vinyl azides. In the latter, the C=C stretching frequency at *ca.* 1625 cm^{-1} is highly intensified as compared to simple olefins.

We have observed that *trans*- and *cis*-stilbene (**7** and **11**) yield *erythro*- and *threo*-1-azido-2-iodo-1,2-diphenylethane (**8** and **12**), respectively. Elimination of hydrogen iodide from these adducts gives vinyl azides **9** and **13**.

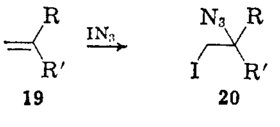


Vinyl azide **9** is quite unstable and could not be obtained pure even when the elimination was carried out with potassium *t*-butylate at 0–5° in ether. The nmr spectrum of this crude product shows in addition to the aromatic hydrogens only two singlets, one being attributed to the ring proton in azirine[5] **10**. The other singlet is due to the vinylic hydrogen of vinyl azide **9**, which is shifted downfield 0.25 ppm with respect to the vinylic hydrogen of azide **13** (τ 3.99).

The addition of IN$_3$ to cyclic olefins also results in *trans* addition. When the iodo azide adduct of cyclohexene (**15**) was reduced with diborane it was shown to be identical with *trans*-1-amino-2-iodocyclohexane (**16**) prepared independently.[6] The addition of iodine azide to 2-cholestene yielded the expected[7] *trans*-diaxial 2β-azido-3α-iodocholestane (**18**). The stereochemistry of this adduct can be deduced from an examination of its nmr spectrum. The hydrogens at C-2 and C-3 occur at τ 5.89 and 5.45 with a half-width each of 7 cps, which fully describes them as being equatorial.[8] The iodine function is, therefore, axial and must be at either the 2β or the 3α position; it is assigned to the 3α position since the C-19 angular methyl group in **18** is shifted downfield to only τ 9.02 as compared to the C-19 absorption in cholestane at τ 9.22.[9] It is known that a 2β-iodo function causes deshielding of the C-19 angular methyl protons by *ca.* 0.4 ppm whereas 2α-nitrogen functions have a much smaller effect.[10]



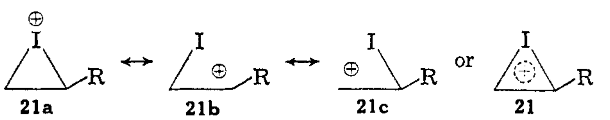
Iodine azide adds stereospecifically to terminal olefins to give an adduct which in the following cases has the iodo function primary and where the azido function occupies the internal position.



	R	R′
a	CH$_3$	CH$_3$
b	H	(CH$_2$)$_3$CH$_3$
c	H	C$_6$H$_5$
d	H	phthalimido
e	H	CH$_2$C$_6$H$_5$
f	H	C$_6$H$_5$CH$_2$CH$_2$
g	C$_6$H$_5$	C$_6$H$_5$
h	(CH$_2$)$_5$	

The stereochemistry of these adducts was clear from their nmr spectra. Examination of the nmr spectra of the iodo azide adducts of cyclic and acyclic internal olefins indicates that the hydrogen geminal to a secondary iodo function has its nmr absorption at approximately τ 5.9–6.1, whereas the hydrogen geminal to a secondary azido function occurs at approximately τ 6.5–6.8. The protons geminal to a primary iodo function absorb at *ca.* τ 6.9. The iodo azide adducts of terminal olefins have both of the geminal hydrogens appearing as a complex multiplet centered at approximately τ 6.9–7.1, indicating a primary iodo function. The position of the azido function, in most cases, has been unequivocally assigned by an examination of the vinylic proton in the nmr spectrum of the corresponding vinyl azide.

All of the above data are self-consistent with an electrophilic addition involving the intervention of a cyclic iodonium ion whose ground state is adequately described by resonance structures **21a–c**. Ring opening of such an intermediate would be expected to occur in a *trans* manner leading to *trans*-addition products. Furthermore, this iodonium ion must be relatively stable, for even when the possibility exists for opening to a benzyl cation, we have observed little or no leakage to such a classical ion. This is evidenced by the fact that *cis*- and *trans*-stilbene give clean *threo* and *erythro* adducts, respectively, and is consistent with our previous reports on cyclic iodonium ion intermediates formed by iodine isocyanate additions to olefins.[11]



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(5) For a report that pyrolysis of vinyl azides gives azirines see G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962); for photolysis see A. Hassner, and F. W. Fowler, *Tetrahedron Letters*, in press.

(6) M. Mousseron and R. Jacquier, *Compt. Rend.*, **229**, 216 (1949).

(7) By analogy to the addition of iodine isocyanate: A. Hassner and C. Heathcock, *J. Org. Chem.*, **30**, 1748 (1965).

(8) A. Hassner and C. Heathcock, *ibid.*, **29**, 1350 (1964).

(9) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 6.

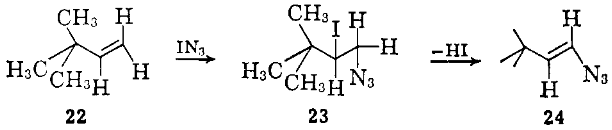
(10) J. E. Kropp, Ph.D. Dissertation, University of Colorado, Boulder, Colo., 1966.

(11) A. Hassner and C. Heathcock, *Tetrahedron Letters*, 1125 (1964).

The iodonium ion derived from unsymmetrical olefins must, however, be unsymmetrical. That is, if from simple carbonium ion theory it would be predicted that resonance structure **21b** would have a lower energy than **21c**, then structure **21b** would contribute to a greater extent in the ground state of the iodonium ion and opening of this ion by nucleophiles, such as azide ion, would occur preferentially at C-2.

The above explanation, in general, gives an adequate rationalization for the observed stereochemistry in the addition of iodine azide to olefins.

We have noted only one terminal olefin that did not yield an adduct with the iodine at the primary position. When IN_3 was added to 3,3-dimethyl-1-butene the only product isolated was 1-azido-2-iodo-3,3-dimethylbutane (**23**). This assignment is indicated from its nmr spectrum which shows, downfield from the singlet for the *t*-butyl group, a complex multiplet centered τ 6.1. If the iodine had occupied the primary position, then an absorption at *ca.* τ 7.0 would have been present. Confirmation of structure **23** was obtained by converting the iodo azide to the vinyl azide **24**, which in the olefinic region shows the two doublets characteristic of an AB system with a coupling constant of 15 cps (*trans*-vinyl hydrogens). In the alternative 2-azido-3,3-dimethyl-1-butene, the geminal methylene protons would be coupled by less than 4 cps.

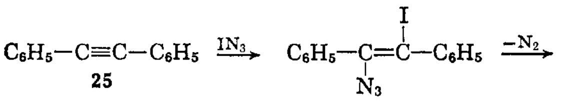


22 **23** **24**

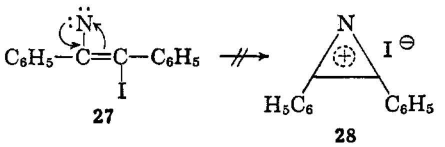
From the above considerations 3,3-dimethyl-2-butene appears to be anomalous since from simple carbonium ion theory the cyclic iodonium ion should open at the secondary rather than the primary position. In this case the *t*-butyl group places a severe steric restriction on the approach of azide ion and, therefore, the iodonium ion is opened at the sterically favorable but electronically unfavorable primary position. This same phenomenon, *anti*-Markovnikov addition, is observed in the bromination of 3,3-dimethyl-2-butene in methanol[12] leading to a bromo ether, as well as in iodine isocyanate additions to this olefin.[10,13]

Steric effects in this electrophilic addition are also obvious since IN_3 adds at least 2.5 times faster to cyclohexene than to 1-methylcyclohexene in spite of the greater nucleophilicity of the more substituted olefin.

We have been successful in adding IN_3 to diphenylacetylene in moderate yield to give the unstable yellow crystalline monoiodo azide adduct **26** which is expected to have *trans* stereochemistry.[14] The synthesis of this vinyl azide is of particular interest since it is a possible precursor to the theoretically interesting azacyclopropenyl cation (**28**). Although all attempts so far to convert vinyl azide **26** into the ion **28** have been unsuccessful, this and other approaches to this system are still under investigation.



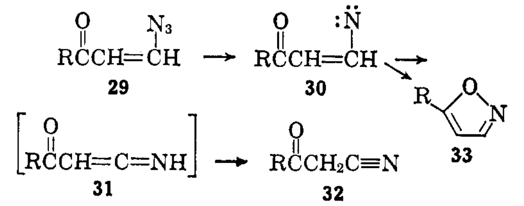
$$\underset{\mathbf{25}}{C_6H_5{-}C{\equiv}C{-}C_6H_5} \xrightarrow{IN_3} \underset{\mathbf{26}}{C_6H_5{-}\underset{N_3}{C}{=}\overset{I}{C}{-}C_6H_5} \xrightarrow{-N_2}$$



27 **28**

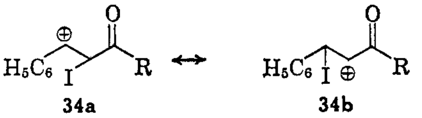
The addition of IN_3 to α,β-unsaturated carbonyl compounds proceeds very well, in contrast to iodine isocyanate which does not add to conjugated ketones or esters.[2] Thus, iodine azide adds stereospecifically in moderate yield to methyl cinnamate and quantitatively to chalcone.

As has been shown above, the elimination of hydrogen iodide from the iodo azide adducts to give unsaturated azides has been very helpful in elucidating the stereochemistry of these adducts. It is known[15] that 2-azidovinyl ketones can be decomposed in the presence of acids to give substituted isoxazoles and nitriles, presumably through a vinyl nitrene intermediate.



29 **30** **31** **32** **33**

Since resonance structure **34a** is expected to be more stable than **34b**, the ground state of the iodonium ion resembles **34a** more than **34b**, and thus the prediction can be made that azide ion would open the iodonium ion intermediate mainly at the benzylic position.

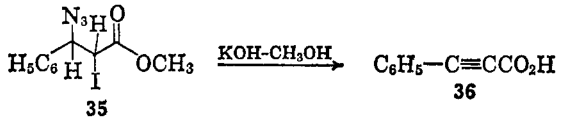


34a **34b**

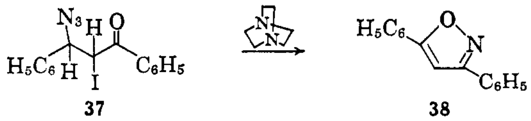
$R = C_6H_5, OMe$

A vinyl azide, obtained from the chalcone or for the methyl cinnamate adduct, in which the azide function occupies the benzylic position should lose nitrogen and give an isoxazole or a ketenimine, thus proving the stereochemistry of the adduct.

When the methyl cinnamate iodo azide adduct (**35**) is treated with potassium hydroxide in methanol at room temperature only propiolic acid (**36**) can be isolated indicating that elimination of hydrazoic as well as hydriodic acid takes place.[16] However, when the iodo azide adduct of chalcone (**37**) is treated with diazabicyclooctane at room temperature 3,5-diphenylisoxazole (**38**) is obtained in 53% yield, suggesting that



35 **36**



37 **38**

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[12] W. H. Puterbausch and M. S. Newman, *J. Am. Chem. Soc.*, **79**, 3469 (1957).

[13] M. Lorber, unpublished results.

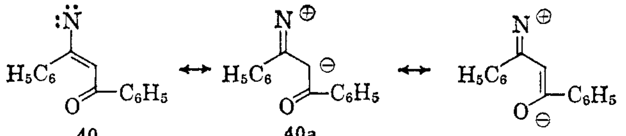
[14] L. D. Bergel'son and L. P. Badenkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1073 (1960); *Chem. Abstr.*, **54**, 24334 (1960).

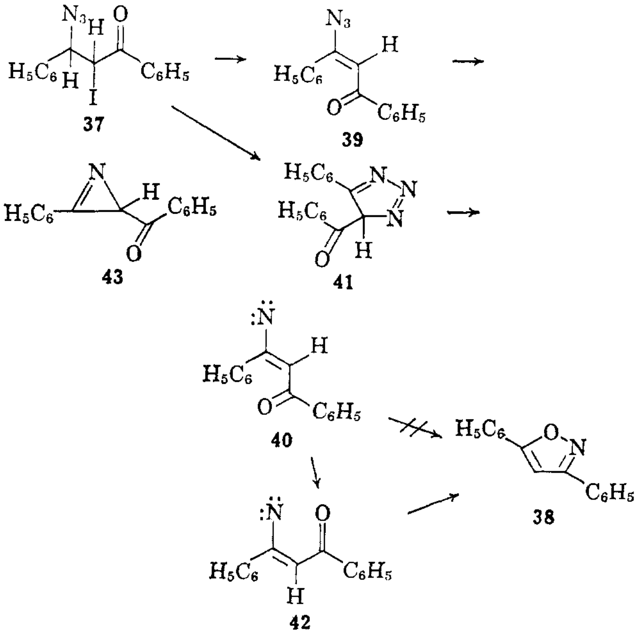
[15] A. N. Nesmeyanov and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 816 (1962).

[16] See J. H. Boyer and F. C. Cantes, *Chem. Rev.*, **48**, 1 (1954), p 27, for examples of HN_3 elimination with base.

indeed the azido function occupies the benzylic position in these adducts. It is interesting to note that we have observed no data to indicate any ketenimine formation which would have to result from phenyl migration.

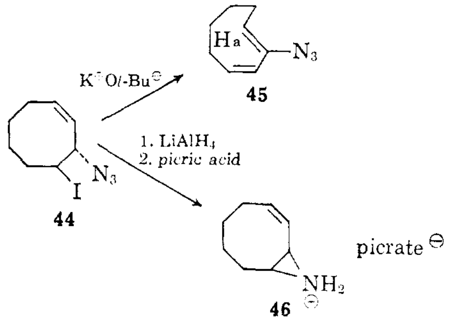
It appears that hydrogen iodide is eliminated from the chalcone adduct in a *trans* manner, to give the unstable *cis*-vinyl azide (**39**)[17] which can cyclize to the 4H-1,2,3-triazole **41** or lose nitrogen to give the *cis*-vinyl nitrene **40**. The ground state of **40** is best represented by the canonical structures **40**–**40b**. It can be seen that the C–C bond order is less than a normal double bond, permitting isomerization to the *trans*-vinyl nitrene **42**, which can cyclize to the isoxazole. Compound **41** can also give the *trans*-vinyl nitrene **42** by loss of nitrogen. The data so far do not permit a differentiation between these two pathways. Cyclization of the *cis*-vinyl nitrene **40** to the isoxazole **38** is unlikely since molecular models indicate the nitrogen–oxygen distance in the *cis*-vinyl nitrene is too large for bond formation.


40 **40a** **40b**

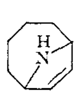


The possibility that the vinyl nitrene cyclizes to the azirine **43**, which can photolyze to the isoxazole **38**,[18] was ruled out since the conversion of **37** to **38** proceeds equally well in the absence of light.

Cyclooctadiene when treated with 1 equiv of IN_3 gives a one-to-one adduct of diene and iodine azide. The available evidence suggests that the addition proceeded to give the 1,2 rather than the 1,4 adduct. First, the nmr spectrum of the adduct shows for the vinylic protons a very complex splitting pattern as expected for **44** rather than a slightly split quartet as expected for a 1,4 adduct. Second, the nmr spectrum of the unsaturated azide **45** shows a one-hydrogen triplet representing the hydrogen (H_a) *trans* to the azido function. This proton is shielded by the diamagnetic current generated in the adjacent double bond and occurs at slightly higher field than the remaining olefinic protons.



Finally, the nmr spectrum for the picrate of the aziridine,[19] formed by lithium aluminum hydride reduction of **44**, shows a two-proton multiplet in the vinylic region, a two-proton multiplet centered at τ 6.8, and an eight-proton multiplet centered at τ 8.3, completely consistent with structure **46** and inconsistent with either **47** or **48**.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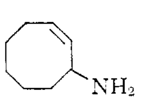
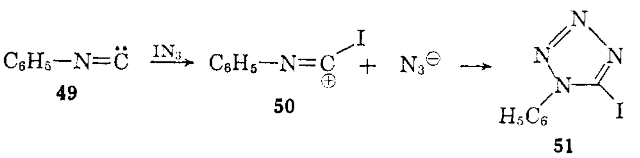

48

Iodine azide adds to acenaphthylene to give a very unstable product which appears to be mainly the *trans* adduct. This assignment is based on the appearance of two doublets centered at τ 4.36 and 4.48 with $J = 2.0$ cps which is in agreement with the coupling constants of known *trans* adducts to acenaphthylene.[20]

In connection with our work on substituted tetrazoles[21] we have discovered that the addition of IN_3 provides a convenient route to 5-iodotetrazoles. In analogy to the synthesis of 1,5-substituted tetrazoles by the addition of carbonium ions to isonitriles in the presence of azide ions,[22] this reaction involves a nitrilium ion (**50**) which adds azide ion to produce the tetrazole **51**.



The above results suggested that the addition of iodine azide to imines followed by elimination of hydrogen iodide to the azomethine might provide another synthesis to 1,5-substituted tetrazoles since imidoyl azides are known to undergo cyclization to tetrazoles.[23] However, exposure of benzalaniline to a solution of iodine azide resulted only in iodination of the activated aromatic nucleus to produce 4-iodobenzalaniline.

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[17] In analogy with the observation that *cis*-1-azido-1,2-diphenylethylene is unstable and loses nitrogen at room temperature whereas the *trans* isomer is stable at room temperature.

[18] E. F. Ullman and B. Singh, *J. Am. Chem. Soc.*, **88**, 1844 (1966); D. W. Kurtz and H. Shechter, *Chem. Commun.*, 689 (1966).

[19] We have observed, in general, that lithium aluminum hydride reduction of iodo azides yields aziridines.

[20] M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2705 (1963).

[21] A. Hassner, L. A. Levy, and R. Gault, *Tetrahedron Letters*, 3119 (1966).

[22] J. Curtins and G. Ehrhart, *Ber.*, **55**, 1559 (1922).

[23] F. R. Benson, *Chem. Rev.*, **41**, 1 (1947).

Experimental Section

General. Both the iodo and azido functions are quite labile in the iodo azide adducts and elemental analysis was generally precluded with the higher molecular weight olefins since extensive decomposition occurred on attempted distillation. However, evidence that addition did take place can be obtained from an examination of the infrared spectrum which shows the strong, asymmetric stretching absorption at *ca.* 2100 cm^{-1}. The nmr spectrum in the olefinic region can be used to ascertain whether any unreacted olefin is present and, if it is, generally the amount is quite small.

All melting points were taken on a Fisher-Johns melting point block and are uncorrected. Infrared measurements were carried out with a Perkin-Elmer IR-21 or Beckman IR-5 whereas nmr spectra were obtained on a Varian A-60 spectrometer in *ca.* 15% solutions using tetramethylsilane as an internal standard. Elemental analyses were performed by A. Bernhardt, Mulheim, Germany, and Huffman Labs, Denver, Colo.

Materials. The acetonitrile was either Matheson Coleman and Bell reagent grade or Eastman practical grade that had been distilled from phosphorus pentoxide. The iodide monochloride was either Matheson Coleman and Bell reagent grade or Eastman practical grade that had been previously distilled. The sodium azide was either practical or reagent grade. The potassium *t*-butylate (MSA Research Corp.) was used without further purification. All olefins were commercially available or were synthesized by known procedures.

General Procedures for Iodine Azide Addition Reactions. To a stirred slurry of 15.0 g (0.25 mole) of sodium azide in 100 ml of acetonitrile in a methanol–ice cold bath was added slowly 18.3 g (0.113 mole) of iodine monochloride over a period of 10–20 min. The reaction mixture was stirred for an additional 5–10 min and, after 0.10 mole of the olefin was added, allowed to warm to room temperature and stirred for 8–20 hr. The red-brown slurry was poured into 250 ml of water, and the mixture was extracted with 250 ml of ether in three portions. These were combined and washed with 150 ml of 5% sodium thiosulfate leaving a colorless, etheral solution. This solution was washed with 900 ml of water in four portions and dried over magnesium sulfate. Removal of the ether *in vacuo* at room temperature produced the iodo azide adduct, now slightly orange in color. Deviations from this procedure for a specific compound are noted later.

For further purification of the iodo azides, distillation is not recommended since generally the iodo function is labile in these adducts and violent decomposition of the azido function can occur when the adducts are heated. However, chromatography using Woelm neutral aluminum oxide activity grade I and elution with Skellysolve F (bp 40–60°) can be used as a method of further purification. The major impurity was usually unreacted olefin and this can be removed in the first few fractions.

General Procedure for the Formation of Unsaturated Azides from Iodo Azides. To 0.10 mole of the azide in 250–300 ml of dry ether cooled in an ice bath was added 13.5 g (20% excess) of potassium *t*-butylate. The reaction was stirred for 15–24 hr and was worked up by washing with 500 ml of water in two portions. The ethereal solution was dried over magnesium sulfate, and the ether was removed *in vacuo* at room temperature. The crude unsaturated azide was purified by passage through 80 g of neutral Woelm aluminum oxide activity I with Skellysolve F, and removal of the solvent *in vacuo* at room temperature produced the pure unsaturated azide.

threo-**2-Azido-3-iodobutane (2)** was prepared from *cis*-2-butene in 90% yield, colorless liquid, bp 68–70° (10 mm), n^{25}D 1.5386. *Anal.* Calcd for $C_4H_8IN_3$: C, 21.25; H, 3.37; N, 18.59. Found: C, 21.43; H, 3.63; N, 18.18. The nmr spectrum (CCl_4) showed peaks at τ 5.84 (one-proton multiplet), 6.50 (one-proton multiplet), and 8.12 (two three-proton doublets, $J = 7$ cps).

erythro-**2-Azido-3-iodobutane (5)** was prepared from *trans*-2-butene in 88% yield, colorless liquid, bp 67–69° (10 mm), n^{25}D 1.5378. *Anal.* Calcd for $C_4H_8IN_3$: C, 21.25; H, 3.37; N, 18.59. Found: C, 21.64; H, 3.57; N, 18.22. The nmr spectrum (CCl_4) showed τ 5.82 (one-proton multiplet), 6.64 (one-proton multiplet), 8.12 (three-proton doublet, $J = 7$ cps), and 8.64 (three-proton doublet, $J = 7$ cps).

erythro-**1-Azido-2-iodo-1,2-diphenylethane (8)** was prepared from *trans*-stilbene. The usual procedure was modified slightly in that the reaction mixture was poured into 200 ml of 5% $Na_2S_2O_3$ instead of water, and the solid which formed was filtered and air dried. The pale yellow iodo azide, mp 110–115°, was obtained in quantitative yield. Recrystallization from methanol produced the pure iodo azide in 73% yield, mp 131–133°. *Anal.* Calcd for $C_{14}H_{12}IN_3$: C, 48.15; H, 3.47; N, 12.03. Found: C, 48.33; H, 3.55; N, 12.30. The nmr spectrum ($CDCl_3$) showed τ 2.70 (ten-proton singlet), 4.81 (one-proton doublet, $J = 9$ cps), and 4.93 (one-proton doublet, $J = 9$ cps).

cis-**1-Azido-1,2-diphenylethylene (9)** was prepared from *erythro*-1-azido-2-iodo-1,2-diphenylethane (**8**). The temperature of the elimination was maintained below 5° during the entire reaction time (14 hr). The presence of the vinyl azide was inferred from the single absorption in the nmr spectrum at τ 3.74 and both azide (2100 cm^{-1}) and double-bond absorption (1640 cm^{-1}) in its infrared spectrum. Also, pyrolysis of this crude azide gave a 94% yield of 2,3-diphenylazirine (**10**).

2,3-Diphenyl-2H-azirine (10). The crude vinyl azide (**9**) was dissolved in dry Skellysolve B (bp 60–80°) and was passed through neutral Woelm aluminum oxide activity I. This was then diluted with more dry Skellysolve B to make a 2% (w/v) solution and refluxed for 2.5 hr. Removal of the solvent gave a 94% yield of pale yellow needles, mp 59–61°; with an analytical sample from hexane, mp 60–62°. *Anal.* Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.90; H, 6.17; N, 6.99.

threo-**1-Azido-2-iodo-1,2-diphenylethane (12)** was prepared from *cis*-stilbene in 80% yield, colorless crystals, mp 89–90°, from ethanol. *Anal.* Calcd for $C_{14}H_{12}IN_3$: C, 48.15; H, 3.47; N, 12.02. Found: C, 47.77; H, 3.50; N, 11.87. The nmr spectrum ($CDCl_3$) showed τ 2.83 (ten-proton singlet), 4.81 (one-proton doublet, $J = 9.4$ cps), and 5.06 (one-proton doublet, $J = 9.4$ cps).

trans-**1-Azido-1,2-diphenylethylene (13)** was prepared from *threo*-1-azido-2-iodo-1,2-diphenylethane (**12**) in 63% yield as yellow crystals, mp 39–43°. Rather than passing the vinyl azide through alumina, recrystallization from hexene was used to obtain the pure vinyl azide, mp 44–46°. *Anal.* Calcd for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 19.00. Found: C, 76.19; H, 4.96; N, 18.46.

trans-**1-Azido-2-iodocyclohexane (15)** was prepared from cyclohexene in 83% yield, bp 73–74° (0.90 mm), n^{25}D 1.5653. *Anal.* Calcd for $C_6H_{10}IN_3$: C, 28.70; H, 4.01; N, 16.73. Found: C, 29.34; H, 4.11; N, 16.72. The nmr spectrum (CCl_4) showed τ 6.1 (one-proton multiplet), 6.4 (one-proton multiplet), and 8.1 (eight-proton multiplet).

A General Procedure for Reduction of Azides to Amine with Diborane. The azide was dissolved in tetrahydrofuran, and the diborane (excess), generated externally, was bubbled into the solution. After standing overnight, the excess diborane was destroyed by the addition of ethanol. Gaseous hydrochloric acid was passed into the solution, and the amine hydrochloride precipitated. For example, *trans*-1-azido-2-iodocyclohexane (**15**) gave the corresponding amine hydrochloride in 50% yield. The benzamide melted at 160–162° and was identical with that prepared by hydrolyzing the iodine isocyanate addition product of cyclohexene.[6] *Anal.* Calcd for $C_{13}H_{16}INO$: 47.43; H, 4.90; I, 38.55. Found: C, 47.45; H, 5.05; I, 38.87.

2β-Azido-3α-iodocholestane (18) was prepared from 2-cholestene.[24] Chromatography of the crude iodo azide on Woelm neutral aluminum oxide activity I and elution with hexane led in 53% yield to colorless crystals, mp 101–102°, from methanol–ether. *Anal.* Calcd for $C_{27}H_{46}IN_3$: C, 60.10; H, 8.59; N, 7.79; I, 23.52. Found: C, 60.80; H, 8.77; N, 7.81; I, 22.83. The nmr spectrum ($CDCl_3$) showed τ 5.45 (broad one-proton singlet, $W_{1/2} =$ 6 cps), 5.89 (broad one-proton singlet, $W_{1/2} = 6$ cps), and 9.34 (three-proton singlet).

2-Azido-1-iodo-2-methylpropane (20a) was prepared from isobutylene in 60% yield, bp 68–69° (7 mm), n^{25}D 1.5292. *Anal.* Calcd for $C_4H_8IN_3$: C, 21.25; H, 3.57; N, 18.59. Found: C, 21.35; H, 3.52; N, 18.08. The nmr spectrum (CCl_4) showed τ 7.14 (two-proton broad singlet) and 9.08 (six-proton singlet).

2-Azido-1-iodohexane (20b) was prepared from 1-hexene in quantitative yield, liquid bp 66° (1.0 mm). The nmr spectrum (CCl_4) showed τ 6.72 (three-proton singlet) and 8.9 (nine-proton multiplet).

2-Azido-1-hexene was prepared from 2-azido-1-iodocyclohexane (**20b**) in 78% yield. The nmr spectrum (CCl_4) showed τ 5.35 (two-proton singlet) and 8.6 (nine-proton multiplet).

α-Azido-β-iodoethylbenzene (20c) was prepared from styrene in 70% yield, colorless liquid, purified by chromatography on Woelm neutral aluminum oxide activity I, n^{25}D 1.6070. *Anal.* Calcd for $C_8H_8ON_3$: C, 35.18; H, 2.95; N, 15.38. Found: C, 36.81; H, 3.03; N, 15.20.

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(24) C. Djerassi, *et al.*, *Chem. Pharm. Bull.* (Tokyo), **11**, 465 (1963).

1-Azido-1-phthalimido-2-iodoethane (20d) was prepared from N-vinylphthalimide in 66% yield, colorless crystals, mp 75–78°, from ethanol. *Anal.* Calcd for $C_{10}H_7IN_4O_2$: C, 35.11; H, 2.06; N, 16.38. Found: C, 34.90; H, 2.07; N, 16.24. The nmr spectrum (CCl_4) showed τ 2.16 (four-proton multiplet), 4.25 (one-proton quartet), and 6.0 (two-proton quartet).

2-Azido-1-iodo-3-phenylpropane (20e) was prepared from allylbenzene; the crude iodo azide was red-brown in color, and this color could be removed by passing the crude adduct through 200 g of Woelm neutral aluminum oxide activity I with Skellysolve F (bp 40–60°) giving a 72% yield of a colorless liquid. The nmr spectrum (CCl_4) showed τ 2.82 (five-proton singlet) and 6.9 (seven-proton multiplet).

2-Azido-3-phenylpropene was prepared from 2-azido-1-iodo-3-phenylpropane (**20e**) in 73% yield as a pale yellow liquid. The nmr spectrum (CCl_4) showed τ 2.80 (five-proton singlet), 5.42 (two-proton doublet further split), and 6.75 (two-proton singlet).

2-Azido-1-iodo-4-phenylbutane (20f) was prepared from 4-phenyl-1-butane in 93% yield as a colorless liquid. The nmr spectrum showed τ 2.72 (five-proton singlet) and 6.9 (seven-proton multiplet).

2-Azido-4-phenylbutene was prepared from 2-azido-1-iodo-4-phenylbutane (**20c**) in 88% yield as a pale yellow liquid. The nmr spectrum (CCl_4) showed τ 2.89 (five-proton singlet), 5.45 (two-proton singlet), and 7.6 (four-proton multiplet).

1-Azido-2-iodo-1,1-diphenylethane (20g) was prepared from 1,1-diphenylethylene in 75% yield, colorless crystals, mp 54.5–55°, from ethanol. *Anal.* Calcd for $C_{14}H_{12}IN_3$: C, 48.15; H, 3.47. Found: C, 48.06; H, 3.40. The nmr spectrum (CCl_4) showed τ 2.71 (ten-proton singlet) and 6.05 (two-proton singlet).

1-Iodomethyl-1-azidocyclohexane (20h) was prepared from methylene cyclohexane in 85% yield as a colorless liquid. The nmr spectrum (CCl_4) showed τ 6.68 (two-proton singlet) and 8.4 (ten-proton multiplet).

1-Azido-1-*t*-butyl-2-iodoethane (23) was prepared from *t*-butylethylene in 76% yield as a colorless liquid. The nmr spectrum (CCl_4) showed τ 5.85–6.40 (three-proton multiplet) and 8.87 (nine-proton singlet).

1-Azido-3,3-dimethyl-1-butene (24) was prepared in 80% yield from 1-azido-1-*t*-butyl-2-iodoethane (**23**). The nmr spectrum (CCl_4) showed τ 4.45 (two-proton quartet with J = 15 cps) and 8.97 (nine-proton singlet).

1-Azido-2-iodo-1,2-diphenylethylene (26) was prepared from diphenylacetylene. The crude iodo azide was titurated with methanol and water to produce a 30% yield of pale yellow crystals, mp 74° dec. An analytical sample obtained from methanol had mp 76° dec. Caution: this should not be heated neat; it is very unstable and decomposes explosively. *Anal.* Calcd for $C_{14}H_{10}IN_3$: C, 48.43; H, 2.90. Found: C, 48.72; H, 3.18.

Competition Reaction with Cyclohexene and Methylcyclohexene. This was carried out in the usual manner only instead of adding 18.3 g of iodine monochloride, 16.25 g (0.100 mole) was added. This was followed by 8.214 g (0.100 mole) of cyclohexene and 9.617 g (0.100 mole) of methylcyclohexene. The reaction ran for 4.33 hr and was worked in the usual manner using one-half the normal amount of ether. The ether was removed *in vacuo* at room temperature. In a separate experiment it was determined that the rate of loss of cyclohexene under these conditions is approximately twice that of methylcyclohexene. The analysis of the olefins was carried out with Aerograph 200 (flame ionization detector) using a 5-ft 5% S.E. 30 on Chromosorb W 60–80 mesh capillary column at 80°. The analysis indicated that the ratio of cyclohexene to methylcyclohexene remaining was 1:2.5 corrected for losses in work-up.

1-Phenyl-1-azido-2-iodo-3-phenyl-3-propanone (37) was prepared from chalcone. The crude reaction mixture was poured into 250 ml of 5% $Na_2S_2O_3$ solution rather than water, and the solid produced was filtered and air-dried producing a quantitative yield of pale yellow crystals, mp 100–103°. An analytical sample from ethanol had mp 100–102°. *Anal.* Calcd for $C_{15}H_{12}IN_3O$: C, 47.76; H, 3.21; N, 11.14; Found: C, 47.91; H, 3.34; N, 11.18. The nmr spectrum ($CDCl_3$) showed τ 2.7 (ten-proton multiplet) and 4.64 (two-proton quartet, J = 11 cps).

Methyl 3-azido-2-iodo-3-phenylpropionate (35) was prepared from methyl cinnamate in 43% yield as colorless crystals obained by triturating the crude iodo azide with methanol and water, mp 45–50°. An analytical sample from benzene–cyclohexane had mp 49.5–50.5°. *Anal.* Calcd for $C_{10}H_{10}IN_3O_2$: C, 36.14; H, 3.22; N, 12.83. Found: C, 36.25; H, 3.02; N, 12.68. The nmr spectrum ($CDCl_3$) showed τ 2.57 (five-proton singlet), 5.24 (two-proton quartet, J = 11 cps), and 6.13 (three-proton singlet).

Elimination of Methyl 3-Azido-2-iodo-3-phenylpropionate (35). To 11.6 g of methyl 3-azido-2-iodo-3-phenylpropionate was added 30 g of potassium hydroxide in 100 ml of methanol. The reaction was stirred at room temperature for 12.5 hr. The solvent was removed *in vacuo* with slight heating, and the colorless paste was dissolved in water and made acidic with 20% HCl. The cloudy suspension was extracted with ether. These extracts were combined and dried over magnesium sulfate. Removal of the ether produces a semisolid that was crystallized from benzene–cyclohexane giving 2.3 g of a pale yellow solid, mp 127–135°. Recrystallization from ethanol produced colorless crystals, mp 136.5–138° (lit.[25] 137°). The infrared spectrum was identical with an authentic sample of phenylpropiolic acid.

3,4-Diphenylisoxazole (38). To 7.52 g of the iodo azide adduct of chalcone was added 2.24 g of 1,4-diazabicyclo[2.2.2.]octane in 80 ml of dry benzene. The reaction mixture was wrapped in aluminum foil and placed in a dark drawer for 49.5 hr. Removal of the benzene *in vacuo* (protected from light) left a brown semisolid that when triturated with cyclohexane produced 2.49 g of light brown crystals, mp 135–140°. Recrystallization from benzene–cyclohexane gave mp 142–143° (lit.[26] 141–142°). Infrared, nmr, and ultraviolet spectral data are in agreement with the known isoxazole structure.

3-Azido-4-iodocyclooctene (44) was prepared from cyclooctadiene in 72% yield. The nmr spectrum (CCl_4) showed τ 4.4 (two-proton multiplet), 5.7 (two-proton multiplet), and 8.0 (eight-proton multiplet).

2-Azido-1,3-cyclooctadiene (45) was prepared from 3-azido-4-iodocyclooctene (**44**) in 50% yield as a pale yellow liquid. The nmr spectrum (CCl_4) showed τ 4.2 (two-proton multiplet) and 4.67 (one-proton triplet, J = 8.5 cps).

3,4-Iminocyclooctene (46). To a stirred slurry of 3.00 g of $LiAlH_4$ in 80 ml of dry ether cooled in an ice bath was added 9.56 g of 3-azido-4-iodocyclooctene in 10 ml of dry ether over 2 hr. The reaction mixture was warmed to room temperature and stirred for a total of 7.75 hr. The reaction mixture was then cooled in an ice bath and the excess $LiAlH_4$ was decomposed with 6 ml of 20% NaOH. The salts were filtered through Celite, and removal of the ether produced 2.13 g (49%) of a colorless liquid. The picrate derivative from ethanol had mp 170–172°. *Anal.* Calcd for $C_{14}H_{14}N_4O_7$: C, 48.00; H, 4.54. Found: C, 47.60; H, 4.54. The nmr spectrum (dimethyl sulfoxide-d_6) showed τ 4.5 (two-proton multiplet), 6.7 (two-proton multiplet), and 8.2 (eight-proton multiplet).

1-Phenyl-5-iodotetrazole (51) was prepared from phenylisonitrile (**49**). Instead of pouring the crude reaction mixture into 250 ml of water, the crude adduct was triturated with water and sodium thiosulfate was added. This produced a semisolid which proved to be 1-phenyl-5-iodotetrazole. The organic phase was diluted with ether and was washed with water. Removal of the solvents produced a semisolid which could be crystallized by the addition of water giving a total yield of 67%, mp 145–147°, from ethanol. *Anal.* Calcd for $C_7H_5IN_4$: C, 30.90; H, 1.85; N, 20.60. Found: C, 31.03; H, 2.14; N, 20.33.

4-Iodobenzalaniline was prepared from benzalaniline and IN_3 as colorless crystals, mp 83–84° (lit.[27] 82–84°), from ethanol. *Anal.* Calcd for $C_{13}H_{11}NI$: C, 50.67; H, 3.60; N, 4.55. Found: C, 50.80; H, 3.43; N, 4.63.

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