filtered and concentrated. The residual solid was recrystallized (acetone–hexane) to separate 343.6 mg (81.2%) of the **diacid 3** as white needles, mp 196.5–198.5° dec. Recrystallization raised the decomposition point to 201–203°; ir (KBr pellet), 1705 cm^{-1} (carboxyl C=O); uv (95% EtOH), 300 mμ (ε 3390) with intense end absorption; nmr (pyridine-d_5), δ 12.8–14.2 (2 H br, carboxyl OH), AB pattern (*J* = 8.5 Hz) with estimated line position at 7.28 and 6.95 (2 H, aryl CH), 4.71 (1 H d, *J* = 7 Hz, $ArCHCO_2R$), 3.78 (3 H s, OCH_3), and 0.8–3.5 (10 H m, aliphatic CH).

Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.19; H, 6.25. Found: C, 66.52; H, 6.44.

A solution of 120 mg (0.415 mmol) of the diacid **3** and 574 mg (8.7 mmol) of KOH in 3.5 ml of $HOCH_2CH_2OH$ was refluxed under N_2 for 2.5 hr and then poured into H_2O, acidified, and extracted with CH_2Cl_2. After the organic extract had been dried and concentrated, the residual crystalline diacid **4** (95.9 mg or 79.8%, mp 184.5–186° dec) was recrystallized (acetone–hexane) to separate the diacid **4**, mp 187–188° dec, identified with the previously described sample by a mixture melting point and comparison of ir spectra.

A 166-mg sample of the diacid **3** was esterified with ethereal CH_2N_2 and the crude neutral product was distilled in a short-path still (0.05 mm and 140–150° bath) to yield 168 mg (92%) of the **diester 38** as a colorless liquid: ir ($CHCl_3$), 1735 cm^{-1} (ester C=O); uv (95% EtOH), 302 mμ (ε 3750) with intense end absorption (ε 27,700 at 210 mμ); nmr ($CDCl_3$), AB pattern (*J* = 8.5 Hz) with estimated line positions at δ 7.27 and 6.90 (2 H, aryl CH), 4.22 (1 H d, *J* = 6 Hz, $ArCHCO_2R$), 3.86, 3.79, 3.68 (three 3 H s, OCH_3), and 0.8–3.5 (10 H m, aliphatic CH); mass spectrum, molecular ion *m/e* 318, abundant fragments *m/e* 220, 206, 205, 126, 84, 83, 55, and 43.

Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.73; H, 7.06.

Metallation of the Alcohol 18.—A suspension of 2.501 g (10.8 mmol) of the alcohol **18** in 55 ml of hexane was treated with a hexane solution containing 11.9 mmol of *n*-BuLi. A solution was formed from which a new precipitate slowly separated. To this stirred suspension was added 1.443 g (12.4 mmol) of $(Me_2NCH_2-)_2$ and 12.4 mmol of *n*-BuLi in hexane solution. The resulting suspension was refluxed for 45 min and then added to excess Dry Ice with thorough agitation. The usual isolation procedure separated 981 mg of crude starting material in the neutral fraction and 2.077 g of crude acid product as an oil. This acidic product was esterified with ethereal CH_2N_2 to give 2.119 g of orange oil which contained[14] three components. Chromatography on SiO_2 separated an additional 326 mg of the starting alcohol **18** (eluted with Et_2O–PhH) followed by 245 mg of a liquid fraction (eluted with Et_2O–PhH) with ir and nmr absorption suggesting it to be a mixture of the ester **32** and the lactone **33**. Our efforts to obtain either of these components pure were unsuccessful.

Later chromatographic fractions (eluted with Et_2O–PhH) afforded 328 mg of crude ester **31** which was recrystallized (CH_2Cl_2–hexane). The pure **ester 31** separated as 246 mg of white needles: mp 115.5–116°; ir ($CHCl_3$), 3590, 3470 (OH), and 1720 cm^{-1} (ester C=O); uv (95% EtOH), 215 mμ (ε 34,500), 244 (9300), and 304 (4750); nmr ($CDCl_3$), δ 7.58 (1 H br s, aryl CH), 7.05 (1 H br s, aryl CH), 4.05 (2 H d, *J* = 3.5 Hz, CH_2OR), 3.88 (6 H s, OCH_3), and 0.7–3.5 (12 H m, OH and aliphatic CH); mass spectrum, abundant fragments *m/e* 57, 45, 44, 43, 41, 31, 29, 28, 18, and 17.

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.38; H, 7.64.

Registry No.—**1,** 19765-79-8; **2,** 19765-80-1; **3,** 19765-81-2; **4,** 19765-82-3; **6,** 19765-83-4; **8,** 19765-84-5; **9,** 19766-18-8; **10,** 19765-85-6; **11,** 19766-19-9; **12,** 19766-20-2; **13,** 19765-86-7; **14,** 19765-87-8; **15,** 19765-88-9; **16,** 19765-89-0; **17,** 19765-90-3; **18,** 19765-91-4; **19,** 19765-92-5; **21b,** 19765-93-6; **22,** 19765-94-7; **23,** 19765-95-8; **24,** 19779-41-0; **25,** 19765-96-9; **26,** 19766-21-3; **27,** 19779-42-1; **28,** 19765-97-0; **30,** 19765-98-1; **31,** 19765-99-2; **34,** 19766-00-8; **35,** 19766-22-4; **36,** 19766-23-5; **37a,** 19766-24-6; **37b,** 19766-01-9; **38,** 19779-43-2; **39,** 19766-02-0; **40,** 19766-03-1; **41,** 19766-04-2; **42,** 19766-05-3; **43,** 19766-25-7.

Notes

Effects of Solvent on the Cyclopropylidene–Allene Conversion[1]

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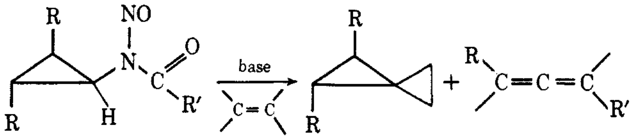
Received December 16, 1968

In previous investigations in these laboratories on the chemistry of substituted diazocyclopropanes and cyclopropylidenes, it was found that treatment of the N-nitrosourea or N-nitrosocarbamate of a cyclopropane with base in the presence of an alkene gives a very clean reaction yielding primarily two products, a spiropentane and an allene.[3-5] In an attempt to gain insight into the precursors of these products, the reaction using the 2,2-diphenylcyclopropyl system was studied in some detail.



From a variety of observations, it was concluded that both the spiropentane and the allene have the carbene as a common precursor. However, if this were the sole progenitor to both products, it was reasoned that a plot of the ratio of spiropentane to allene *vs.* the concentration of alkene should be linear. In fact, when such a plot was made (Figure 1), it showed a strong curvature.[5] Furthermore, although it was recognized that the curvature could arise from a solvent effect as a result of the large change in alkene concentration (1.14–11.35 *M*) the exceptionally good fit to

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[1] Based partly upon a dissertation submitted by J. M. Walbrick to the Faculty of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Alfred P. Sloan Fellow, 1963–1967.

[3] W. M. Jones, M. H. Grasley, and D. G. Baarda, *J. Am. Chem. Soc.*, **86**, 912 (1964); D. L. Muck and W. M. Jones, *ibid.*, **88**, 74 (1966); 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); for additional work on cyclopropylidenes, see P. S. Skell and R. R. Engel, *ibid.*, **89**, 2912 (1967), and references included therein.

[4] W. M. Jones, *ibid.*, **82**, 6200 (1960); W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *ibid.*, **85**, 2754 (1963).

[5] W. M. Jones and M. H. Grasley, *Tetrahedron Letters*, 927 (1962).

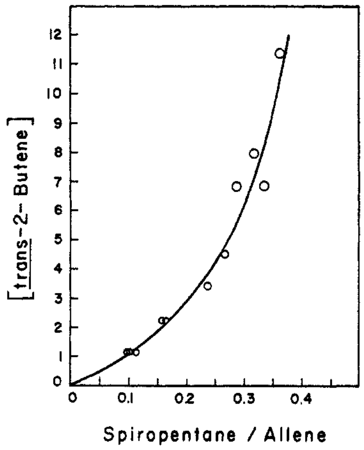
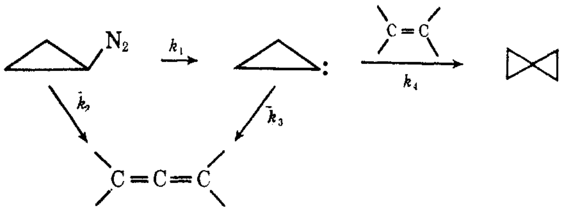


Figure 1.—Dependence of spiropentane/allene ratio on 2-butene concentration (diluted with n-heptane).

SCHEME I



the curve calculated from the more complex scheme (Scheme I) involving two different intermediates led us to prefer a reaction scheme in which both the diazocyclopropane and the carbene gave the allene.[5] At this time we report a variety of recent observations that lead us to the conclusion that the curve in Figure 1 does, in fact, result from a medium effect and, as a result, two distinct allene precursors are not required in this reaction.

We were led to this new conclusion in a somewhat circuitous way. During an investigation of the formation of optically active 1,3-diphenylallene from the corresponding optically active ethyl N-nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate[6] it was found that the activity of the allene did not change as the solvent was varied over the range from pure cyclohexane to cyclohexene. The allene was obtained with rotations of 686 ± 30° and 683 ± 30° in cyclohexane and cyclohexene, respectively. If Scheme I were operative, increased cyclohexene concentration would decrease the amount of allene resulting from the carbene. Since it is highly unlikely that the ring opening of both the carbene and the diazocyclopropane, with their different steric circumstances[6] as well as different symmetry-allowed ring-opening modes[7] would lead to allene of the same optical purity, it was necessary to consider the possibility that the allene in fact has only one precursor. To this end a plot of the ratio of spiropentane to allene *vs.* olefin concentration was carried out on the 2,3-diphenylcyclopropyl system in essentially the same manner as that reported for the 2,2-diphenylcyclopropyl system. In fact, when the reaction was carried out in varying mixtures of cyclohexane and cyclohexene, once

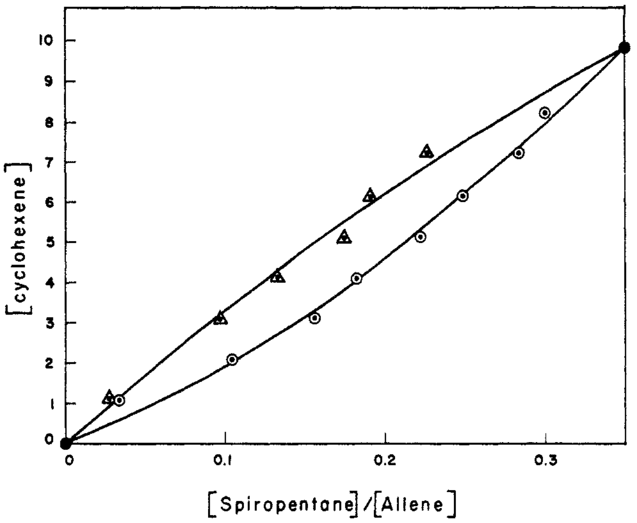


Figure 2.—Dependence of spiropentane/allene ratio on cyclohexene concentration: ⊙ diluted with cyclohexane, Δ diluted with benzene.

again a marked curvature in the plot was observed (Figure 2), albeit less severe.

As a possible resolution to the apparent dichotomy created by the optical activity studies which pointed to a single allene precursor and the competition studies which favored a dual mechanism, we looked to a possible solvent effect as the cause of the latter. To test this hypothesis, a solvent was sought which would meet two basic requirements: (1) polarity equal to or greater than cyclohexene and (2) inertness to the intermediate (most certainly the carbene). The solvent that was finally found to meet these requirements was benzene. Polarity was determined for cyclohexane, cyclohexene, and benzene using the Berson Ω criterion.[8] Ω values were found to be 0.595, 0.506, and 0.497, respectively. Inertness of the carbene to benzene was evidenced by the complete absence (<1%) of new products. The results of this investigation using cyclohexene–benzene mixtures are shown in Figure 2. It will be noted that the resulting curve is actually in the opposite direction from the cyclohexane case. For this to be consistent with Scheme I, k_1/k_2 must be negative. Since this is a physical impossibility, it must be concluded that Scheme I is not a proper description of the reaction under consideration. Furthermore, when a few points were taken for an evaluation of the effect of using benzene as the diluting solvent on the previously reported 2,2-diphenylcyclopropyl system, it was found that again the direction of the curvature was reversed. It was also found that, in the 2,3-diphenylcyclopropyl system (the only one studied under the following conditions) the direction of curvature became even more severe as solvent polarity was increased beyond benzene. For example, the spiropentane/allene ratios resulting from the generation of the 2,3-diphenylcyclopropylidene in 1.03 M cyclohexene in cyclohexane, benzene, and methylene bromide were found to be 0.034, 0.028, and 0.013, respectively. In other words, the rate of addition of the carbene to olefin relative to its collapse to the allene appears to be sensitive to solvent polarity, the more polar the solvent, the more the

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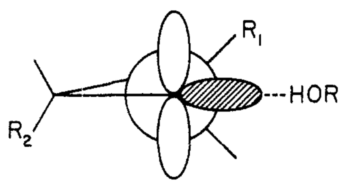
(6) J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Am. Chem. Soc.*, **90**, 2895 (1968); W. M. Jones, J. W. Wilson, Jr., and F. B. Tutwiler, *ibid.*, **85**, 3309 (1963).

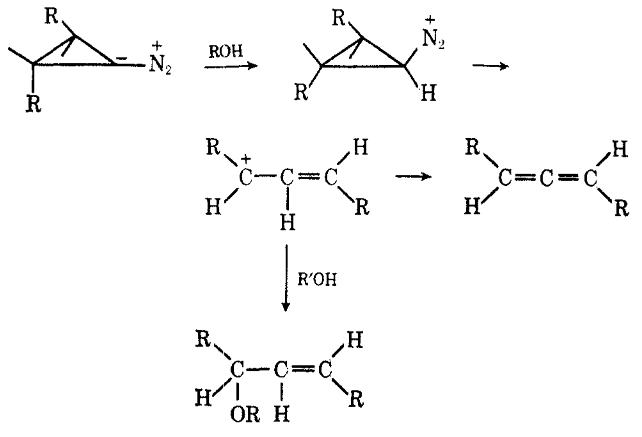
(7) Private communication from Professor R. Hoffmann, Cornell University.

(8) A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

ring opening is favored.[9-11] This could arise either from an increase in the rate of ring opening, a decrease in the rate of spiropentane formation, or a combination of both. At this time, these two possibilities cannot be distinguished. However, it should be noted that due to the differences in symmetry of the two cyclopropanes the greater degree of curvature in Figure 1 relative to Figure 2 would be anticipated if the ring-opening transition state were more polar than the carbene. However, it is difficult to understand why the rate of the electrocyclic ring opening of the symmetrical 2,3-diphenylcyclopropylidene would be affected by changes in solvent polarity in view of the observations of both Battiste[12] and Criegee,[13] who have found that the rate of comparable ring openings of cyclobutenes is insensitive to the nature of the medium.



It was also found that, in contrast to the insensitivity of the stereochemistry of the ring opening to minor variations in solvent polarity (cyclohexane, cyclohexene, and benzene gave nearly identical rotations), protonic solvents showed dramatic effects on this property. Thus, the 1,3-diphenylallene obtained from reactions in benzene, *t*-butyl alcohol, and methanol was found to have rotations of 607 ± 30°, 350 ± 30°, and 197 ± 30°, respectively. Inasmuch as the direction of ring opening is apparently controlled by steric repulsion of the 2,3 substituents, this decrease in activity with increased acid strength may simply reflect an increase in the effective bulkiness at C-1 resulting from solvation. This effect can be seen by using a Newman projection and sighting down the 1,2 bond of I. Factors that promote rotation of R_1 in a clockwise direction should lead to increased activity while any effect that could promote counterclockwise rotation would cause a decrease in activity. Thus, if the alcohol solvates the carbene by hydrogen bonding to the nonbonded pair, the effective bulkiness should be increased in such a way as to promote counterclockwise rotation of R_1 and a net decrease in activity.[14]



Finally it should be noted that these reactions are extremely "clean" reactions and yields are essentially quantitative. Glpc analyses of the reaction products show that in addition to 1,3-diphenylallene the reactions in benzene and methylene bromide yielded no other reaction products (<1% detectable), the reaction in pure cyclohexane yielded only one additional product (2.6%, presumably the corresponding insertion product), the reaction in methanol yielded only one other product, 1-methoxy-*trans*-2,3-diphenylcyclopropane (33%), and the reaction in cyclohexene yielded only one other product, the spiropentane (26%). The optically active spiropentane, $[\alpha]^{25}\text{D}$ +135°, isolated from the reaction in cyclohexene is to our knowledge the first optically active spiropentane to be reported.

In conclusion, one final point should be emphasized. Whereas the results presented in this paper eliminate the necessity for two different precursors in this reaction, and, in fact, support a single intermediate, they do not define its structure. However, from the previously reported properties of the spiropentane precursor,[3-5] there can be little doubt but that it is the carbene in the singlet (ground ?) state.

Experimental Section

General.—Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Model 1R10 infrared spectrophotometer. Nuclear magnetic resonance spectra were run in dilute carbon tetrachloride solution on a Varian A-60A spectrometer using tetramethylsilane as 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, 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/100 ml. The elemental analyses were performed by 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 (glpc) was performed on two instruments manufactured by Wilkins Instrument and Research, Inc., Walnut Creek, Calif. The analytical glpc was accomplished on a Model 600-D Hi-Fi gas chromatograph, equipped with a hydrogen flame ionization detector and employing nitrogen as a carrier gas. 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 carrier 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 an Hitachi Perkin-Elmer Model RMU6E mass spectrometer. Ultraviolet determinations were run on a Cary Model 15 double-beam recording spectrophotometer employing silica cells.

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[9] The increased rate of ring opening in CH_2Br_2 is particularly striking since spin-orbit coupling[10] between the carbene and the heavy atom solvent would be expected to promote intersystem crossing to the triplet cyclopropylidene which apparently does not open to allene.[11] This observation may reflect a singlet ground state for this carbene or inefficient coupling between the carbene and the heavy atom. Both of these possibilities are under investigation.

[10] *Cf.* N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, pp 27–29.

[11] P. S. Skell and R. R. Engle, *J. Am. Chem. Soc.*, **88**, 3749 (1966), and references cited therein; W. T. Borden, *Tetrahedron Letters*, 447 (1967).

[12] Private communication from Professor M. A. Battiste, University of Florida.

[13] R. Criegee, *Angew. Chem. Intern. Ed. Engl.*, **7**, 559 (1968).

[14] Partial reaction involving the following represents an alternative explanation for the decreased optical purity of the allene in the experiments that were run in alcohol as a solvent. Complete absence of the ether and independent demonstration of its stability to reaction conditions argue against this.

Ethyl (−)-N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate.—The procedure as described in an earlier publication[6] was utilized to yield the N-nitrosocarbamate as a yellow oil, $[\alpha]^{25}\text{D}$ −251° (*c* 7.4, ether). This material was homogeneous as shown by tlc (pentane–ether eluent) and had identical ir and nmr spectra with those reported.[3] The racemic material was prepared in an identical manner.

Decomposition of Ethyl (±)-N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate in Cyclohexane–Cyclohexene and Benzene–Cyclohexene Mixtures. Determination of Spiropentane/Allene Ratios.—A 47.8-ml, magnetically stirred, water-jacketed, volumetric reaction flask connected to a pressure-compensated gas buret and a constant-temperature circulator at 30.0° was thoroughly flushed with dry nitrogen. After addition of 0.0620 g (0.20 mmole) of the N-nitrosocarbamate and the appropriate solvent mixture, a 0.38-ml (0.20 mmole) portion of 5.6 *M* sodium methoxide in methanol was added. The reaction was allowed to continue until nitrogen evolution was complete; this normally required 3 hr and gave 80–100% gas evolution. The mixture was then analyzed by glpc using the 600-D instrument with a $^1/_8$ in. × 6 ft column packed with 10% SE 30 on 60–80 mesh Chrom W with DMCS at 156° with temperature programming for elution of the spiropentane. In each case the chromatogram showed no components in addition to the standard, allene, and spiropentane (<1% detectable) with the exception of reactions in which cyclohexane was the solvent. In pure cyclohexane 2.6% of another component was observed, and the amount of this material observed was proportionate to the amount of cyclohexane used in the reactions.

Decomposition of Ethyl (−)-N-Nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate in Various Solvents. Determination of the Optical Rotation of the 1,3-Diphenylallene.—A procedure identical with that for the determination of spiropentane to allene ratios was utilized except that the (−)-N-nitrosocarbamate, $[\alpha]^{25}\text{D}$ −251° (*c* 7.4, ether), was used. After the reaction was complete (nitrogen evolution ceased) the reaction mixtures from the cyclohexane and benzene reactions were poured into equal volumes of cyclohexene, and the reaction mixtures from reactions in cyclohexene, methanol, and *t*-butyl alcohol were poured into equal volumes of cyclohexane. These mixtures were evaporated *in vacuo* to an oil, which was immediately chromatographed over 10 g of silica (hexane eluent). The resulting chromatography fractions which were shown to contain only 1,3-diphenylallene by glpc were then used for specific rotation determination. The concentration of the allene in these fractions was determined by glpc by comparison to a standard of approximately equal concentration using the 600-D instrument with a $^1/_8$ in. × 6 ft column packed with 10% SE 30 on 60–80 mesh Chrom W with DMCS at 156°. Using this procedure the specific rotation (+30°) of the (+)-1,3-diphenylallene was obtained for identical reactions in the following solvents: cyclohexene, 683°; cyclohexane, 686°; benzene, 607°; *t*-butyl alcohol, 350°; methanol, 197. Control experiments showed (+)-1,3-diphenylallene to be optically stable when exposed to sodium methoxide in the above solvents at comparable concentrations and exposure times.

Determination of Relative Solvent Polarities.—The procedure of Berson, Hamlet, and Mueller[8] was used. In a nitrogen-flushed, water-jacketed flask kept at 30.0° by use of a constant-temperature circulator was placed 30 ml of the appropriate solvent and 1.3 ml of freshly distilled methyl acrylate. A freshly distilled 1.3-ml portion of cyclopentadiene was then added by use of a syringe through a rubber septum. The reaction mixture was allowed to stir for 24 hr and then evaporated to an oil by use of a rotary evaporator at room temperature. A small portion of ether was added to the oil and again the solvent was removed. Ether was added to the resulting oil and this solution was analyzed by glpc on the 600-D instrument using a $^1/_8$ in. × 10 ft column packed with TCEP on 60–80 mesh Chrom W with DMCS and a nitrogen pressure of 24 psig at 103°. The following *endo*/*exo* ratios (±2%) were obtained for the solvents listed: acetone, 0.414; benzene, 0.497; cyclohexene, 0.506; hexane, 0.577; cyclohexane, 0.595. Control experiments for reaction time and work-up procedure did not alter the observed ratios.

(+)-*trans*-1,2-Diphenyl-1′,2′-tetramethylenespiropentane.—To a solution of 1.54 g (4.98 mmoles) of ethyl (+)-N-nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate, $[\alpha]^{25}\text{D}$ +210° (*c* 5.8, ether), in 100 ml of cyclohexene at 22° was added 1.035 ml (5.96 mmoles) of a 5.79 *M* solution of sodium methoxide in methanol. After gas evolution was complete (1 hr), analysis of an aliquot of the reaction mixture by glpc on the 600-D instrument with a $^1/_8$ in. × 5 ft column packed with 6% apiezon L on 60–80 mesh Gas-Chrom Z at 233° and an inlet pressure of 30 psig showed a 26% yield of the spiropentane. After addition of 150 ml of heptane to the reaction mixture and evaporation *in vacuo* to a volume of approximately 60 ml, the mixture was chromatographed over 220 g of silica (hexane eluent). Incomplete separation was obtained as glpc analysis of the chromatography fractions showed elution of the allene, followed by fractions containing both allene and spiropentane, then followed by fractions containing only the spiropentane. These latter fractions were combined and evaporated to an oil. Crystallization of this oil from 95% ethanol at −78° gave 66 mg of the spiropentane: $[\alpha]\text{D}^{25}$ +135° (*c* 19.54, hexane); mp 97–97.5°; infrared, $\lambda_{\text{max}}^{\text{KBr}}$ 1600, 750, and 700 cm^{-1} (phenyls); nmr, τ 2.85 (m) ten phenyls, 7.67 (pair of doublets, 3.8 cps) two hydrogens of spiropentane adjacent to phenyls, 8.0–9.2 (m) ten remaining protons; mass spectrum, *m/e* 274 (parent peak), 192, 191, 183, 141, 115, and 91; ultraviolet, $\lambda_{\text{max}}^{95\%\ \text{EtOH}}$ 238 mμ (log ϵ 4.2), $\lambda_{\text{sh}}^{95\%\ \text{EtOH}}$ 268 mμ (log ϵ 3.2), 275 mμ (log ϵ 3.0).

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 91.65; H, 8.07.

1-Methoxy-*trans*-2,3-diphenylcyclopropane.—To a solution of 1.65 g (5.32 mmoles) of ethyl (±)-N-nitroso-N-(*trans*-2,3-diphenylcyclopropyl)carbamate in 200 ml of anhydrous methanol was added 1.0 ml (5.6 mmoles) of a 5.6 *M* solution of sodium methoxide in methanol. Gas was rapidly and vigorously evolved. After gas evolution was complete, glpc of the reaction mixture showed the presence of only two components, 1,3-diphenylallene (67%) and 1-methoxy-*trans*-2,3-diphenylcyclopropane (33%). Evaporation of the reaction mixture to a volume of 30 ml and separation of the second component by preparative glpc on the A-350-B instrument with a 0.5 in. × 6 ft column packed with 20% SE 30 on 60–80 mesh Gas-Chrom Z at 190° and an inlet pressure of 50 psig gave the ether as a white solid: mp 60–62°; infrared, $\lambda_{\text{max}}^{\text{KBr}}$ 1600, 750, 700 (phenyls), 1110 cm^{-1} (ether); nmr, τ2.83 (m) ten phenyls, 6.42 (q) one hydrogen of cyclopropane adjacent to methoxy group, 6.81 (s) three methyls, 7.57 (m) two hydrogens of cyclopropane adjacent to phenyls; mass spectrum, *m/e* 224 (base and parent peak), 209, 193, 192, 147, and 77.

Anal. Calcd for $C_{16}H_{16}O$: C, 85.67; 7.19. Found: C, 85.58; H, 7.10.

Registry No.—Cyclopropylidene, 2143-70-6; allene, 463-49-0; spiropentane, 157-40-4; (+)-*trans*-1,2-diphenyl-1′,2′-tetramethylenespiropentane, 19817-59-5; 1-methoxy-*trans*-2,3-diphenylcyclopropane, 19817-60-8.

Acknowledgment.—The authors most gratefully acknowledge the support for this work which they received from the National Science Foundation.

Stereoselectivity of Carbene Intermediates. VI. Selectivity of Phenylchlorocarbene[1]

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Received November 8, 1968

At least formally, phenylhalocarbenes can be generated by the action of base on benzal halides **1**,[4] or by photoinduced elimination of nitrogen from phenyl-

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[1] Part V: R. A. Moss and J. R. Przybyla, *Tetrahedron*, **25**, 647 (1969).

[2] National Science Foundation Summer Undergraduate Research Participant, 1968 (GY-4154).

[3] Henry Rutgers Fellow, 1968–1969.

[4] See R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962), for example.