The acetylide was then immediately treated with 1 ml of 10% sulfuric acid in 10 ml of ethanol and allowed to stand overnight. The solution was concentrated *in vacuo* and diluted with benzene. The benzene solution was extracted with 10% sodium bicarbonate solution and dried over anhydrous sodium sulfate. Evaporation of the solvent *in vacuo* gave 231 mg of crude oil. The product was chromatographed in benzene over neutral Woelm alumina (activity grade 2, 10 g). Elution of the column with benzene gave 72.4 mg of oil (one spot on tlc). Elution with ether–hexane gave 11.3 mg more of the above compound **33**: ν_{max} ($CHCl_3$) 1748, 1724, 1642, and 1235 cm^{-1}; the nmr spectrum contained, besides the usual signals due to methyls and acetates, a low-field proton at τ 4.67 ascribable to the hydrogen α to the ester group.

A second compound was obtained (31.1 mg) by elution of the column with 150 ml of ether: ν_{max} ($CHCl_3$) 3534 (OH), 1750–1700, and 1235 cm^{-1} (broad).

A third compound was eluted with methanol–ether (1:1, 200 ml): ν_{max} ($CHCl_3$) 3675 (OH), 1705 (unsaturated ester), and 1630 cm^{-1} (C=C), no acetate absorption. Treatment of this compound (56.4 mg) with acetic anhydride and pyridine in the usual manner gave a crude oil. The acetate derivative proved to have an infrared spectrum identical with that of the first compound eluted from the column (**33**).

A solution of the above ester **33** (79 mg) in glacial acetic acid (5 ml) was refluxed 4 hr with 27 mg of freshly sublimed selenium dioxide. The acetic acid was removed *in vacuo* leaving 74 mg of darkly colored oil; chromatography over 5 g of activity grade 3 neutral alumina and elution with benzene yielded 51 mg of a pure solid compound, **34**, mp 144–145°; ν_{max} (KBr) 1760 (lactone), 1740 (acetate), 1640 (C=C), and 1240 cm^{-1} (acetate). The infrared (CCl_4) and mass spectra and mobilities on tlc were identical with those of an authentic sample obtained by the degradation of andrographolide.

Acknowledgment. We wish to thank Professor M. P. Cava for providing a sample of the naturally derived unsaturated lactone **3** and Dr. Robert Highet for determination of several mass spectra. We acknowledge the helpful suggestions of Dr. P. C. Parthasarathy in preliminary phases of this work. We thank Mr. Lawrence Pelavin for the preparation of compounds **18a** and **18b**. This work was supported in part by Grant GP-690 from the National Science Foundation.

A General Method for Synthesizing Optically Active 1,3-Disubstituted Allene Hydrocarbons[1,2]

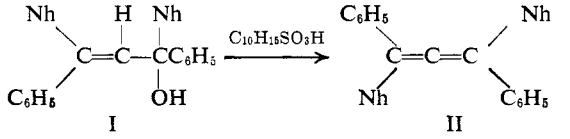
Johnny M. Walbrick, John W. Wilson, Jr., and W. M. Jones[3]

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32601. *Received October 25, 1967*

Abstract: Optically active 1,3-diphenylallene, $[\alpha]^{25}D$ +459°, 5,6-nonadiene, $[\alpha]^{28}D$ −7.5°, 3,4-heptadiene, $[\alpha]^{25}D$ +11.2°, and 2,3-pentadiene, $[\alpha]^{25}D$ −25.3°, have each been prepared in high yield from the corresponding ethyl N-nitroso-N-(*trans*-2,3-disubstituted cyclopropyl)carbamates *via* the corresponding diazocyclopropanes. The nitrosocarbamates were prepared from the *trans*-2,3-disubstituted cyclopropanecarboxylic acids which were resolved using standard bases. This method appears to be the first general route into optically active 1,3-disubstituted allene hydrocarbons. Routes through other diazocyclopropane precursors were shown to be lower yield processes.

Although molecular dissymmetry, and hence potential optical activity, in allenes was recognized as early as 1875,[4] they have been found to be surprisingly difficult to synthesize.[5] This has been especially true in the case of allene hydrocarbons (in which the molecule contains no resolving "handle"). In fact, although isolated cases have appeared, no general method for their preparation has been reported to date.

The first resolution of an active allene hydrocarbon involved the asymmetric synthesis of (+)- and (−)-1,3-diphenyl-1,3-di-α-naphthylallene (II) from the tetraarylallyl alcohol I using *d*-camphorsulfonic acid as the dehydrating agent.[6] The resulting allene was reported as being "feebly dextrorotatory." That this represented



I II

low optical purity was demonstrated by simple recrystallization to give the allene of high optical rotation, $[\alpha]^{17}_{5641}$ +437°. An attempted generalization of this method (replacement of one naphthyl by tolyl or pentadeuteriophenyl) was not successful.[7]

A particularly ingenious synthesis of optically active allene hydrocarbons is that of Jacobs, in which two active 1,3-diarylallenes, IV, were obtained by chromatographing inactive 1,3-diarylpropynes, III, on a column

(1) Based upon dissertations submitted by J. M. Walbrick and J. W. Wilson, Jr., to the Faculty of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) A preliminary account of this work has been presented: W. M. Jones, J. W. Wilson, Jr., and F. B. Tutwiler, *J. Am. Chem. Soc.*, **85**, 3309 (1963).

(3) Alfred P. Sloan Fellow, 1963–1967.

(4) For a comprehensive review of the chemistry of allenes, see H. Fischer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, Chapter 13.

(5) For reports in the literature before 1930 of unsuccessful attempts to prepare optically active allenes, see K. Zeigler and W. Sauermilch, *Chem. Ber.*, **63**, 1851 (1930); A. Lapworth and E. Wechsler, *J. Chem. Soc.*, 38 (1910); O. Dimroth and H. Feuchter, *Chem. Ber.*, **36**, 2238 (1903); C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, **49**, 546 (1927). For examples of resolutions of allenes containing resolving groups, see E. P. Kohler, J. T. Walker, and M. Tishler, *ibid.*, **57**, 1743 (1935); E. P. Kohler and W. J. Whitcher, *ibid.*, **62**, 1489 (1940); J. H. Wotiz and R. J. Palchak, *ibid.*, **57**, 2619 (1935).

(6) P. Maitland and W. H. Mills, *J. Chem. Soc.*, 987 (1936).

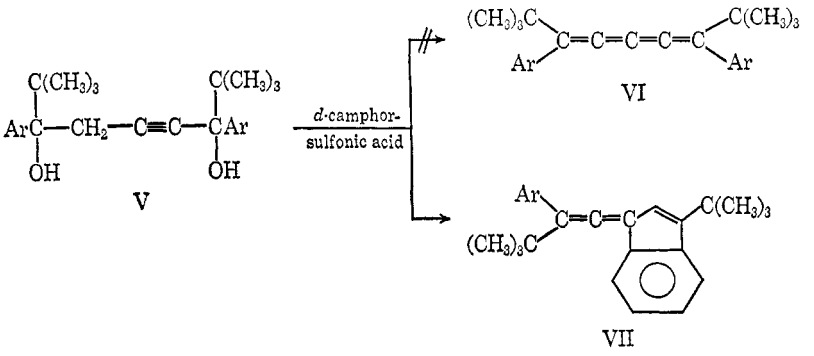
(7) G. R. Clemo, R. Raper, and A. C. Robson, *ibid.*, 431 (1939).

of alumina impregnated with brucine.[8] Again, at least one (*vide infra*) and probably both of the allenes

$$\underset{\text{III}}{ArC{\equiv}CCH_2Ar} \xrightarrow[\text{alumina}]{\text{brucine on}} \underset{\text{IV}}{ArCH{=}C{=}CHAr}$$

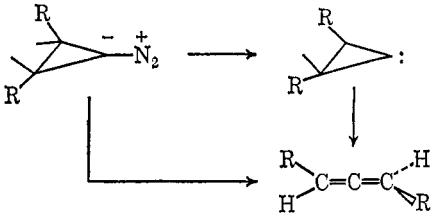
were of low optical purity ($[\alpha]^{23}D$ +2.48° for 1,3-diphenylallene and $[\alpha]^{24}D$ +8.5° for 1-(*p*-biphenyl)-3-phenylallene).

Finally, a group of Japanese workers reported the preparation of optically active 1,5-diphenyl-1,5-di-*t*-butylpentatetraene (VI) by dehydration of the dialcohol V with *d*-camphorsulfonic acid.[9] However, this was later shown to be the indenoallene VII, another example of an optically active allene hydrocarbon,[10] and again, the allene was of low optical rotation ($[\alpha]_{5641}$ +11°) even after fractional recrystallization.



Thus, to the best of our knowledge, in all cases the method of preparation of optically active allene hydrocarbons has involved asymmetric induction and, as is rather typical of resolutions involving asymmetric induction, all products (initially isolated) were probably of very low optical purity.

In previous studies on the chemistry of diazocyclopropanes and cyclopropylidenes, it has been found that both species collapse to allenes.[11-14] It occurred



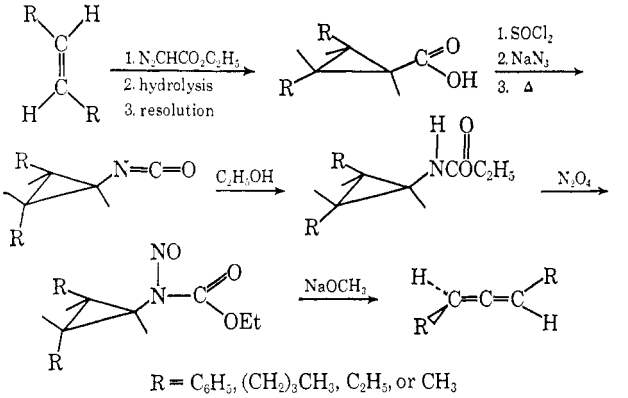
to us that if the dissymmetry in optically active diazocyclopropanes and/or the corresponding carbenes were retained during the collapse to the allene, then this could afford a simple route to optically active allene hydrocarbons. As a synthetic method, this seemed highly attractive for several reasons. First, cyclopropanecarboxylic acids, the diazocyclopropane precursors (Scheme I), are readily available by simple addition of carbethoxycarbene to an appropriate alkene. Second, the acid contains an excellent resolving handle which is removed as a natural course of the steps that follow. Third, although conversion of the cyclopropane acids to the corresponding allenes involves several steps, they are all straightforward reactions that would be expected to occur in high yields.

The purpose of this paper is to report the results of a study of the conversion of a series of optically active *trans*-2,3-dialkyl- and -diaryl-substituted cyclopropanecarboxylic acids to the corresponding 1,3-disubstituted allenes in which it has been found that the above-mentioned expectations were fulfilled.

Results and Discussion

The *trans*-2,3-diphenylcyclopropyl system was chosen to test the feasibility of this method as well as to optimize experimental conditions. The desired optically active acid[15] was prepared from *trans*-stilbene and ethyl diazoacetate, followed by resolution *via* its quinine salt, as shown in Scheme I (R = C_6H_5). Further steps to the

Scheme I



R = C_6H_5, $(CH_2)_3CH_3$, C_2H_5, or CH_3

isocyanate were also essentially routine. Reaction of the isocyanate with alcohols, ammonia, or Grignard reagents gave the corresponding methyl, ethyl, benzyl, and benzhydryl carbamates, the urea, the acetamide, and the benzamide. Of these, the corresponding carbamates were found to give the highest over-all yields in the combined steps including nitrosation and conversion to the allene. Several carbamates were prepared in an attempt to obtain the N-nitroso derivative as a crystalline material; however, each was obtained as an uncrystallizable yellow oil. The ethyl carbamate was arbitrarily chosen for further study. Using this carbamate, 1,3-diphenylallene was obtained from optically active *trans*-2,3-diphenylcyclopropanecarboxylic acid in an over-all yield of

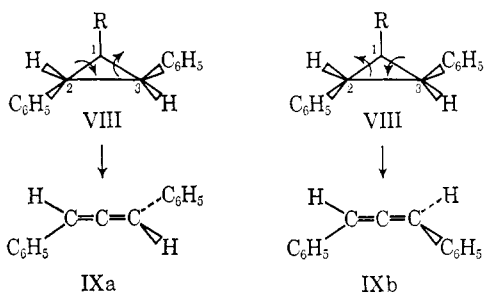
(8) T. L. Jacobs and D. Danker, *J. Org. Chem.*, **22**, 1424 (1957).
(9) M. Nakagawa, K. Shingu, and K. Naemura, *Tetrahedron Letters*, 802 (1961).
(10) R. Kuhn and B. Schulz, *Angew. Chem.*, **74**, 292 (1962).
(11) W. M. Jones and M. H. Grasley, *Tetrahedron Letters*, 927 (1962); W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).
(12) W. M. Jones, M. H. Grasley and D. G. Baarada, *ibid.*, **86**, 912 (1964); D. L. Muck and W. M. Jones, *ibid.*, **88**, 74 (1966).
(13) W. M. Jones, D. L. Muck, and T. K. Tandy, Jr., *ibid.*, **88**, 68 (1966); W. M. Jones and D. L. Muck, *ibid.*, **88**, 3798 (1966).
(14) P. S. Skell and R. R. Engel, *ibid.*, **89**, 2912 (1967), and references included therein.
(15) I. A. D'yakonov, M. I. Komendantov, K. H. Fu, and G. L. Korichev, *J. Gen. Chem. USSR*, **32**, 917 (1962).

56% in two crops of crystals showing specific rotations of +459 and 405° ([α]^{25}D in hexane). Although the activity is relatively high, the allene is apparently far from optically pure as evidenced by the fact that simple recrystallization from hexane raised the specific activity of one sample to 1020°.[16]

The generality of this synthetic route was tested by changing the nature of the R groups (Scheme I). Since the retention of dissymmetry probably has a steric origin,[2,17] attention was focused on smaller groups. Specifically, the *trans*-2,3-di-*n*-butyl, -diethyl, and -dimethylcyclopropyl systems were prepared by the addition of ethyl diazoacetate to the appropriate *trans* olefins and subjected to the same reaction sequence as shown in Scheme I. For the *trans*-2,3-di-*n*-butyl system, the acid, [α]^{25}D −2.78°, gave 5,6-nonadiene, [α]^{28}D −7.5°. *trans*-2,3-Diethylcyclopropanecarboxylic acid, [α]^{23}D +1.74°, gave 3,4-heptadiene, [α]^{25}D +11.2°, and *trans*-2,3-dimethylcyclopropanecarboxylic acid, [α]^{25}D −10.0°, gave 2,3-pentadiene, [α]^{25}D +25.3°. In all cases optically active allenes were obtained in good yield; thus, this method appears to be general for the synthesis of optically active 1,3-disubstituted allene hydrocarbons. Furthermore, it is potentially applicable to the synthesis of other types of optically active allenes. Work is in progress to explore its generality.

The factors governing the maintenance of molecular dissymmetry in the ring-opening process as well as the relative configurations of the cyclopropane and the allene have been discussed previously for the *trans*-2,3-diphenylcyclopropyl system[2,17] and hence will not be dealt with in detail at this point. However, to briefly review the principal points, the formation of an optically active product indicates that in at least one of the allene precursors (diazocyclopropane or cyclopropylidene)[18] some rotation around the 1–2 and 1–3 bonds must occur prior to or concomitant with the ring-opening process which involves breaking of the 2–3 bond. Furthermore, the orthogonality of the double bonds in the product requires that this rotation be conrotatory; a disrotatory mode would lead to a planar product. As shown in Scheme II each of the two distinguishable conrotatory ring-opening processes leads to a different enantiomer of the allene. The preferred direction of conrotatory opening cannot be predicted

Scheme II



R = N_2 or electron pair

on symmetry grounds[19] but can be predicted using the simple steric argument that the controlling factor during the ring-opening process is the interaction between groups on C-2 and C-3. Thus in Scheme II a preference for the formation of enantiomer IXa over enantiomer IXb from VIII would be predicted. In accord with this proposal is the finding that *trans*-2,3-diphenyldiazocyclopropane (or *trans*-2,3-diphenylcyclopropylidene) of absolute configuration VIII (as determined by an unequivocal chemical correlation on the starting acid[17]) yielded predominantly (+)-1,3-diphenylallene of structure IXa (as determined by circular dichroism studies of Mason and Vane[20]). Investigation of this reaction sequence as a possible method to determine the absolute configurations of 1,3-dialkylallenes is in progress.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected; boiling points are also uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137B Infracord or a Beckman Model IR10 infrared spectrophotometer. Unless otherwise specified, the infrared data are given for the IR10 instrument. Nuclear magnetic resonance spectra were run in dilute carbon tetrachloride solution (unless otherwise stated) on a Varian A-60A or 4300-2 spectrometer using tetramethylsilane as an internal reference. Chemical shifts are recorded as parts per million on the τ scale, coupling constants as cycles per second. Nuclear magnetic resonance data are recorded in the order: chemical shift (multiplicity, where s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, coupling constant) integration and interpretation. Optical rotations were measured in 1-dm tubes with a Perkin-Elmer Model 141 high-precision digital read-out polarimeter. Concentrations are given in g/ml. The elemental analyses were performed by Dr. Harry W. Galbraith, Galbraith Laboratories, Inc., Knoxville, Tenn. Analytical thin layer chromatography was accomplished on 2 × 8 in. plates coated in this laboratory with 0.25-mm layers of Merck silica gel HF_{254} using ultraviolet detection. Gas–liquid partition chromatography was performed on three instruments manufactured by Wilkins Instrument and Research, Inc., Walnut Creek, Calif. The analytical gas–liquid partition chromatography (glpc) was accomplished on Models 600-B and 600-D "Hi-Fi" gas chromatographs, each equipped with a hydrogen flame ionization detector and employing nitrogen as a carrier gas. The majority of the preparative work was accomplished on a Model A-350-B dual-column, temperature-programming-gas chromatograph fitted with a thermistor detector and employing helium as a carried gas. The instrument was fitted by the manufacturers with accessory parts from a Model A-700 automatic preparative gas chromatograph which allowed automatic injection and collection of samples. Column specifications and operating conditions of these instruments are specified in the individual experiments. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU6E mass spectrometer. Ultraviolet determinations were run on a Cary Model 15 double-beam recording spectrometer employing silica cells.

(±)-1-Carbethoxy-*trans*-2,3-diphenylcyclopropane. The procedure of D'yakonov, *et al.*,[15] was used for the addition of ethyl diazoacetate to *trans*-stilbene (Koch-Light Laboratories, Pure Grade) to yield 62 g (70% based on reacted stilbene) of the ester as a light yellow liquid, bp 175–193° (3.5 mm), n^{21}D 1.5639 (lit.[15] bp 136–142° (0.2 mm), n^{20}D 1.5623).

(±)-*trans*-2,3-Diphenylcyclopropanecarboxylic Acid. Saponification of 63 g of the corresponding ethyl ester according to the procedure of D'yakonov, *et al.*,[15] yielded, after crystallization from ethanol–water, 42.3 g (75%) of the acid as a white crystalline solid, mp 156.5–157.5° (lit.[15] mp 155–157°).

Resolution of *trans*-2,3-Diphenylcyclopropanecarboxylic Acid. The procedure of D'yakonov[15] was used. From 10.0 g of racemic acid, 3.92 g (39%) of the (−) acid, [α]^{27}D −22.8° (*c* 0.0136, 95% ethanol), mp 134–137° (lit.[15] [α]^{20}D −23.87° (*c* 0.00023, alcohol), mp 136–137°), and 3.47 g (35%) of the (+) acid, [α]^{25}D +21.9° (*c* 0.0183, 95% ethanol), mp 134–136° (lit.[15] [α]^{20}D +23.70° (*c* 0.00021, alcohol), mp 136–137°), were obtained.

(16) The starting acid was probably optically pure. This point is being tested by the isotope dilution method.

(17) W. M. Jones and J. W. Wilson, Jr., *Tetrahedron Letters*, 1587 (1965).

(18) Experiments are in progress.

(19) Private communication from R. Hoffmann.

(20) S. F. Mason and G. W. Vane, *Tetrahedron Letters*, 1593 (1965).

(−)-Ethyl N-(*trans*-2,3-Diphenylcyclopropyl)carbamate. In a typical preparation, 40 ml (0.56 mol) of thionyl chloride was added to 13.3 g (0.0559 mol) of (−)-*trans*-2,3-diphenylcyclopropanecarboxylic acid, $[\alpha]^{25}D$ −20.8° (*c* 0.0288, 95% ethanol). The mixture was stirred at room temperature for 1 hr, after which all traces of thionyl chloride were removed by distillation under reduced pressure. To the residual acid chloride was added 150 ml of dry acetone. The mixture was stirred and cooled in an ice bath. To the cold solution was rapidly added 5.2 g (0.080 mol) of sodium azide dissolved in a minimum amount of water. The mixture was stirred with cooling for 1 hr after which it was poured into water and extracted with ether. The ether layer was dried over magnesium sulfate. This ether solution of the acid azide was added dropwise to 200 ml of dry refluxing benzene. After the addition was complete the benzene solution was refluxed until nitrogen evolution ceased. The benzene solution was cooled in an ice bath and 100 ml of absolute ethanol added. The mixture was then heated to 40–50° for 1 hr. Removal of the solvent by use of a rotary evaporator and crystallization of the resulting brown oil from ethanol–water gave 13.9 g (89%) of the carbamate as a white solid, mp 82–84°, $[\alpha]^{28}D$ −68.2° (*c* 0.0269, 95% ethanol). Successive recrystallizations from ethanol–water gave an analytical sample, mp 85.5–86°; infrared: λ_{max}^{KBr} 3350 (N–H), 1690 (carbonyl), 1600, 750, 690 cm^{-1} (phenyls); nmr: τ 2.70 (m) 10 phenyls, 5.33 (s) 1 hydrogen attached to nitrogen, 5.92 (q) 2 methylene adjacent to oxygen, 6.82 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.40 (m) 2 hydrogens of cyclopropane carbons adjacent to phenyls, 8.84 (t) 3 methyl.

Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.53; H, 6.95; N, 5.10.

(−)-Ethyl N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate. The general procedure of White and Aufdermarsh[21] was used with modifications. A mixture of 0.200 g (0.712 mmol) of (−)-ethyl N-(*trans*-2,3-diphenylcyclopropyl)carbamate, $[\alpha]^{25}D$ +67.0° (*c* 0.0186, 95% ethanol), 0.50 g of anhydrous sodium acetate, 0.35 g of anhydrous sodium sulfate, and 20 ml of dry methylene chloride was cooled to −20°, and a solution of 1.5 *M* dinitrogen tetroxide in ether (prepared by bubbling the gas into a tared volumetric flask about one-half full of ether at −50° and noting the increase in weight) was added with a syringe through a rubber septum in 0.30-ml portions until the blue color remained over a 5-min period. The excess dinitrogen tetroxide and some solvent were removed *in vacuo*, and 15 ml of cold ether was added. The reaction mixture was then washed once with cold saturated sodium chloride solution, twice with cold 5% sodium bicarbonate–saturated sodium chloride solution, and once again with cold saturated sodium chloride solution. The organic layer was dried over sodium sulfate and evaporated at room temperature by use of a rotary evaporator to a yellow oil. This oil was chromatographed over a column of deactivated silica (prepared by slowly packing the silica with water-saturated ether and eluted with dry 50% pentane–ether) to give 0.205 g (93%) of the N-nitrosocarbamate as a yellow oil, $[\alpha]^{25}D$ −240° (*c* 0.051, ether); infrared: λ_{max}^{film} 1760 (carbonyl), 1600, 760, 695 cm^{-1} (phenyls); no N–H absorption of the unnitrosated carbamate was present; nmr: τ 2.69 (m) 10 phenyls, 5.79 (q) 2 methylene adjacent to oxygen, 7.11 (s) 3 cyclopropane hydrogens, 8.77 (t) 3 methyl. The N-nitrosocarbamate was shown to be homogeneous by tlc (pentane–ether eluent).

(+)-1,3-Diphenylallene. To a solution of 0.890 g (2.87 mmol) of ethyl N-(*trans*-2,3-diphenylcyclopropyl)carbamate, $[\alpha]^{25}D$ −240° (*c* 0.051, ether), in 75 ml of hexane at room temperature in a closed reaction vessel, there was added 0.45 ml of a 5.60 *M* solution of sodium methoxide in methanol with a syringe through a rubber septum. Gas evolution began in 2 min and continued for 1 hr, at which time 70 ml (99%) of gas had been evolved. Analysis of an aliquot by glpc using a 0.125 in. × 5 ft column packed with 6% Apieson L on 60–80 mesh Gas-Chrom Z at 150° with an inlet pressure of 30 psig showed a 93% yield of the allene. The chromatogram showed only one other component with a retention time greater than that of the allene when programmed to 250°, and this component amounted to only 2% of the amount of the allene by integral ratio. The reaction mixture was column chromatographed over silica (purified hexane eluent). Concentration of the allene-containing fractions *in vacuo* and cooling overnight in a Dry Ice bath yielded 0.267 g of the allene, $[\alpha]^{25}D$ +459° (*c* 0.0076, hexane). Concentration of the filtrate yielded a second crop of the allene, 0.081 g, $[\alpha]^{25}D$ +405° (*c* 0.0062, hexane), mp 51–52° (lit.[7] for racemic allene, mp 49–51°; found for racemic allene, mp 53–54°). Combination of the two crops yielded 0.348 g (63%) of 1,3-diphenylallene: infrared: λ_{max}^{KBr} 1930 cm^{-1} (allene) (lit.[6] 1947 cm^{-1}); nmr: τ 2.75 (m) 10 phenyls, 3.57 (s), 2 olefinic hydrogens; mass spectrum: parent ion peak *m/e* 192; ultraviolet: $\lambda_{max}^{95\% \text{ ethanol}}$ 255 mμ (ε 38,100) (lit.[7] $\lambda_{max}^{95\% \text{ ethanol}}$ 255 mμ (ε 52,200)). Three recrystallizations from hexane yielded 1,3-diphenylallene, $[\alpha]^{25}D$ +1020° (*c* 0.0055, absolute ethanol).

(+)-*trans*-2,3-Di-*n*-butylcyclopropanecarboxylic Acid. The procedure of D'yakonov and Kostikov[22] was used. From 29.0 g of *trans*-5-decene (Aldrich Chemicals) 15.8 g (48% based on reacted decene, 39% over-all) of the acid was obtained as a colorless liquid, bp 127° (1.20 mm) (lit.[21] 116° (1 mm)).

Resolution of (±)-*trans*-2,3-Di-*n*-butylcyclopropanecarboxylic Acid. A mixture of 3.60 g (18.2 mmol) of (±)-*trans*-2,3-di-*n*-butylcyclopropanecarboxylic acid and 3.00 g (18.1 mmol) of ephedrine was dissolved in 100 ml of benzene and heated to 60° for 45 min. The mixture was then evaporated to a volume of 25 ml by passing a stream of dry nitrogen over the warm solution. Addition of 75 ml of hexane and cooling in the refrigerator overnight gave 0.90 g of the diastereomer as a solid white mass, mp 89–90°. Concentration and cooling of the filtrate yielded a second crop of the diastereomer, 2.20 g, to give a total 3.1 g (47%). This diastereomer was then dissolved in 50 ml of a 2% sodium hydroxide in 50% methanol–water solution, and the mixture was heated at 40–50° for 2 hr. Approximately one-half of the solvent was removed, and the mixture was allowed to cool overnight. The precipitated ephedrine was then removed by filtration. The filtrate was washed with ether to remove the final traces of ephedrine. The water layer was acidified to pH 2 with 10% sulfuric acid and extracted with ether. Drying over magnesium sulfate and removal of the solvent yielded 1.52 g (89% from diastereomer) of the acid, $[\alpha]^{25}D$ −2.78° (*c* 0.4005, 95% ethanol). Saponification of the filtrate in like manner yielded the enantiomeric acid, $[\alpha]^{25}D$ +2.37° (*c* 0.1023, 95% ethanol).

(+)-Ethyl N-(*trans*-2,3-Di-*n*-butylcyclopropyl)carbamate. This carbamate was prepared in an identical manner with that described for ethyl N-(*trans*-2,3-diphenylcyclopropyl)carbamate. From 2.00 g (10.1 mmol) of (−)-*trans*-2,3-di-*n*-butylcyclopropanecarboxylic acid, $[\alpha]^{25}D$ −2.37° (*c* 0.1023, 95% ethanol), 2.34 g (96%) of the carbamate was obtained as a light tan liquid, $[\alpha]^{25}D$ +33.1° (*c* 0.031, 95% ethanol). Analytical glc using the 600-B instrument with a 0.125 in. × 5 ft column packed with 5% SE 30 on 60–80 mesh Chromosorb W with DMCS at 134° and an inlet pressure of 20 psig showed a major peak with a retention time of 12.2 min and a minor peak at 4.3 min. The minor peak was 7.8% of the mixture by area integration. An analytical sample was prepared by preparative glpc using a A-350-B instrument with a 0.25 in. × 10 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 173° and an inlet pressure of 50 psig. The carbamate was obtained as a colorless liquid; infrared: λ_{max}^{KBr} 3300 (N–H), 1705 cm^{-1} (carbonyl); nmr: τ 5.91 (q) 2 methylene adjacent to oxygen, 7.69 (p) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 8.3–9.7 (m) 23 remaining protons.

Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.67; H, 11.27; N, 5.80. Found: C, 69.51; H, 11.35; N, 5.59.

(−)-Ethyl N-Nitroso-N-(*trans*-2,3-di-*n*-butylcyclopropyl)carbamate. This N-nitrosocarbamate was prepared in an identical manner with that described for ethyl N-nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate. From 0.450 g (1.87 mmol) of (−)-ethyl N-(*trans*-2,3-di-*n*-butylcyclopropyl)carbamate, $[\alpha]^{25}D$ +33.1° (*c* 0.031, 95% ethanol), 0.503 g (100%) of the nitrosocarbamate was obtained as a yellow oil, $[\alpha]^{25}D$ +24.8° (*c* 0.1342, hexane); infrared (infracord): λ_{max}^{film} 1750 cm^{-1} (carbonyl), no absorption in the N–H region; nmr: τ 5.74 (q) 2 methylene adjacent to oxygen, 7.90 (q) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, and 8.3–9.7 (m) 23 remaining protons. The instability of this compound precluded its analysis.

(+)-5,6-Nonadiene. A solution of 0.450 g (1.67 mmol) of (+)-ethyl N-nitroso-N-(*trans*-2,3-di-*n*-butylcyclopropyl)carbamate, +24.8° (*c* 0.1342, hexane), in 25 ml of anhydrous ether was cooled to 0° in a closed reaction vessel for minitoring gas evolution. A 0.088-g (0.00165 mol) portion of sodium methoxide was then added and the reaction flask quickly stoppered. After the induction period of 1 min, 36 ml (90%) of gas was given off in a 30-min period. The mixture was then stirred for an additional 30-min.

(21) E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174, 1179 (1961).

(22) I. A. D'yakonov and R. R. Kostikov, *J. Gen. Chem. USSR*, **34**, 1385 (1964).

The reaction mixture was chromatographed over 15 g of silica (hexane eluent). The first 120 ml of eluent contained two major and one minor components as shown by glpc using the 600-D instrument with a 0.125 in. × 5 ft column packed with 5% SE 30 on 60–80 mesh Chromosorb W with DMCS at 82° and an inlet pressure of 20 psig. These components had retention times of 0.2, 1.3, and 2.2 min in the integral ratio of 1:6:30. The third component of the mixture, (+)-5,6-nonadiene, was separated by preparative glpc using the A-350-B instrument with a 0.25 in. × 10 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 106° and an inlet pressure of 50 psig. Under these conditions the allene had a retention time of 5.0 min. Separation yielded 0.620 g (51%) of (+)-5,6-nonadiene as a colorless liquid, $[\alpha]^{28}D$ +6.1° (*c* 0.022, carbon tetrachloride); infrared (Infracord): λ_{max}^{film} 1950 cm^{-1}; nmr: τ 5.01 (m) 2 olefinic hydrogens, 8.02 (m) 4 allylic methylenes, 8.68 (m) 8 central methylenes of butyl groups, 9.10 (m) 6 methyls. The allene was shown to be homogeneous by glpc using the above given conditions. The enantiomeric allene, (+)-5,6-nonadiene, $[\alpha]^{28}D$ −7.5° (*c* 0.0080, carbon tetrachloride), was obtained in an identical manner from the N-nitrosocarbamate, $[\alpha]^{25}D$ −38.5° (*c* 0.329, carbon tetrachloride).

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.53; H, 13.03.

(±)-Ethyl *trans*-2,3-Diethylcyclopropanecarboxylate. To a stirred solution of 51.5 g (0.613 mol) of *trans*-3-hexene (Farchan Research Laboratories) and 0.6 g of anhydrous copper sulfate heated to reflux by use of an oil bath, 51.0 g (0.447 mol) of ethyl diazoacetate was added at a rate of one drop every 2–12 sec. During the addition the heating bath was removed since the heat of reaction was sufficient to maintain reflux of the olefin. The mixture was allowed to reflux for an additional hour, allowed to cool to room temperature, and filtered to remove the catalyst. The residue was distilled to give 40.1 g (52%) of the ester as a colorless liquid, bp 63–80° (10 mm). Analytical glpc of this material on the 600-D instrument with a 0.125 in. × 5 ft column packed with 5% SE 30 on 60–80 mesh Chromosorb W with DMCS at 144° and an inlet pressure of 20 psig showed a major component with a retention time of 1.8 min and four minor components, one of which had a retention time identical with that of diethyl fumarate. The 63–80° fraction was dissolved in 200 ml of ether and shaken with portions of a 1% potassium permanganate solution until the permanganate solution was no longer decolorized. The mixture was filtered and the layers separated. The organic layer was dried over magnesium sulfate, the solvent removed on a rotary evaporator, and the remaining oil distilled to yield 29 g (38%) of the ester as a colorless liquid, bp 74° (13 mm); infrared (Infracord): λ_{max}^{film} 1710 cm^{-1} (carbonyl); nmr: τ 5.95 (q) 2 methylene adjacent to oxygen, 8.5–9.3 (m) 16 remaining protons.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 11.66. Found: C, 70.22; H, 11.47.

(±)-*trans*-2,3-Diethylcyclopropanecarboxylic Acid. A mixture of 27.9 g (0.196 mol) of (±)-ethyl *trans*-2,3-diethylcyclopropanecarboxylate, 11 g (0.275 mol) of sodium hydroxide, 15 ml of water, and 125 ml of methanol was heated at mild reflux for 8 hr. The solvent was removed by use of a rotary evaporator and the residue dissolved in 100 ml of water. Addition of 10% sulfuric acid to pH 2, extraction with ether, drying with magnesium sulfate, and removal of solvent by use of a rotary evaporator gave a dark oil which was distilled. The desired acid was obtained as a colorless liquid, 16.85 g (72%), bp 81° (0.40 mm); infrared (Infracord): λ_{max}^{film} 2650 (carboxyl), 1690 cm^{-1} (carbonyl); nmr: τ −1.15 (s) 1 carboxyl hydrogen, 8.3–9.3 (m) 13 remaining protons. Glpc analysis showed the acid to be homogeneous with a retention time of 0.9 min using the 600-D instrument with a 0.125 in. × 5 ft column packed with 20% SE 30 on 60–80 mesh Chromosorb W at 137° and an inlet pressure of 20 psig.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.80; H, 9.97.

Resolution of (±)-*trans*-2,3-Diethylcyclopropanecarboxylic Acid. To a solution of 9.85 g (30.3 mmol) of quinine in 100 ml of 95% ethanol, 8.0 g (56.2 mmol) of (±)-*trans*-2,3-diethylcyclopropanecarboxylic acid was added. The solution was heated to reflux for 10 min and then diluted with 250 ml of 20% ethanol. Slow cooling to room temperature followed by cooling in the refrigerator overnight yielded 12.0 g of the diastereomer as a white solid. Recrystallization of this material from hot 60% ethanol yielded 5.8 g (59%) of the diastereomer, mp 126–127°. A mixture of 5.8 g (12.4 mmol) of the diastereomer dissolved in 30 ml of methanol, 60 ml of a solution of 4% sodium hydroxide in methanol, and 60 ml of water was heated at 50° for 3 hr. The mixture was evaporated at reduced pressure to a volume of 50 ml, cooled to room temperature, and filtered to remove the precipitated quinine. The filtrate was washed with ether to remove the last traces of quinine, then acidified to pH 2 with 10% sulfuric acid. Extraction with ether, drying with magnesium sulfate, and removal of the solvent by use of a rotary evaporator yielded 2.05 g (25%) of the acid as a colorless liquid, $[\alpha]^{26}D$ −4.55° (*c* 0.0314, 95% ethanol). The filtrates from the first two crystallizations of the diastereomer were combined and saponified in an identical manner to give 5.19 g (65%) of the acid, $[\alpha]^{23}D$ +1.74° (*c* 0.110, 95% ethanol).

(−)-Ethyl N-(*trans*-2,3-Diethylcyclopropyl)carbamate. This carbamate was prepared in an identical manner with that described for ethyl N-(*trans*-2,3-diphenylcyclopropyl)carbamate. From 2.0 g (14.1 mmol) of (+)-*trans*-2,3-diethylcyclopropanecarboxylic acid, $[\alpha]^{23}D$ +1.74° (*c* 0.110, 95% ethanol), 1.714 g (66%) of the carbamate was obtained as a light brown liquid, $[\alpha]^{24}D$ +44.2° (*c* 0.0184, methanol). Glpc analysis on the 600-D instrument using a 0.125 in. × 5 ft column packed with 5% SE 30 on 60–80 mesh Chromosorb W with DMCS at 128° and an inlet pressure of 20 psig showed a major component (90%) with a retention time of 4.5 min and a minor component (10%) with a retention time of 0.9 min. The major peak was isolated by preparative glpc using the A-350-B instrument with a 0.25 in. × 10 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 163° and an inlet pressure of 50 psig (retention time 5.6 min) as a colorless liquid; infrared (Infracord): λ_{max}^{film} 3270 (N–H), 1690 cm^{-1} (carbonyl); nmr: τ 5.94 (q) 2 methylene adjacent to oxygen, 7.70 (p) 1 hydrogen on cyclopropane carbon adjacent to oxygen, 8.3–9.8 (m) 15 remaining protons.

Anal. Calcd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56. Found: C, 65.03; H, 10.51; N, 7.64.

(+)-Ethyl N-Nitroso-N-(*trans*-2,3-diethylcyclopropyl)carbamate. This N-nitrosocarbamate was prepared in an identical manner with that described for ethyl N-nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate. From 0.104 g (0.562 mmol) of (−)-ethyl N-(*trans*-2,3-diethylcyclopropyl)carbamate, $[\alpha]^{24}D$ +44.2° (*c* 0.0184, methanol), 0.118 g (98%) of the N-nitrosocarbamate, $[\alpha]^{25}D$ +35.7° (*c* 0.112, ether), was obtained as a yellow liquid; infrared (Infracord): λ_{max}^{film} 1750 cm^{-1} (carbonyl), no absorption in the N–H region; nmr: τ 5.33 (q) 2 methylene adjacent to oxygen, 7.98 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 8.3–9.5 (m) 15 remaining hydrogens. The instability of this compound precluded its analysis.

(+)-3,4-Heptadiene. To a solution of 0.347 g (1.62 mmol) of (+)-ethyl N-nitroso-N-(*trans*-2,3-diethylcyclopropyl)carbamate, $[\alpha]^{25}D$ +35.7° (*c* 0.122, ether), in 15 ml of petroleum ether, bp 20–40°, in a closed reaction vessel at 25°, 0.281 ml of a 5.76 *M* solution of sodium methoxide in methanol was added with a syringe through a rubber septum. After gas evolution ceased, the reaction mixture was evaporated to one-half of its original volume and chromatographed over 5 g of silica (petroleum ether, bp 20–40°, eluent). Two components were rapidly eluted as was shown by glpc analysis of the chromatography fractions on the 600-D instrument on a 0.125 in. × 5 ft column packed with 5% SE 30 on 60–80 mesh Chromosorb W with DMCS at 43° and inlet pressure of 20 psig (retention times of 1.8 and 1.4 min). Isolation of the allene (the 1.8-min peak) was accomplished on the A-350-B instrument using a 0.25 in. × 10 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 67° with an inlet pressure of 50 psig to yield 0.070 g (45%) of the allene as a colorless liquid, $[\alpha]^{25}D$ +11.2° (*c* 0.00738, carbon tetrachloride); infrared (Infracord): λ_{max}^{film} 1970 cm^{-1} (allene); nmr: τ 4.90 (pentet with second-order splitting) 2 olefinic hydrogens, 8.05 (m) 4 methylenes of ethyl groups, 9.00 (triplet with second-order splitting) 6 methyls.

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.64; H, 12.35.

(±)-*trans*-2,3-Dimethylcyclopropanecarboxylic Acid. This synthesis was carried out in a cylindrical reaction vessel fitted with a quartz-jacketed, Hanovia Type L, 450-W, high-pressure (immersion type) mercury arc lamp with an outer Pyrex sleeve. Stirring was provided by bubbling a stream of dry nitrogen through the solution from a sintered-glass filter at the base of the vessel. The cooling jacket of the immersion assembly was cooled by circulating cold methanol which was cooled in a copper coil immersed in a Dry Ice–acetone bath. The outer portion of the reaction vessel was cooled in a Dry Ice–acetone bath. After flushing the vessel with dry nitrogen, 150 ml of *trans*-2-butene (Matheson, CP) was condensed into it. Ethyl diazoacetate was then added in approximately 6-ml portions, each followed by photolysis until the infrared spectrum of an evaporated aliquot showed only a weak 2050-cm^{-1} absorption.

After a total of 46 hr of photolysis, 34.7 ml (0.326 mol) of ethyl diazoacetate had been added. Evaporation of the solvent yielded 60 g of the crude ester as a dark oil, to which 60 g of potassium hydroxide, 250 ml of methanol, and 200 ml of water were added, and the mixture was heated on the steam bath for 3 hr. The methanol was removed by use of a rotary evaporator and the resulting aqueous solution acidified with 10% sulfuric acid to pH 2. Continuous extraction of this mixture with ether for 24 hr, followed by removal of the ether by distillation through a 15-cm Vigreux column, gave an oil which was distilled at reduced pressure through a 10-cm Vigreux column. The acid, 16.9 g (48% from ethyl diazoacetate), was obtained as a colorless liquid, bp 123° (47 mm); infrared (Infracord): λ_{max}^{film} 2600 (broad, carboxyl), 1695 cm^{-1} (carbonyl); nmr: τ −1.83 (s) 1 carboxyl hydrogen, 9.0 (m) 9 remaining protons. The acid was analyzed as its *p*-phenylphenacyl derivative, mp 84–85°.

Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 78.07; H, 6.77.

Resolution of (±)-*trans*-2,3-Dimethylcyclopropanecarboxylic Acid. To a solution of 12.0 g (37 mmol) of quinine in 100 ml of hot 95% ethanol, 8.0 g (70 mmol) of the acid was added. The mixture was heated to reflux for 15 min, then 400 ml of water was added. Cooling in the refrigerator for 2 days yielded 9.75 g (92%) of the white crystalline diastereomer, mp 133–135°. Recrystallization yielded 5.79 g (54%) of the diastereomer as clusters of white needles, mp 139–141°. This diastereomer and 5.61 g of potassium hydroxide were dissolved in 200 ml of 50% methanol–water and the solution heated on a steam bath for 5 hr. The methanol was removed by use of a rotary evaporator and the resulting aqueous solution continuously extracted with ether for 48 hr. The ether solution thus obtained was dried over magnesium sulfate and the ether removed by use of a rotary evaporator to yield 1.48 g (35%) of the acid, $[\alpha]^{25}D$ −10.0° (*c* 0.190, absolute ethanol). The filtrates from the first two crystallizations were combined and saponified in like manner to yield 4.36 g (54%) of the acid, $[\alpha]^{24}D$ +4.56° (*c* 0.0473, 95% ethanol).

(−)-Ethyl N-(*trans*-2,3-Dimethylcyclopropyl)carbamate. This carbamate was prepared in an identical manner with that described for ethyl N-(*trans*-2,3-diphenylcyclopropyl)carbamate with the exception that during the removal of excess thionyl chloride from the acid chloride, the oil was pumped at 60 mm for 1 hr, then at 30 mm for 10 min. From 1.47 g (12.9 mmol) of (−)-*trans*-2,3-dimethylcyclopropanecarboxylic acid, $[\alpha]^{25}D$ −10.0° (*c* 0.190, absolute ethanol), 0.641 g (32%) of a light brown liquid was obtained. Glpc analysis of this liquid on the 600-D instrument using a 0.125 in. × 7 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 131° and an inlet pressure of 20 psig showed a major component (92%) with a retention time of 2.8 min and a minor component (8%) with a retention time of 1.1 min. The major component was isolated by preparative glpc on the A-350-B instrument using a 0.25 in. × 6 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 121° and an inlet pressure of 50 psig as a colorless liquid, $[\alpha]^{25}D$ −54.2° (*c* 0.0430, methylene chloride); infrared (Infracord): λ_{max}^{film} 3350 (N–H), 1700^{-1} (carbonyl); nmr: τ 5.92 (q) 2 methylene adjacent to oxygen, 7.77 (p) 1 hydrogen on cyclopropane carbon adjacent to nitrogen, 8.6–9.7 (m) 11 remaining hydrogens.

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 61.32; H, 9.45; N, 8.64.

(−)-2,3-Pentadiene. Optically active ethyl N-nitroso-N-(*trans*-2,3-dimethylcyclopropyl)carbamate was prepared from the corresponding carbamate, $[\alpha]^{25}D$ −54.2° (*c* 0.0430, methylene chloride), by the same procedure used to prepare the corresponding *trans*-2,3-diphenyl compound. This N-nitrosocarbamate was dissolved in 35 ml of tetraglyme (distilled from lithium aluminum hydride) and the solution pumped on a vacuum system at 0.1 mm for 0.5 hr to remove any volatile impurities. After releasing the vacuum, 3.0 ml of a 1.93 *M* solution (5.79 mmol) of sodium triethyleneglycolate in triethylene glycol (prepared by treating sodium metal with dry triethylene glycol and pumping at 0.1 mm to remove volatile impurities) was added at room temperature. After 1 min, vigorous gas evolution began and continued for 10 min. The vacuum was then reapplied for 10 min while condensing the volatile materials in a 8 × 160 mm cold trap cooled in liquid nitrogen and located between the reaction vessel and the mechanical pump. Glpc analysis of the liquid collected (approximately 1 ml) on a Varian Aerograph A90-P3 gas chromatograph equipped for manual collection of samples using a 0.25 × 10 ft column packed with 10% TCEP on 60–80 mesh Chromosorb P at 27° and an inlet pressure of 20 psig showed three components with retention times of 2.2, 10.3, and 22.3 min in the integral ratio of 5:8:1. Collection of the 2.2-min peak in a cold trap cooled in liquid nitrogen gave 0.0529 g (20%) of the allene as a colorless liquid, $[\alpha]^{25}D$ −25.3° (*c* 0.0265, carbon tetrachloride); infrared (Infracord): λ_{max}^{film} 1970 cm^{-1} (allene) (lit.[23] 5.05 μ); nmr: τ 5.07 (pentet with second-order splitting) 2 olefinic hydrogens, 8.37 (pair of doublets, 6.8) 6 methyls (identical with both the calculated and experimental literature[24] values).

(±)-Methyl N-(*trans*-2,3-Diphenylcyclopropyl)carbamate. To a benzene solution of (±)-*trans*-2,3-diphenylcyclopropyl isocyanate prepared in the usual manner from 5.0 g (21 mmol) of the corresponding acid was added 50 ml of 1% sodium methoxide in methanol, and the mixture was refluxed for 48 hr. The solvent was removed by use of a rotary evaporator, and 50 ml of dry benzene was added to the remaining solid. The mixture was filtered to remove the sodium methoxide, and pentane added to the filtrate until the solution reached the cloud point. Cooling of this solution yielded 4.02 g (72% from the acid) of the light tan carbamate, mp 93–95°. Chromatography over silica (benzene eluent) followed by successive recrystallizations from benzene–pentane gave an analytical sample, mp 97–98°; infrared: λ_{max}^{KBr} 3400 (N–H), 1690 (carbonyl), 1600, 750, and 695 cm^{-1} (phenyls); nmr: τ 2.74 (m) 10 phenyls, 5.36 (s) 1 N–H, 6.43 (s) 3 methyl, 6.84 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.44 (m) 2 hydrogens of cyclopropane carbons adjacent to phenyls.

Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.20; H, 6.20; N, 5.38.

(±)-Benzyl N-(*trans*-2,3-Diphenylcyclopropyl)carbamate. To a benzene solution of (±)-*trans*-2,3-diphenylcyclopropyl isocyanate made in the usual manner from 4.0 g (16.8 mmol) of the corresponding acid was added 10.0 g (92.8 mmol) of benzyl alcohol. The mixture was stirred at room temperature for 3 hr and then refluxed for 12 hr. The solvent was removed by use of a rotary evaporator to yield a light-tan oil, which on crystallization from benzene–hexane gave 3.07 g (53% based on starting acid) of the carbamate as a white crystalline solid, mp 92–95°. Successive recrystallizations from ethanol–water gave an analytical sample in the form of white needles, mp 95–96°: infrared: λ_{max}^{KBr} 3390 (N–H), 1690 cm^{-1} (carbonyl); nmr ($CDCl_3$ solution): τ 2.75 (m) 15 phenyls, 4.98 (q, 12.9) 2 methylene adjacent to oxygen, 5.34 (s) 1 N–H, 6.81 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.42 (m) 2 hydrogens of cyclopropane carbons adjacent to phenyls.

Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.54; H, 6.32; N, 3.97.

(±)-Benzhydryl N-(*trans*-2,3-Diphenylcyclopropyl)carbamate. To a benzene solution of (±)-*trans*-2,3-diphenylcyclopropyl isocyanate made in the usual manner from 4.0 g (16.8 mmol) of the corresponding acid was added 10.0 g (54.4 mmol) of benzhydrol. The mixture was stirred at room temperature for 12 hr. The solvent was removed by use of a rotary evaporator to yield a light yellow oil which solidified when kept at a reduced pressure of 0.10 mm for 2 hr. Chromatography of this light yellow solid over silica (benzene eluent) to remove the excess benzhydrol yielded 4.50 g (64% based on starting acid) of the carbamate in the form of a white, fluffy solid, mp 137–139°. Successive recrystallizations from ethanol–water gave an analytical sample, mp 140–141; infrared: λ_{max}^{KBr} 3400 (N–H), 1690 (carbonyl), 1600, 749, and 696 cm^{-1} (phenyls); nmr ($CDCl_3$ solution): τ 2.73 (m) 20 phenyls, 3.10 (s) 1 benzhydryl methine, 5.26 (s) 1 N–H, 6.77 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.41 (m) 2 hydrogen of cyclopropane carbons adjacent to phenyls.

Anal. Calcd for $C_{29}H_{25}NO_2$: C, 83.03; H, 6.01; N, 3.34. Found: C, 83.20; H, 5.94; N, 3.34.

(±)-*trans*-2,3-Diphenylcyclopropylurea. Petroleum ether, 50 ml, bp 60–80°, was added to the benzene solution of (±)-*trans*-2,3-diphenylcyclopropyl isocyanate made in usual manner from 5.0 g (21.0 mmol) of the corresponding acid in a mechanically stirred reaction vessel. The solution was cooled to 0° and dry ammonia passed into the solution for 1 hr. During the course of the addition a voluminous light tan solid appeared. Another 50 ml of petroleum ether (bp 60–80°) was added and ammonia passed into the solution for an additional 3 hr. The light tan solid was filtered, washed with cold pentane, and dried under vacuum to give 4.25 g (81% based on starting acid) of the urea. Recrystallization from hot *t*-butyl alcohol yielded white platelets, mp 96–97.5°. Successive recrystallizations from hot butyl alcohol gave an analytical sample, mp 98–99°; infrared: λ_{max}^{KBr} 3440 (N–H), 3270 (N–H), 1650 (car-

(23) W. von E. Doering and P. M. La Flamme, *Tetrahedron*, **2**, 75 (1958).

(24) D. F. Koster and A. Danti, *J. Phys. Chem.*, **69**, 486 (1965).

bonyl), 1600, 750, and 690 cm^{-1} (phenyls); nmr ($CDCl_3$ solution): τ 2.74 (m) 10 phenyls, 4.84 (s) 1 hydrogen of secondary nitrogen, 5.15 (s) 2 $-NH_2$, 6.95 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.47 (m) 2 hydrogens of cyclopropane carbons adjacent to phenyls.

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.92; N, 6.36; N, 10.94.

(±)-N-(*trans*-2,3-Diphenylcyclopropyl)benzamide. A benzene solution of (±)-*trans*-2,3-diphenylcyclopropyl isocyanate made in the usual manner from 5.0 g (21.0 mmol) of the corresponding acid was cooled to 0° and maintained in an atmosphere of dry argon as 35.2 ml of a 2.2 *M* solution of phenylmagnesium bromide in ether was slowly added with stirring. After stirring 1 hr at 0°, the mixture was allowed to warm to room temperature and stirred an additional 3 hr, then cooled to 0° and 15 ml of a 5.4 *M* aqueous ammonium chloride solution slowly added. This mixture was stirred at 0° for 1 hr and at room temperature for 2 hr. The addition of 50 ml of water and 50 ml of benzene facilitated the separation of layers. The organic layer was separated and washed successively with 5% hydrochloric acid, 5% sodium bicarbonate, and water. Drying with magnesium sulfate and removal of solvent with a rotary evaporator yielded a light brown oil. This oil solidified when kept at reduced pressure (0.01 mm) overnight. The solid was leached with pentane and vacuum dried to give 4.30 g (62%) of the benzamide as a white solid, mp 149–152°. Successive recrystallizations from benzene–pentane gave analytically pure product, mp 157°; infrared: λ_{max}^{KBr} 3330 (N–H), 1630 (carbonyl), 1600, 750, and 695 cm^{-1} (phenyls); nmr ($CDCl_3$ solution): 2.70 (m) 15 phenyls, 3.64 (s) 1 N–H, 6.48 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.26 (m) 2 hydrogens of cyclopropane carbons adjacent to phenyls.

Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.19; H, 6.05; N, 4.38.

(±)-N-(*trans*-2,3-Diphenylcyclopropyl)acetamide. A benzene solution of (±)-*trans*-2,3-diphenylcyclopropyl isocyanate made in the usual manner from 5.0 g (21.0 mmol) of the corresponding acid was cooled to 0° and maintained in an atmosphere of dry argon as a solution of 0.0315 mol of methylmagnesium bromide in ether was slowly added with stirring. The mixture was stirred at 0° for 1 hr and then allowed to warm to room temperature, at which it was stirred for an additional hour. The mixture was then cooled to 0° and 8.6 ml of a 4.7 *M* aqueous ammonium chloride solution slowly added. This mixture was stirred at 0° for 0.5 hr and then allowed to warm to room temperature, at which it was stirred for an additional 2 hr. The organic layer was separated and washed successively with 5% hydrochloric acid, 5% sodium bicarbonate, and water. Drying over magnesium sulfate and removal of the solvent by use of a rotary evaporator yielded a dark oil which would not solidify. Chromatography of this oil over silica (eluted with pentane–benzene mixtures over the range of 100% pentane to 100% benzene) gave 1.48 g (28%) of the acetamide as a white solid, mp 106–131°. Successive recrystallizations from benzene–hexane gave analytically pure material, mp 128–130°; infrared: λ_{max}^{KBr} 3250 (N–H), 1640 (carbonyl), 1600, 740, and 695 cm^{-1} (phenyls); nmr ($CDCl_3$ solution): τ 2.77 (m) 10 phenyls, 3.89 (s) 1 N–H, 6.67 (m) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.44 (m) 2 hydrogens of cyclopropane carbons adjacent to phenyls, 8.29 (s) 3 methyls.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.45; H, 6.79; N, 5.68.

(±)-Methyl N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate. An identical procedure with that for the corresponding ethyl N-nitrosocarbamate was used to give an 83% yield of this N-nitrosocarbamate as a yellow oil; infrared: λ_{max}^{film} 1770 (carbonyl), 1600, 750, 695 cm^{-1} (phenyls), no absorption in the N–H region; nmr ($CDCl_3$ solution): τ 2.86 (m) 10 phenyls, 6.16 (s) 3 methyls, 7.08 (s) 3 cyclopropane hydrogens; homogeneous by tlc (pentane–ether eluent). The instability of this compound precluded its analysis.

(±)-Benzyl N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate. An identical procedure with that for the corresponding ethyl N-nitrosocarbamate was used to give an 80% yield of this N-nitrosocarbamate as a yellow oil; infrared: λ_{max}^{film} 1750 (carbonyl), 1600, 745, and 695 cm^{-1} (phenyls); no absorption in the N–H region; nmr ($CDCl_3$ solution): τ 2.70 (m) 15 phenyls, 4.79 (q, 12.7) 2 methylenes adjacent to oxygen, 7.15 (s) 3 cyclopropane hydrogens; homogeneous by tlc (pentane–ether eluent). The instability of this compound precluded its analysis.

(±)-Benzhydryl N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)-carbamate. An identical procedure with that for the corresponding ethyl N-nitrosocarbamate was used to give an 85% yield of this N-nitrosocarbamate as a yellow oil; infrared: λ_{max}^{film} 1760 (carbonyl), 1600, 760, and 695 cm^{-1} (phenyls); no absorption in the N–H region; nmr ($CDCl_3$ solution): τ 2.83 (m) 21 phenyls, 7.11 (s) 3 cyclopropane hydrogens; homogeneous by tlc (pentane–ether eluent). The instability of this compound precluded its analysis.

(±)-N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)urea. To a solution of 0.966 g (3.84 mmol) of (±)-*trans*-2,3-diphenylcyclopropylurea in 3.0 ml of a mixture of 70% acetic acid and 30% acetic anhydride was added 0.528 g (7.66 mmol) of sodium nitrite in 0.6 ml of distilled water over a 40-min period. The clear, light-green solution was then stirred at 0° for 6 hr. Addition of water caused the nitrosourea to precipitate as a light yellow gummy solid. This material was washed with a copious amount of water until the odor of acetic acid was no longer detectable. Grinding of the crude nitrosourea under 15 ml of petroleum ether and subsequent filtration yielded 0.43 g (40%) of a light yellow amorphous solid, mp 91–94.5° dec. Recrystallization from chloroform–petroleum ether yielded 0.15 g of the N-nitrosourea as a pale yellow amorphous solid, mp 109–110° dec; infrared: λ_{max}^{KBr} 3570 (N–H), 3400 (N–H), 1740 (carbonyl, split), 1600, 755, and 690 cm^{-1} (phenyls); nmr ($CDCl_3$ solution): τ 2.71 (m) 10 phenyls, 4.5 (m) 2 N–H, 6.73 (t) 1 hydrogen of cyclopropane carbon adjacent to nitrogen, 7.03 (d) 2 hydrogens of cyclopropane carbons adjacent to phenyls.

Anal. Calcd for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.37; N, 14.94. Found: C, 68.10; H, 5.47; N, 15.00.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.