Nitrene Insertion into a C–H Bond at an Asymmetric Carbon Atom with Retention of Optical Activity. Thermally Generated Nitrenes

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This work is concerned with the nature of the electronic state of the reacting nitrene. Three different types of optically active azides were prepared, an o-azidoalkylbenzene, an alkyl azidocarbonate, and an alkanesulfonyl azide. Pyrolysis of the azides led in each case to cyclization at the asymmetric carbon atom to give an indoline, an oxazolone, and a sultam, respectively. The indoline and oxazolone were shown still to be optically active, and thus it was concluded that cyclization occurs by a one-step process involving a singlet state nitrene.

Introduction

During the past several years, there has been a growing interest in the chemistry of the electron-deficient monovalent nitrogen species widely referred to as a nitrene.[1] The chemistry of a nitrene depends very much upon the group bonded to the nitrogen atom. Five kinds of nitrenes have been recognized: aryl,[2] sulfonyl,[3] acyl,[4] possibly vinyl,[5] and, tentatively, alkyl.[6] A good illustration of the effect a substituent has on a nitrene reaction is seen in the different reactions of benzene with benzenesulfonylnitrene (I)[3b,c] and carbethoxynitrene (II).[4c]
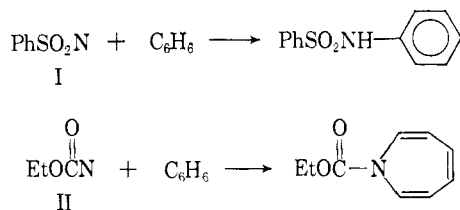
The former leads merely to a substitution at the C–H bond by the nitrene nitrogen, while the latter involves attack of the nitrene on one of the double bonds of the benzene ring. A reasonable explanation of these observed differences is that the two nitrenes, I and II, are reacting in different electronic states, in one case as a triplet and in the other as a singlet. The available evidence concerning the nature of arenesulfonylnitrene reactions is somewhat contradictory. A case for radical-like reactions, presumably involving the triplet state, can be made from the results of a study of orientation effects and relative rate factors in the reaction of I with substituted benzenes.[3b,c] However, the distribution of products from the reaction of I with anthracene[3a] —which leads mainly to substitution at the 1- rather than the 9- position—was rationalized by postulating a single-state nitrene intermediate. Recent kinetic

evidence obtained from a study[7] of the reaction of aryl and alkyl nitrenes supports the triplet state or radical hypothesis for these reacting nitrenes.

With but one exception,[4c] nitrenes have been generated either by photolysis or pyrolysis of organic azides. Under the usual conditions, the nitrenes thus formed appear to have a short life time. However, at liquid nitrogen temperatures, solid solutions of aryl and sulfonyl nitrenes prepared by photolysis of the corresponding azides appear to be stable indefinitely, and, indeed, are believed to possess triplet electronic ground states.[8]

Nothing definitive is known about the electronic state of the reacting nitrene. This work was undertaken with the objective of examining this point. By studying the insertion reaction of various types of thermally generated nitrenes at an asymmetric carbon atom and determining the extent of retention of configuration, one could gain some insight into the nature of the reacting species.

Results

The three optically active azides, 1-azido-2-(2-methylbutyl)benzene (III), 2-methylbutyl azidoformate (IV), and 3-methylpentane-1-sulfonylazide (V), were synthesized and thermally decomposed to give the products indicated.
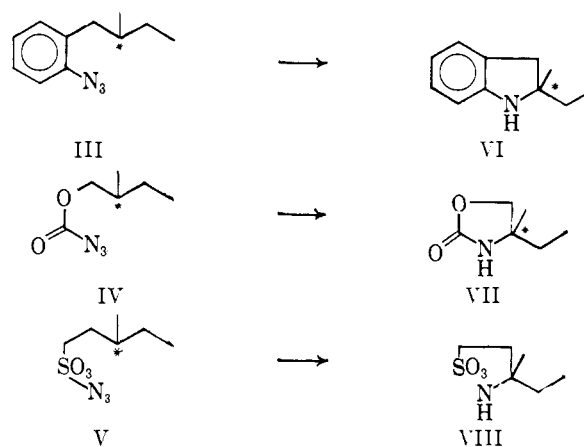
Pyrolysis of III in the vapor phase or in diphenyl ether solution resulted in formation of optically active 2-ethyl-2-methylindoline (VI) in yields of 50–60%. Vapor phase pyrolysis of IV gave 4-ethyl-4-methyloxazol-2-one (VII) in 68% yield, while pyrolysis of V gave

(1) For a review see L. Horner, Angew. Chem. Intern. Ed. Engl., 2, 599 (1963); R. A. Abromovitch and B. A. Davis, Chem. Rev., 64, 149 (1964).

(2) G. Smolinsky, J. Org. Chem., 26, 4108 (1961); (b) J. Am. Chem. Soc., 83, 2489 (1961); (c) ibid., 82, 4717 (1960); (d) P. A. S. Smith, et al., ibid., 84, 480 (1962); (e) J. Org. Chem., 23, 524 (1958); (f) J. Am. Chem. Soc., 75, 6335 (1953); (g) ibid., 73, 2545, 2626 (1951); (h) ibid., 73, 2438 (1951); (i) L. Horner, A. Christmann, and A. Gross, Chem. Ber., 96, 399 (1963).

(3) (a) J. F. Tilney-Bassett, J. Chem. Soc., 2517 (1962); (b) J. F. Heacock and M. T. Edmison, J. Am. Chem. Soc., 82, 3460 (1960); (c) O. C. Dermer and M. T. Edmison, ibid., 77, 70 (1955).

(4) (a) J. W. ApSimon and O. E. Edwards, Can. J. Chem., 40, 896 (1962); (b) L. Horner and A. Christmann, Chem. Ber., 96, 388 (1963); (c) W. Lwowski, et al., J. Am. Chem. Soc., 85, 1200 (1963); (d) Tetrahedron Letters, No. 7, 277 (1962); (e) K. Hafner and C. Koenig, Angew. Chem., 75, 89 (1963).

(5) (a) G. Smolinsky, J. Org. Chem., 27, 3557 (1962); (b) J. Am. Chem. Soc., 83, 4483 (1961).

(6) The results reported in the paper on the photolysis of alkyl azides by D. H. R. Barton and L. R. Morgan, Jr., (J. Chem. Soc., 3313 (1961)) have been found to be nonreproducible.

(7) P. Walker and W. A. Waters, ibid., 1632 (1962).

(8) (a) G. Smolinsky, E. Wasserman, and W. A. Yager, J. Am. Chem. Soc., 84, 3220 (1962); (b) G. Smolinsky, I. C. Snyder, and E. Wasserman, Rev. Mod. Phys., 35, 576 (1963); (c) E. Wasserman, G. Smolinsky, and W. A. Yager, J. Am. Chem. Soc., in press.

a mixture of sultams which resisted all attempts at separation.

Products VI and VII were purified by gas phase chromatography and were shown to be free of any contaminants. The structure of each of the products was established by elemental analysis and n.m.r. spectroscopy. The n.m.r. spectra of VI and VII (Table II) clearly show the pattern associated with a methyl and ethyl group bonded to a quaternary carbon atom. Table I lists the optical rotations of the pyrolysis products and also the rotation of 2-amino-2-methylbutanol-1 (IX), which was obtained by alkaline hydrolysis of VII.

TABLE I

OPTICAL ROTATIONS AT SEVERAL WAVE LENGTHS[a]

Compd.	[M]²⁵λ in degrees			
	589 mμ	546 mμ	500 mμ	436 mμ
VI (vapor reaction)[b]	−15.0	−17.4	−20.7	−24.4
VI (soln. reaction)[c]	−9.71	−11.2	−13.2	−15.6
VII[d]	+0.457	+0.661	+1.01	+1.98
IX[e]	+3.49	+4.12	+4.98	+6.59

[a] The rotations were determined with a Rudolph photoelectric spectropolarimeter using a 1 dm. × 0.4 m. tube, water jacketed, with silica end-plates. [b] Concentrate = 25.655 g./100 ml. of cyclohexane. [c] Concentrate = 22.675 g./100 ml. of cyclohexane. [d] Concentrate = 32.437 g./100 ml. of ethanol. [e] Concentrate = 26.547 g./100 ml. of ethanol.

TABLE II

N.M.R. SPECTRAL ASSIGNMENTS[a]

τ	Assignments[b]	Remarks
		Compound VI
3.4[c]	Ph	Complex multiplet
6.70	−NH−	Singlet
7.25[c]	Ph−CH₂−	An AB-type spectrum with main band splitting, J = 1, and very weak satellites having J = 29[d]
8.41[c]	−CH₂CH₃	Quartet, J ≈ 6.1
8.80	−CH₃	Singlet
9.19[c]	−CH₂CH₃	Triplet, J ≈ 6.1
		Compound VII
2.48	−NH−	Singlet, broadband
6.02[c]	−OCH₂−	An AB-type spectrum with main band very slightly split[d]
8.45[c]	−CH₂CH₃	Quartet, J ≈ 7.4
8.70	−CH₃	Singlet
9.05[c]	−CH₂CH₃	Triplet, J ≈ 7.4

[a] Spectra determined in carbon tetrachloride solutions. [b] All the assigned peaks had the required values for the integrated areas. [c] Center of multiplet. [d] Cf. J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 55, 56.

One of the by-products from the pyrolysis of III was 2,3-dimethyl-1,2,3,4-tetrahydroquinoline. This finding of closure to a six-membered ring is in contrast to an earlier report[2a] that pyrolysis of 1-azido-2-butylbenzene did not yield a six-membered ring product. Preliminary results from a reinvestigation of this earlier work indicates that the five-membered ring product is formed in approximately 40% yield while the six-membered ring product is formed in 10% yield.

The preparation of azide III began with a Friedel–Crafts acylation of benzene using the acid chloride prepared from optically active 2-methylbutanoic acid (X).[9] The resulting ketone XI[10] was reduced to the hydrocar-

bon XIIa[11] with sodium and alcohol in liquid ammonia.[12] Fractional distillation of the mononitrated[13] hydrocarbon gave 25% of the *ortho* derivative XIII, which was hydrogenated over palladized carbon to 2-(2-methylbutyl)aniline (XIV). This was converted to azide III in the usual way.[2h]

(+)(S)-2-Methylbutyl azidoformate (IV) was prepared from commercially available (−)(S)-2-methylbutanol-1 by allowing the alcohol to react first with phosgene followed by heating the resulting chloroformate with sodium azide in aqueous methanol.

Again starting with (−)(S)-2-methylbutanol-1, (+)-(S)-3-methylpentanol-1 (XV) was prepared.[14] This, after conversion to the tosylate, was heated with potassium thiocyanate[15] to give (+)(S)-3-methylpentyl-1-thiocyanate (XVI). Oxidation of XVI with an aqueous chlorine solution[16] to the sulfonyl chloride followed by treatment with sodium azide gave sulfonyl azide V.

Attempts to resolve racemic VI and VII with *d*-10-camphorsulfonic acid and *d*-tartaric acid in a variety of solvents were completely unsuccessful. Nor was any resolution achieved with brucine or ephedrine and the phthalamide derivative of VI.

The resolution of compounds whose asymmetry depends upon the presence of an ethyl and methyl group can prove difficult in spite of the fact that 2-aminobutane has been resolved with tartaric acid.[17] This type of compound has often been resolved indirectly. For example, optically active 2-butanol was prepared by first resolving 1-buten-3-ol followed by hydrogenation.[18]

Discussion

We are reporting the first examples of retention of optical activity during the insertion of a nitrene into a C–H bond at an asymmetric carbon atom. We believe this to be the first published report of maintenance of stereospecificity during an insertion reaction.[19] A complete mechanistic interpretation of these results necessitates the resolution of racemic VI and VII; however, it is worthwhile at this time to mention several implications of the work.

In the past, reactions of aryl nitrenes have been explained as free-radical reactions.[2a,b,7] The present work suggests that this assumption may not always be valid, and that nitrenes may also undergo direct insertion reactions. This situation is analogous to that in carbene chemistry where there appears to be more than one mechanism for bond formation.[20]

Triplet-state nitrenes very likely react by abstracting hydrogen atoms, forming separate radicals which eventually couple. However, a singlet-state nitrene might undergo direct insertion into a carbon–hydrogen bond.

(9) F. L. Weissenborn, *et al.*, *J. Am. Chem. Soc.*, **76**, 1792 (1954).

(10) P. J. Kohlbrenner and C. Schuerch, *ibid.*, **77**, 6066 (1955).

(11) D. Bryce-Smith and E. E. Turner, *J. Chem. Soc.*, 1975 (1950).

(12) A. J. Birch, *ibid.*, 809 (1945).

(13) K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951).

(14) (a) P. Pino, L. Lardicci, and L. Centoni, *J. Org. Chem.*, **24**, 1399 (1959); (b) L. Lardicci and P. Pino, *Gazz. chim. ital.*, **91**, 441 (1961).

(15) J. Kenyon, H. Phillips, and V. P. Pittman, *J. Chem. Soc.*, 1072 (1935).

(16) T. B. Johnson and I. B. Douglass, *J. Am. Chem. Soc.*, **61**, 2548 (1939).

(17) P. Bruck, I. N. Denton, and A. H. Lamberton, *J. Chem. Soc.*, 921 (1956).

(18) W. G. Yong and F. F. Caserio, *J. Org. Chem.*, **26**, 245 (1961).

(19) W. von E. Doering, in a paper presented at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, discussed the results of the reaction of methylene with optically active *sec*-butyl chloride and found the insertion product at the C–Cl bond to be 20% optically pure.

(20) See the discussion in J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 24.

One can argue that this latter process probably would result in retention of configuration about the reacting carbon atom, while the former process would not. The fact that the product from the vapor phase reaction of III has retained a greater degree of optical activity than that from the liquid phase reaction (see Table I) is consistent with the interpretation that it is the singlet state which is responsible for the stereospecificity observed during bond formation. This statement is based on the assumption that the rotation of VI obtained from the vapor phase reaction is very nearly that of optically pure VI, and thus the rotation of VI from the solution phase reaction differs significantly (see Table I). We feel moderately confident about the above assumption since the molecular rotation of 2-methylindoline is reported to be approximately $+10°$ in ethanol and in benzene solution and about $-18°$ in ether.[21] It is believed that aryl nitrenes are ground-state triplets,[8] and it is reasonable to expect a more facile singlet–triplet transition in solution than in the vapor phase.

An alternative, but we feel less likely, explanation for the observed retention of optical activity involves a biradical mechanism in which a triplet state nitrene abstracts the hydrogen atom from the asymmetric carbon atom followed by rapid radical recombination. This latter process would have to proceed faster than rotation about the carbon–carbon bond. This type of radical recombination could be due to a solvent cage effect in the case of the solution reaction or, in the case of the vapor reaction, to a surface effect. The result, however, is indistinguishable from that of a direct insertion process.

We feel that a reasonable picture of the transition state for the nitrene insertion process is

and
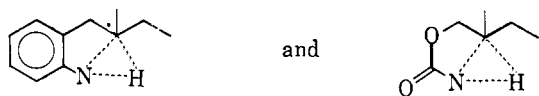
This mechanism predicts retention of configuration at the reaction site.

Work, now in progress, involves a system in which the optical activity is due to the presence of methyl and butyl, rather than methyl and ethyl groups, for it is felt that such a system will afford a greater chance of resolving racemic products. Thus, it is hoped, a more definitive conclusion concerning the nature of the nitrene reaction will be possible.

Experimental

$(+)(S)$-α-**Methylbutyric Acid (X).**—Commercially available, optically active 2-methylbutanol-1 was oxidized with alkaline permanganate[9] to the acid X, $\alpha^{29}D$ $+13.04°$ (l 1 dm., neat) (optical purity 93%).[22]

$(+)(S)$-α-**Methylbutyrophenone (XI).**—A solution of 102 g. (1 mole) of acid X in 100 ml. of thionyl chloride containing a drop of pyridine was stirred with gentle warming for 2 hr. and then distilled at atmospheric pressure. The fraction boiling 100–122° was added dropwise to a well stirred suspension of 150 g. (1.12 moles) of aluminum chloride in 2000 ml. of dry benzene maintained in a nitrogen atmosphere and cooled in an ice bath. When all the acid chloride had been added, the reaction turned dark green in color and became essentially homogeneous. Stirring was continued overnight at room temperature. In the morning the dark red reaction solution was cooled in an ice bath and decomposed with dilute hydrochloric acid. The organic

layer was separated, washed with water and 1 N potassium carbonate solution, dried over anhydrous potassium carbonate, and evaporated at reduced pressure. The residue was distilled at 20 mm. and the fraction boiling 110–130° weighed 120 g. (79%). The combined ketone XI[10] from several runs was fractionated through a 2-ft. spinning band column and the fraction boiling 132–133° (32 mm.) was collected: $\alpha^{25}D$ $+24.43°$ (l 1 dm., neat).

$(+)(S)$-(2-**Methylbutyl)benzene (XIIa).**—Hydrogenation of ketone XI in ethanol with 5% palladized carbon at ambient temperatures and 50 p.s.i. pressure proceeded to the alcohol stage and stopped. This alcohol in liquid ammonia containing 2 equivalents of ethanol was reduced to the hydrocarbon with 2 equivalents of sodium following the method of Birch.[12]

The combined hydrocarbon XIIa from several runs was fractionated through a 2-ft. spinning band column and the fraction boiling 100–101° (38 mm.) was collected: $n^{20}D$ 1.4884, $\alpha^{20}D$ $+5.80°$ (lit.[11] $n^{20}D$ 1.4891), total yield 70%.

dl-(2-**Methylbutyl)benzene (XIIb).**—dl-(1-Hydroxy-2-methylbutyl)benzene (b.p. 110–130° (22 mm.)) was prepared in 80% yield via a Grignard reaction of 2-bromobutane and benzaldehyde in ether solution. Hydrogenation of this alcohol in ethanol containing 1% perchloric acid with 5% palladized carbon at 60° gave the hydrocarbon XIIb, which after fractionation through a 2-ft. spinning band column had the properties. b.p. 101.5–102° (40 mm.), $n^{20}D$ 1.4883 (lit.[11] $n^{20}D$ 1.4891). The infrared spectra of the racemic and optically active (2-methylbutyl)-benzenes (XII) were identical.

Nitration of (2-Methylbutyl)benzene (XII).—Using the method of Nelson and Brown[13] both racemic XIIb and active XIIa, (2-methylbutyl)benzene, were mononitrated. The o- and p-nitro(2-methylbutyl)benzenes were separated by fractionation through a 2-ft. spinning band column. o-Nitro(2-methylbutyl)-benzene (XIII) was isolated in 25% yield, b.p. 159° (32 mm.), $n^{20}D$ 1.51868.

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.59; H, 7.85; N, 7.14.

p-Nitro(2-methylbutyl)benzene had b.p. 177° (32 mm.), $n^{20}D$ 1.52792.

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68,61; H, 7.60; N, 7.12.

(2-**Methylbutyl)aniline (XIV).**—Nitro compound XIII was hydrogenated in ethanol solution with 5% palladized carbon at ambient temperatures and 50 p.s.i. pressure. The amine XIV boiled at 141° (28 mm.) and had $n^{20}D$ 1.53112.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 81.07; H, 10.52; N, 8.41.

2-**Azido-1-(2-methylbutyl)benzene (III).**—Amine XIV was converted to azide III using procedure B of Smith and Brown[2h] with the following modifications: sodium nitrite was used in place of amyl nitrite in the diazotization step. The crude azide was extracted from the aqueous reaction mixture with petroleum ether (b.p. 30–60°) and the extracts washed well with water and carbonate solution, dried, and evaporated at reduced pressure at 40–45°. Azide III was purified by passing its petroleum ether solution through a column of Merck alumina (wt. ratio 10:1). The infrared spectrum of III (neat) showed the usual[23] azide band at 4.7 μ. The active azide III had $[\alpha]D$ $+11.3°$.

$(+)(S)$-2-**Methylbutyl Azidoformate (IV).**—Eighty-five grams (0.97 mole) of commercially available $(-)(S)$-2-methylbutanol-1 $[\alpha^{22}D$ $-3.71°$ (l 1 dm., neat), 77% optically pure] was added rapidly to 1000 g. of a stirred, cooled 12.5% benzene solution of phosgene (125 g., 1.26 moles) maintained in a nitrogen atmosphere. After all the alcohol had been added, cooling was continued for 30 min. and then the reaction was allowed to stand at room temperature overnight. In the morning, the benzene was removed at reduced pressure and the residue was stirred overnight with a solution of 70 g. of sodium azide in 400 ml. water–100 ml. methanol. This mixture was extracted with petroleum ether (b.p. 30–60°), the extracts were washed with water and carbonate solution, dried, and evaporated. The crude azidoformate weighed 117 g. (75%) and had infrared (neat) absorption at 4.64 (N_3) and 5.76 μ ($C=O$); the rotation, neat, in a 1-dm. tube was $\alpha^{21}D$ $+4.86°$.

2-**Methyl-2-nitrobutanol-1.**—To a paste formed from 650 mg. of calcium oxide and a few drops of water was added 200 g. (1.94 moles) of 2-nitrobutane.[24] To this stirred mixture was added

(21) W. J. Pope and G. Clarke, Jr., *J. Chem. Soc.*, **85**, 1332 (1904).

(22) A. Kjaer and S. E. Hansen, *Acta Chem. Scand.*, **11**, 898 (1957).

(23) E. Lieber, *et al.*, *Anal. Chem.*, **29**, 916 (1957).

(24) We wish to thank Mr. L. A. Seifert, Jr., of the Commercial Solvents Corp. for a generous sample of this compound.

dropwise over a period of about an hour 348 g. (4.1 moles) of 35% aqueous formaldehyde. The reaction mixture was warmed with a water bath and maintained at 25–30°. After 3 hr., the reaction solution was diluted with about 700 ml. of water, saturated with sodium chloride, and extracted with ether. The ether extract was dried over sodium sulfate and concentrated at reduced pressure. The residue on Claisen distillation was separated into two fractions: the first (b.p. 25–55° (25 mm.)) consisted mainly of starting nitrobutane, and the second (b.p. 110–123° (25 mm.)) of 2-methyl-2-nitrobutanol-1. A fractionation of the latter through a 2-ft. spinning band column resulted in obtaining relatively pure nitroalcohol in yields ranging between 50 and 70% as the fraction boiling 97–99° (12 mm.).

2-Amino-2-methylbutanol-1 (IX).—A solution of 25 g. (0.19 mole) of 2-methyl-2-nitrobutanol-1, 31 g. (0.38 mole) of sodium acetate, and 22 ml. (0.38 mole) of glacial acetic acid in 100 ml. of water–100 ml. of ethanol was shaken in a Parr apparatus in a hydrogen atmosphere in the presence of a few grams of Raney nickel. When hydrogen uptake ceased (about 10 hr.) the reaction was filtered and the filtrate diluted with 600 ml. of 1 M sodium hydroxide, saturated with potassium carbonate, and extracted with ether. The ether extract was dried over potassium carbonate and concentrated. A Claisen distillation at reduced pressure (12 mm.) gave material ot better than 98% purity as the fraction boiling 80–82°. The analytical sample was purified by gas phase chromatography (10 ft. × $^3/_8$ in. column packed with 10% Ucon Polar on HMDS-W) at 185°.

Anal. Calcd., for $C_6H_{13}NO$: C, 58.21; H, 12.70; N, 13.58. Found, C, 58.07; H, 12.93; N, 13.31.

The amino alcohol in benzene, containing 2 equivalents of triethylamine, was converted to racemic 4-ethyl-4-methyloxazol-2-one (VII) with a slight excess of phosgene.

(+)(S)-1-Chloro-2-methylbutane.—Commercially available (−)(S)-2-methylbutanol-1 (α^{22}D −4.12° (neat, l 1 dm.)) was converted to the chloride with thionyl chloride.[25]

(+)(S)-3-Methylpentanol-1 (XV).—The Grignard reagent[14a] of (+)(S)-1-chloro-2-methylbutane was treated with gaseous carbon dioxide to give 3-methylpentanoic acid which was reduced with lithium aluminum hydride (mole:mole) in ether using the method of Lardicci and Pino.[14b] The alcohol was obtained in 65% over-all yield: b.p. 152–153°, n^{25}D 1.4176, α^{24}D +6.31° (neat, l 1 dm.).[14a]

(S)-3-Methylpentyl 1-Tosylate.—Toluenesulfonyl chloride (152 g., 0.80 mole) was added in small portions with stirring to a solution of 73.6 g. (0.73 mole) of (+)(S)-3-methylpentanol-1 (XV) in 500 ml. of dry pyridine maintained at −5 to −10°. The reaction solution was then placed in the refrigerator overnight. In the morning the reaction mixture was poured onto 700 g. of cracked ice. This mixture was extracted twice with methylene chloride and the extracts washed successively with ice–water, cold 1 M sulfuric acid, and cold 1 M potassium bicarbonate solution, dried over sodium sulfate, and evaporated at reduced pressure at 40–45°.

(+)(S)-3-Methylpentyl 1-Thiocyanate (XVI).—Using the method of Kenyon, Phillips, and Pittman,[15] thiocyanate XVI was prepared by the action of potassium thiocyanate on (+)-(S)-3-methylpentyl 1-tosylate in ethanol; XVI was obtained in 90% yield, b.p. 93° (11 mm.), n^{26}D 1.4641, α^{27}D +27.5° (neat, l 1 dm).

Anal. Calcd. for $C_7H_{13}NS$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.91; H, 9.46; N, 10.01.

(S)-3-Methylpentane-1-sulfonyl Chloride (XVII).—Chloride XVII was prepared using the method of Johnson and Douglass[16] by bubbling chlorine into a cold aqueous mixture of (+)(S)-3-methylpentyl 1-thiocyanate (XVI); XVII was purified by fractionation through a 2-ft. spinning band column (b.p. 98° (7 mm.)) during which process it readily decomposed; yield 22%.

Anal. Calcd. for $C_6H_{13}SO_2Cl$: C, 39.02; H, 7.09; Cl, 19.20; S, 17.36. Found: C, 40.35; H, 7.27; Cl, 19.84; S, 16.96.

(S)-3-Methylpentane-1-sulfonyl Azide (V).—3-Methylpentane-1-sulfonyl chloride (XVII, 27.0 g., 0.15 mole) was added dropwise to 23.8 g. (0.29 mole) of potassium azide in 200 ml. of 50% aqueous ethanol. The reaction was stirred overnight in a nitrogen atmosphere. After dilution with an equal volume of water, the product was extracted with petroleum ether (b.p. 30–60°). The extract was washed twice with 1 N potassium carbonate and

water, dried, and evaporated at reduced pressure (40–45°). The weight of azide V was 26.4 g. (95% yield). The infrared spectrum (neat) showed azide absorption[23] at 4.65 μ.

Pyrolysis of Azides.—Solution phase pyrolysis of the azides was accomplished in diphenyl ether as described previously.[2b] Vapor phase pyrolysis of the azides was accomplished in an apparatus described earlier[2a] with a few minor modifications: the products were trapped at ice–acetone temperatures, and the two azides III and V were sucked into the top of the reaction tube through a fine capillary.

Pyrolysis of 1-Azido-2-(2 methylbutyl)benzene (III).—It was found that 10-g. vapor-phase runs could be made before it proved necessary to clean the pyrolysis tube of decomposition products. The pyrolysate was Claisen distilled (b.p. 105–125° (20 mm.)) and accounted for 80% of the material. Preparative scale gas phase chromatography (10 ft. × $^3/_8$ in. column packed with 10% Ucon Polar on 68/80 HMDS-W) at 200° separated the distillate into five components. The first, a cleanly eluted compound, in 60% yield, proved to be 2-methyl-2-ethylpyrrolidine (VI). The ultraviolet spectrum[26] in cyclohexane had two maxima: ϵ_{244} 8900, ϵ_{299} 3000; two minima: ϵ_{223} 2800, ϵ_{267} 570; in ethanol, again, two maxima: ϵ_{243} 7900, ϵ_{296} 2500; and minima: ϵ_{221} 2900, ϵ_{243} 1000. The remaining four components overlapped considerably.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.93; H, 9.38; N, 8.69. Found for VI: C, 81.81; H, 9.23; N, 8.49. Found for combined fractions 2–5: C, 82.11; H, 9.66; N, 8.59.

The benzamide of VI separated very slowly (24 hr.) from hexane in dense crystals, m.p. 78°.

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.24; H, 6.96; N, 5.09.

The derivative prepared from phthalic anhydride and VI recrystallized from ethanol–water and had m.p. 148–150°.

Anal. Calcd. for $C_{19}H_{19}NO_3$; C, 73.76; H, 6.19; N, 4.53. Found: C, 73.91; H, 6.18; N, 4.49.

After separating the diphenyl ether,[2b] the products obtained from the solution phase pyrolysis were purified as described above. The yield of VI was again about 50–60%.

Dehydrogenation.—Two milliliters ot the combined fractions 2–5 obtained from the above reaction were heated at 200° for 20 hr. in the presence of 50 mg. of 10% palladized carbon while sweeping the mixture with nitrogen. The cooled reaction mixture was diluted with benzene, filtered, and the filtrate concentrated. Gas phase chromatography (as described above) resolved the concentrate into four compounds (1, 65, 11, 23%). The second compound was shown to be o-(2-methylbutyl)-aniline (XXX) while the last was identified by mixture melting point and an infrared comparison with an authentic sample[27] as 2,3-dimethylquinoline.

Pyrolysis of (+)(S)-2-Methylbutyl Azidoformate (IV).—The azidoformate (20 g., 0.14 mole) was introduced into the pyrolysis tube in the vapor phase (see above). The pyrolysate (14.5 g., 81%) was subjected to gas phase chromatography (10 ft. × $^3/_8$ in. column packed with 10% Versamide 900 on 60/80 KOH washed W) and resolved into five components over a programmed temperature range of 195–240°. The first compound eluted in 68% yield was 4-ethyl-4-methyloxazol-2-one (VII). The infrared spectrum (neat) shonwed absorption at 3.1 (NH) and 5.7 μ (C=O).

Anal. Calcd. for $C_6H_{11}NO_2$: C, 55.79; H, 8.58; N, 10.85. Found: C, 55.94; H, 8.51; N, 10.99.

A mixture of 1.92 g. (14.9 mmoles) of the oxazolone VII was boiled for 17 hr. with 60 ml. of 3 M sodium hydroxide in a nitrogen atmosphere. After saturating with potassium carbonate, the reaction mixture was extracted with ether. The ether extracts were washed with dilute hydrochloric acid, the acid wash was made alkaline with sodium hydroxide saturated with carbonate and extracted with ether. After drying over potassium carbonate, the ether extracts were evaporated at reduced pressure to give 1.4 g. (94%) of 2-amino-2-methylbutanol-1 (IX); IX was subjected to gas phase chromatography (10 ft. × $^3/_8$ in. column packed with 10% Ucon Polar on HMDS-W) at 180° and was eluted in approximately 12 min. This material was identical with that synthesized *via* the nitro alcohol (see above).

(25) H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2566 (1942).

(26) T. Masamune, *ibid.*, **79**, 4418 (1957).
(27) H. B. Nisbet and A. M. Pryde, *J. Inst. Fuel*, **27**, 58 (1954). We wish to thank Dr. H. B. Nisbet for a sample of the dimethylquinoline.