by placing a glass rod in the capillary tubing leading to the bulb and heating the tubing with heating tape to a temperature near that of the bath.

The sample was vaporized into the bulb as a mixture with *n*-heptane; this operation required less than 30 sec. Timing was started as soon as the stopcock leading to the bulb was opened. Samples were removed by allowing the material in the bulb to expand into a 10-ml volume; the stopcock was allowed to remain open for 12 sec. The material was then condensed with liquid nitrogen and analyzed by a capillary glpc. The shortest reaction time examined was 16 min.

The flow system employed was a Chemical Data Systems Model 1100 Pyrochrom used in conjunction with capillary glpc.

Analysis in both cases was by a Varian Associates Series 1220-2 chromatograph using a 200 ft × 0.01 in. i.d. didecyl phthalate column operated at room temperature and 15 psi helium pressure. Integration of the signal was by a Vidar Model 6210 digital integrator.

The 1,4-dimethylspiropentanes were prepared as described earlier[13] and purified immediately prior to use by preparative glpc using a 12 ft × 0.25 in. di-*n*-butyl tetrachlorophthalate column operated at 70° and 100 ml/min helium flow. Distal **20** and medial **2** were homogeneous by capillary glpc. Proximal **18** contained a 3% impurity which was neither of the two other isomers.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Alkyl Shifts in Thermolyses. VI.[1] Synthesis and Characterization of the 2,4- and 4,5-Dimethyl-1-carbethoxyspiropentanes and the 2-Methyl-3-ethylidene-1-carbethoxycylopropanes[2]

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Abstract: In order to examine the complete stereochemistry of a spiropentane to methylenecyclobutane thermal rearrangement, three stereoisomeric 4,5-dimethyl-1-carbethoxyspiropentanes were prepared by copper-catalyzed addition of ethyl diazoacetate to *cis*- and *trans*-2,3-dimethylmethylenecyclopropane. Only one isomer was found in the former case while two, in a 3:1 ratio, were produced from the latter. The structures were assigned primarily on the basis of anticipated steric effects in the additions. Seven of the eight possible 2,4-dimethyl-1-carbethoxyspiropentanes were prepared by Gaspar–Roth cyclopropanation of the four 2-methyl-3-ethylidene-1-carbethoxycyclopropanes whose structures were partly assigned by pmr spectroscopy. Chemical degradation of the 2,4-dimethyl-1-carbethoxyspiropentanes to the various 1,4-dimethylspiropentanes established the relationships between the methyls of these esters and their precursors.

The spiropentane to methylenecyclobutane thermal rearrangement[4] appears to be closely related to the cyclopropane to propylene thermal isomerization,[1] a reaction which has received considerable experimental[5] and theoretical[6] attention. Since both interconversions could be envisioned as proceeding *via* either a concerted conservation of orbital symmetry controlled pathway[7a] or a two-step pathway involving biradicals,[7b] a complete stereochemical study of the former reaction appeared to be essential. In order to determine the stereochemical outcome at the migration origin, terminus, and migrating carbon, it was necessary to prepare and to assign the stereostructures of a number of 4,5-dimethyl- and 2,4-dimethyl-1-carbethoxyspiropentanes whose pyrolytic behavior is described in the next paper of this series. In addition to the impetus provided by the thermal rearrangements of the spiropentane system, the further possibility of examining the stereochemistry of multiple cyclopropylcarbinyl cation, anion, and radical rearrangements of spiropentylcarbinyl derivatives motivated this endeavor.

Results and Discussion

Synthesis of the 4,5-Dimethyl-1-carbethoxyspiropentanes. Slow addition of ethyl diazoacetate to *cis*-2,3-dimethylmethylenecyclopropane (**1**)[8] in octane containing cupric sulfate and copper bronze at reflux gave mostly one spiropentane ester, **3**, as evidenced by vpc and pmr. Since the product of attack from the least hindered side of the olefin usually predominates in these additions,[9] the *cis*-4,5-dimethyl-*anti*-1-carbethoxyspiropentane structure was assigned to **3**. Inspection of molecular models reveals the large degree to which the side of the π bond syn to the cis, vicinal methyls is shielded from attack by reagents, so the fact that *cis*-4,5-dimethyl-*syn*-1-carbethoxyspiropentane (**4**) was not formed to any appreciable extent is not unreasonable.

Under the same reaction conditions, *trans*-2,3-di-

(1) For part V see J. J. Gajewski and L. T. Burka, *J. Amer. Chem Soc.*, **94**, 8857 (1972).

(2) Taken from the thesis of L. T. B. submitted in partial fulfillment of the Ph.D. requirements, Indiana University, Jan 1972.

(3) Fellow of the Alfred P. Sloan Foundation, 1971–1973.

(4) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 5550 (1961); P. J. Burkhardt, *Diss. Abstr.*, **23**, 1524 (1962).

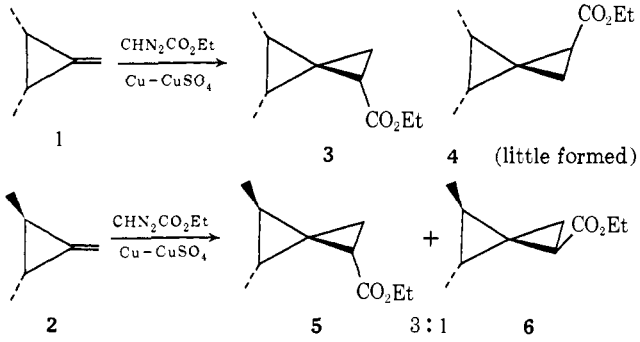
(5) For a review see W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 7343 (1968).

(6) R. Hoffmann, *ibid.*, **90**, 1475 (1968); L. Salem, *Bull. Soc. Chem. Fr.*, 3101 (1970); Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971); L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(7) (a) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

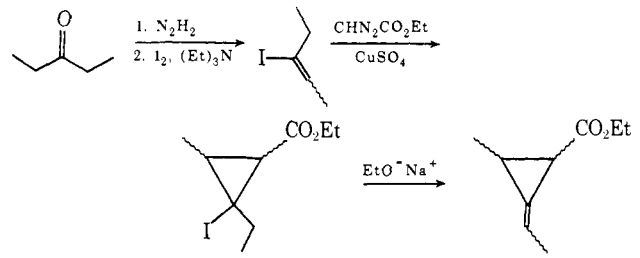
(8) J. J. Gajewski, *J. Amer. Chem. Soc.*, **93**, 4450 (1971).

(9) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

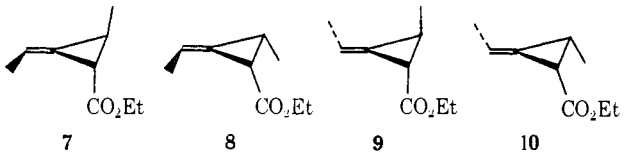


methylmethylenecyclopropane (**2**) and ethyl diazoacetate gave two spiropentane esters, **5** and **6**, in a 3:1 ratio, respectively. On the assumption of steric effects dominating the addition, the major product, **5**, was assigned the *medial,syn*-4-methyl-*medial,anti*-5-methyl-1-carbethoxyspiropentane structure,[10] and the minor product, **6**, was assigned the *distal*-4-methyl-*proximal*-5-methyl-1-carbethoxyspiropentane structure.

Synthesis and Characterization of 2-Methyl-3-ethylidene-1-carbethoxycyclopropanes. Synthesis of 2,4-dimethylcarbethoxyspiropentanes was accomplished by adding diazomethane to the appropriate 2-methyl-3-ethylidenecarbethoxycyclopropane using the Gaspar–Roth procedure. The synthesis of the olefin followed along lines previously developed[10b] and is outlined below. The dehydroiodination of the crude cyclo-

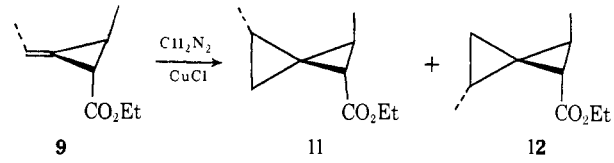


propyl iodide produced the four isomers of 2-methyl-3-ethylidenecarbethoxycyclopropane, **7**, **8**, **9**, and **10**, in a ratio of 2:1:8:6, which could be separated by preparative vpc. The *cis*- and *trans*-2-methyl-*anti*-3-ethylidene compounds (**9** and **10**) were assumed to be the major



components of the mixture in analogy to the dehydrobromination of 2-bromo-2-ethylcarbethoxycyclopropane.[10b] This assumption was supported by nmr data and *substantiated* by subsequent degradative studies. Thus, the stereochemistry of **7**, **8**, **9**, and **10** could be assigned from the pmr data using the previously described ethylidene compounds as models.[2] The assumption that the major components were the *anti*-ethylidene compounds, **9** and **10**, was indicated by the vinyl methyl signals at δ 1.84 and 1.83 which favorably compare to that at δ 1.87 in *anti*-2-ethylidenecarbethoxycyclopropane.[10b] The vinyl methyl absorptions in the minor components **7** and **8** were at δ 1.74 and 1.76, which can be compared to δ 1.78 for that in *syn*-2-ethylidenecarbethoxycyclopropane.[10b] The major component of the *anti*-ethylidenes was predicted to be the trans compound **9** for steric reasons.[11] This was substantiated by the relative upfield shift of the 1-H due to the usual shielding effect of the 2-methyl group cis to it.[8] This shift was from δ 2.18 in the second most abundant component **10** to δ 1.73 in the major isomer **9**. The upfield shift was also evident in the pair of minor isomers with a shift from δ 2.16 in the least abundant component, **8**, to δ 1.72 in the third most abundant one, **7**. On the basis of the pmr assignments, the major component was *trans*-2-methyl-*anti*-3-ethylidenecarbethoxycyclopropane (**9**). The other three components in order of decreasing abundance were assigned as *cis*-2-methyl-*anti*-3-ethylidenecarbethoxycyclopropane (**10**), *trans*-2-methyl-*syn*-3-ethylidenecarbethoxycyclopropane (**7**), and *cis*-2-methyl-*syn*-3-ethylidenecarbethoxycyclopropane (**8**).

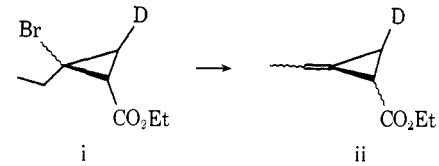
Synthesis and Characterization of 2,4-Dimethyl-1-carbethoxyspiropentanes. Reaction of **9** with diazomethane in the presence of cuprous chloride[12] gave two dimethylcarbethoxyspiropentanes, **11** and **12**, in nearly



equal quantities which could be separated by preparative glpc. Inspection of the pmr allowed no clear-cut determination of the stereochemistry of the two products. Since all three 1,4-dimethylspiropentanes had been made and characterized,[6] the relative stereochemistry of the methyl groups in these dimethylcarbethoxyspiropentanes could be determined easily by removal of the carbethoxy group and comparison of the product with the known 1,4-dimethylspiropentanes. In order to make this correlation, one of the isomers was degraded as shown below. Reaction of the spiropentanecarboxylic acid with lead tetraacetate (LTA) and iodine by the method of Barton[13] gave the cor-

(10) (a) Since existing stereochemical designations cannot define the relationships in substituted spirosystems, we have defined a set applicable to spiropentanes by recognizing that two substituents can be either proximal, medial, or distal to one another according to the distance, on a line, between the substituents; only three different distances are possible.[10b] When two substituents are identical, only the three stereochemical relations above exist. However, for nonidentical substituents, two medial compounds are possible, and are further distinguished by the terms syn or anti, depending on whether they are on the same or opposite sides of a plane defined by the cyclopropane ring bearing the higher priority substituent.[10b] In the case of **5** and **6**, the relationships between each of the methyls and the carbethoxy group are given. (b) J. J. Gajewski and L. T. Burka, *J. Org. Chem.*, **35**, 2190 (1970).

(11) Under the conditions of the dehydrohalogenation reactions cis–trans isomerization of substituents on the cyclopropane ring is relatively rapid; the thermodynamically most stable product should predominate. This was illustrated by the fact that attempts to dehydrohalogenate i to form ii resulted in epimerization of the label, or more properly, its reference substituent, the carbethoxy group, with a variety of bases and



conditions of reactions.

(12) W. von E. Doering and W. R. Roth, *Tetrahedron*, 19, 715 (1963).

(13) D. H. R. Barton, H. P. Faro, E. P. Serebeyakov, and N. F. Woosey, *J. Chem. Soc.*, 2438 (1965).

responding iodide. The iodide was reduced by reaction with tri-*n*-butyltin hydride to yield a single dimethylspiropentane whose pmr was identical with that of *proximal*-1,4-dimethylspiropentane (**13**). Since the methyls bore a proximal relationship to one another and since the carbethoxy group was trans to one of them because **11** was derived from **9**, **11** must have been *trans*-2-methyl-*distal*-4-methylcarbethoxyspiropentane (**11**).[14] The other isomer from the cyclopropanation of **9** must, therefore, be *trans*-2-methyl-*medial,syn*-4-methylcarbethoxyspiropentane (**12**), since these methylenations are cis additions.[9] This degradation also substantiated the assignment of **9** as being an *anti*-ethylidene compound since only an anti compound such as **9** and **10** could give a dimethylcarbethoxyspiropentane with the two methyl groups in a proximal relationship upon methylenation in a cis fashion. The assignment of the 2-methyl group as trans to the carbethoxy group in **11** and **13** ultimately rests upon the pmr assignment in **9** discussed above.

Methylenation of **7** produced two dimethylcarbethoxyspiropentanes in a 3:1 ratio which were separable by preparative glpc. Again pmr did not allow an unambiguous assignment of stereochemistry for the products; however, degradation of the major isomer in the same manner as for **11** resulted in the isolation of only *medial*-1,4-dimethylspiropentane (**16**).

There are only two 2,4-dimethyl-*trans*-1-carbethoxyspiropentanes that could give rise to *medial*-1,4-dimethylspiropentane, namely **12** or **15**, but **12** was on hand from **9** and was clearly different from **15**. Therefore, the major isomer from methylenation of **7** must be *trans*-2-methyl-*medial,anti*-4-methylcarbethoxyspiropentane (**15**) and the minor one *trans*-2-methyl-*proximal*-4-methylcarbethoxyspiropentane (**14**).

The cis-anti compound, **10**, was also subjected to methylenation; one major product was formed which was assumed to be **17**. This assignment was made in consideration of the steric effect of the carbethoxy and methyl groups hindering attack of the carbene species on the endo side of the double bond. The other isomer, **18**, was also isolated from the reaction but in only small quantities.

Methylenation of the cis-syn compound, **8**, gave two products in a 4:1 ratio which could be separated only with difficulty on a capillary chromatograph and not at all preparatively. The major product in the mixture was probably **19**, the product of addition of methylene from the least hindered side of **8**.

Experimental Section

General. Nuclear magnetic resonance spectra were recordedon Varian A-60 and HR-220 spectrometers. Carbon tetrachloride was used as solvent with TMS as internal standard; chemical shifts are reported as δ values in ppm downfield from TMS. Infrared spectra were obtained with a Perkin–Elmer Model 621 spectrophotometer using 0.5 to 5% solutions in carbon tetrachloride. Vapor phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using the following columns: 20 ft × 0.38 in. 25% UCON 50 HB 2000 Polar on 60–80 Chromosorb W (UCON), 20 ft × 0.25 in. 20% tris(cyanoethoxy)-propane on 60–80 Chromosorb W (TCEP), 15 ft × 0.25 in. 30% di-*n*-butyl tetrachlorophthalate on 60–80 Chromosorb W (DBTCP), and 250 ft × 0.01 in. i.d. UCON 50 HB 2000 polar (UCON capillary). Operating temperature and helium flow rate or pressure are given in parentheses after the column. Mass spectra were recorded on an A.E.I. Model MS-9.

***cis*-4,5-Dimethyl-*anti*-1-carbethoxyspiropentane (3).** *cis*-2,3-Dimethylmethylenecyclopropane (**1**) was prepared as described previously.[8] The olefin (4.0 g, 49 mmol) was dissolved in 1 ml of octane containing 25 mg of copper bronze and 25 mg of cupric sulfate. To the stirred, refluxing mixture 12 g (105 mmol) of ethyl diazoacetate dissolved in 4 ml of octane was added over a period of 4 hr. After this time, the unreacted olefin was removed by distillation, and the residue was filtered. Distillation of the residue using an 18-in. spiral wire packed column gave 1.8 g of material (bp 90.5–92° at 20 Torr). Glpc on the UCON capillary (130°, 55 psi) indicated one major component comprising about 95% of the mixture. Part of this material was further purified using the UCON column (170°, 100 ml/min) and identified as *cis*-4,5-dimethyl-*anti*-1-carbethoxyspiropentane (**3**): ir 3055, 2970, etc., 1715, 1440, 1365, 1345, 1300, 1255, 1160, 1060, 1025, 975, 945, 890, and 850 cm^{-1}; nmr (220 MHz) δ 0.96 (d, J = 6 Hz) and 1.02 (d, J = 6 Hz) superimposed on a third small signal, total of 7 H, 1.14 (t, J = 4 Hz) and 1.22 (t, J = 7 Hz) superimposed on a multiplet extending from 1.1 to 1.3, total of 6 H, 1.83 (d of d, J = 8 and 4 Hz, 1 H) and 4.02 (m, 2 H); *m/e* 168.1146 (calcd for $C_{10}H_{16}O_2$, 168.1150).

***trans*-4,5-Dimethylcarbethoxyspiropentanes (5 and 6).** *trans*-2,3-Dimethylmethylenecyclopropane (**2**) was prepared as described previously.[8] Ethyl diazoacetate (15 g, 131 mmol) in 5 ml of octane was added over a 4-hr period to a refluxing mixture of 6 g (73 mmol) of dimethylmethylenecyclopropane, 3 ml of octane, 25 mg of copper bronze, and 25 mg of cupric sulfate. After this time unreacted olefin was removed by distillation; the residue was filtered and then

(14) Distal, in this case, refers to the spatial distance between the 4-methyl group and the carbethoxy group; see ref 10.

distilled through an 18-in. spiral wire column to yield 2.15 g of material, bp 84–86° (23 Torr), which glpc (20 ft UCON column) indicated to be two components in a 3:1 ratio. Part of the mixture was separated using the UCON (155°, 100 ml/min).

The major component was identified as *medial,syn*-4-methyl-*medial,anti*-5-methylcarbethoxyspiropentane (**5**): ir 3060, 2975, etc., 1715, 1443, 1368, 1342, 1308, 1255, 1160, 1125, 1068, 1025, 975, 945, 890, and 855 cm^{-1}; nmr (220 MHz) δ 0.71 (7 line multiplet, 2 H), 1.0–1.28 (d, J = 6 Hz at 1.06 and d, J = 6 Hz, at 1.10 superimposed on a small multiplet, total of 7 H), 1.23 (t, J = 7 Hz, 3 H), 1.36 (t, J = 7 Hz, 1 H), 1.77 (d of d, J = 7 and 4 Hz, 1 H), and 4.04 (m, 2 H); *m/e* 168.1163 (calcd for $C_{10}H_{16}O_2$, 168.1150).

The minor product was identified as *distal*-4-methyl-*proximal*-5-methylcarbethoxyspiropentane (**6**): ir 2985, etc., 1715, 1420, 1443, 1368, 1348, 1295, 1257, 1168, 1145, 1082, 1062, 1031, 1019, 971, 950, 922, 887, and 853 cm^{-1}; nmr (220 MHz) δ 0.71 (m, 1 H), 1.03 (d, J = 6 Hz, superimposed on a multiplet centered at 0.97, total of 7 H), 1.13 (d of d, J = 8 and 4 Hz, 1 H), 1.23 (t, J = 7 Hz, 3 H), 1.34 (t, J = 4 Hz, 1 H), 1.76 (d of d, J = 7 and 4 Hz, 1 H), and 4.01 (m, 2 H); *m/e* 168.1153 (calcd for $C_{10}H_{16}O_2$, 168.1150).

3-Iodo-2-pentene. 3-Iodo-2-pentene was prepared from 3-pentanone using the method of Pross and Sternhell.[15] 3-Pentanone (33 g, 0.38 mol) was added, with stirring, over a 4-hr period to 163 g (3.3 mol) of hydrazine hydrate. The reaction mixture was then extracted with 300 ml of chloroform. The chloroform solution was washed with water, dried with anhydrous potassium carbonate, then added to 200 ml (1.4 mol) of triethylamine and cooled to 0°. A saturated solution of iodine in tetrahydrofuran was added until the color persisted (*ca.* 175 g, 0.7 mol). After stirring an additional 15 min at room temperature, water was added until the precipitate dissolved. The organic layer was washed with saturated sodium sulfate and dried with magnesium sulfate. After distillation of the solvent, the residue was distilled under reduced pressure to give 20 g (10%) of material, bp 76–82° (90–100 Torr). Nmr indicated a 1:4 mixture of isomers. No attempt was made to further purify the compounds. Nmr of the major component (60 MHz) showed peaks at δ 1.08 (t, J = 7 Hz, 3 H), 1.72 (d of t, J = 7 and 1 Hz, 3 H), 2.42 (m, 2 H) and 5.52 (q of t, J = 7 and 1 Hz, 1 H).

2-Methyl-3-ethylidenecarbethoxycyclopropanes (7–10). Ethyl diazoacetate (20 g, 170 mmol) was added, with stirring, over a 20-hr period to 17 g (87 mmol) of 3-iodo-2-pentene and 100 mg of cupric sulfate heated to 100°. Excess olefin was removed by distillation; the residue was distilled under reduced pressure to yield 8.35 g of material, bp 78–85° (2.5 Torr). The crude 2-iodo-2-ethyl-3-methylcarbethoxycyclopropane was added to a well-stirred slurry of 3 g (125 mmol) of sodium hydride in 50 ml of ether containing 0.2 ml of ethanol and allowed to stir at room temperature for 2 hr. Excess acetic acid was added to the reaction mixture, followed by enough water to cause two layers to form. The ether solution was washed with sodium bicarbonate and dried with magnesium sulfate. Removal of the solvent and distillation of the residue under reduced pressure gave 2.6 g of material, bp 85–95° (25 Torr), containing four compounds in the ratio of 2:1:8:6. This could be separated into four components using the UCON column (140°, 150 ml/min). There were obtained 0.20 g of component 1, 0.25 g of component 2, 0.6 g of component 3, and 0.7 g of component 4. Components 1, 2, and 3 overlapped somewhat and were further purified using the UCON column (130°, 150 ml/min).

The first component was identified as *trans*-2-methyl-*syn*-3-ethylidenecarbethoxycyclopropane (**7**): ir 2980, etc., 1720, 1440, 1370, 1310, 1250, 1150, 1090, 1035, 965, 900, 860, and 840 cm^{-1}; nmr (220 MHz) δ 1.18 (d, J = 7 Hz), 1.24 (t, J = 7 Hz), total of 6 H, 1.72 (m) superimposed on a doublet of triplets (J = 7 and 2 Hz) centered at 1.76, total of 4 H, 2.02 (broad multiplet, 1 H), 4.05 (q, J = 7 Hz, 2 H) and 5.78 (m, 1 H); *m/e* 154.0985 (calcd for $C_9H_{14}O_2$, 154.0993).

The second component was identified as *cis*-2-methyl-*syn*-3-ethylidenecarbethoxycyclopropane (**8**): ir 2980, etc., 1720, 1440, 1370, 1330, 1295, 1255, 1160, 1135, 1045, 950, 895, and 850 cm^{-1}; nmr (220 MHz) δ 1.21 (d, J = 7 Hz) superimposed on a triplet centered at 1.24 (J = 7 Hz), total of 6 H, 1.74 (d of t, J = 7 and 2 Hz, 3 H), 1.96 (broad multiplet, 1 H), 2.16 (two 3-line multiplets with 8 and 2 Hz spacing between lines), 4.06 (q, J = 7 Hz, 2 H), and 5.77 (m, 1 H); *m/e* 154.0985 (calcd for $C_9H_{14}O_2$, 154.0993).

The third component was identified as *trans*-2-methyl-*anti*-3-ethylidenecarbethoxycyclopropane (**9**): ir 2980, etc., 1720, 1445, 1380, 1370, 1305, 1255, 1155, 1085, 1045, 970, 950, 895, and 860 cm^{-1}; nmr (220 MHz) δ 1.21 (d, J = 6 Hz) superimposed on a triplet (J = 7 Hz) centered at 1.24, total of 6 H, 1.73 (7-line multiplet with 2-Hz spacing between lines, 1 H), 1.83 (d of t, J = 7 and 2 Hz, 3 H), 2.00 (broad multiplet, 1 H), 4.03 (q, J = 7 Hz, 2 H), and 5.74 (m, 1 H); *m/e* 154.0985 (calcd for $C_9H_{14}O_2$, 154.0993).

The fourth component was subsequently identified as *cis*-2-methyl-*anti*-3-ethylidenecarbethoxycyclopropane (**10**): ir 2970, etc., 1720, 1445, 1375, 1330, 1290, 1250, 1155, 1145, 1105, 1090, 1030, 1020, 930, 890, and 860 cm^{-1}; nmr (220 MHz), δ 1.24 (t, J = 7 Hz) superimposed on a doublet (J = 6 Hz) at 1.25, total of 6 H, 1.84 (d of t, J = 7 and 2 Hz, 3 H), 1.94 (broad multiplet, 1 H), 2.18 (two 3-line multiplets with 9- and 2-Hz spacing, 1 H), 4.05 (q, J = 7 Hz, 2 H), and 5.75 (m, 1 H); *m/e* 154.0095 (calcd for $C_9H_{14}O_2$, 154.0993).

***trans*-2-Methyl-*distal*- and -*medial,syn*-4-methylcarbethoxyspiropentane (11 and 12).** Gaseous diazomethane generated from 20 g (194 mmol) of *N*-methyl-*N*-nitrosourea was added to a stirred mixture of 2.3 g (15 mmol) of *trans*-2-methyl-*anti*-3-ethylidenecarbethoxycyclopropane (**9**) in 3 ml of pentane containing 0.1 g of cuprous chloride in the manner described by Doering and Roth.[12] Filtration and removal of solvent gave a residue which contained three components in the ratio 2:3:2; the major component was starting material. The compounds were separated using the TCEP column (100°, 100 ml/min).

The first component was subsequently identified as *trans*-2-methyl-*medial,syn*-4-methylcarbethoxyspiropentane (**12**): ir 3050, 2975, etc., 1718, 1450, 1377, 1465, 1345, 1317, 1255, 1115, 1098, 1062, 1038, 1000, 950, 920, and 837 cm^{-1}; nmr (220 MHz) δ 0.40 (unsymmetrical triplet, 1 H), 0.95 (unsymmetrical triplet, 1 H), 1.05–1.27 (s at 1.09; d, J = 6 Hz, at 1.14; t, J = 7 Hz, at 1.23 superimposed on a multiplet, 10 H), 1.42 (d, J = 4 Hz, 1 H), 1.63 (m, 1 H), and 4.01 (m, 2 H); *m/e* 168.1146 (calcd for $C_{10}H_{16}O_2$, 168.1150).

The third component was subsequently identified as *trans*-2-methyl-*distal*-4-methylcarbethoxyspiropentane (**11**): ir 3055, 2975, etc., 1718, 1450, 1441, 1421, 1380, 1365, 1312, 1257, 1160, 1125, 1090, 1038, 945, 915, 890, and 840 cm^{-1}; nmr (220 MHz) δ 0.54 (unsymmetrical triplet, 1 H), 0.90 (d of d, J = 8 and 4 Hz, 1 H), 1.13 (d, J = 6 Hz), 1.21 (d, J = 6 Hz), 1.26 (t, J = 7 Hz), total of 10 H, 1.43 (d, J = 4 Hz, 1 H), 1.76 (m, 1 H), and 4.00 (m, 2 H); *m/e* 168.1147 (calcd for $C_{10}H_{16}O_2$, 168.1150).

Degradation of *trans*-2-Methyl-*distal*-4-methylcarbethoxyspiropentane (11). The ethyl ester, **11** (0.37 g), was saponified with 1 g of potassium hydroxide in 3 ml of water and 0.5 ml of methanol at room temperature for 12 hr. After acidification, extraction with ether, drying, and removing solvent, 0.30 g of crude acid (mp 57–59°) was obtained. Treatment with lead tetraacetate and iodine as described by Barton[13] gave the corresponding iodide. Thus, the crude acid was dissolved in 20 ml of benzene and placed in a three-necked flask. After sweeping the system with argon, 1.0 g of lead tetraacetate was added and the mixture was heated to reflux. Iodine (0.53 g) was slowly added while the flask was irradiated with a 300-W lamp. Irradiation was continued for 30 min after the iodine had been added. Filtration, followed by successive washes with sodium sulfite and sodium bicarbonate and drying and removing solvent produced 0.4 g of crude iodide. The iodide was then immediately reduced with tri-*n*-butyltin hydride.[16] The iodide was stirred and irradiated with a sunlamp while 1 g of tri-*n*-butyltin hydride was slowly added. The system was evacuated and the volatile material was collected in a cold trap. Preparative glpc with the DBTCP column (70°, 100 ml/min) gave 40 μl of *proximal*-1,4-dimethylspiropentane (**13**):[10] nmr (220 MHz) δ 0.30 (J = 3 Hz, 2 H), 0.77 (m, 2 H), 0.95–1.15 (doublet superimposed on a multiplet, total of 8 H).

***trans*-2-Methyl-*proximal*- and -*medial,anti*-4-methylcarbethoxyspiropentanes (14 and 15).** In the same manner as described above, 770 mg (5 mmol) of *trans*-2-methyl-*syn*-3-ethylidenecarbethoxycyclopropane (**7**) was treated with diazomethane generated from 15 g (145 mmol) of *N*-methyl-*N*-nitrosourea to give 0.9 g of crude product. Glpc (250 UCON capillary, 125°, 55 psi) indicated about 75% reaction to give two products in a 3:1 ratio which could be separated preparatively using the UCON column (150°, 150 ml/min).

The major product was subsequently identified as *trans*-2-methyl-*medial,anti*-4-methylcarbethoxyspiropentane (**15**): ir 3055, 2980, etc., 1720, 1442, 1421, 1363, 1342, 1318, 1255, 1160, 1900, 1038, 912, 872, and 852 cm^{-1}; nmr (220 MHz) δ 0.46 (unsymmetrical

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triplet, 1 H), 1.00–1.14 (s at 1.07 and d at 1.11 superimposed on a multiplet, 8 H), 1.23 (t, J = 7 Hz, 3 H), 1.39 (d, J = 4 Hz, 1 H), 1.73 (m, 1 H), and 4.03 (m, 2 H); *m/e* 168.1146 (calcd for $C_{10}H_{16}O_2$, 168.1150).

The minor product was subsequently identified as *trans*-2-methyl-*proximal*-4-methylcarbethoxyspiropentane (**14**): ir 3050, 2975, etc., 1717, 1450, 1365, 1310, 1255, 1155, 1090, 1038, 955, 920, 870, and 845 cm^{-1}; nmr (220 MHz) δ 0.33 (t, J = 4 Hz, 1 H), 0.81 (d of d, J = 8 and 4 Hz, 1 H), 0.98 (d, J = 6 Hz, 3 H), 1.10 (d, J = 6 Hz, 3 H), 1.16–1.35 (triplet at 1.22 superimposed on a multiplet, 4 H), 1.41 (d, J = 4 Hz, 1 H), 1.74 (m, 1 H), and 4.03 (m, 2 H); *m/e* 168.1146 (calcd for $C_{10}H_{16}O_2$, 168.1150).

Degradation of *trans*-2-Methyl-*medial*,*anti*-4-methylcarbethoxyspiropentane (15). The ethyl ester **15** (0.2 g) was saponified and allowed to react with LTA and iodine as above. Reduction of the iodide gave 30 μl of *medial*-1,4-dimethylspiropentane[10] which was purified by preparative glpc using the DBTCP column (70°, 100 ml/min): nmr (220 MHz) δ 0.25 (m, 1 H), 0.34 (s, J = 4 Hz, 1 H), 0.74 (m, 1 H), 0.86 (m, 1 H), and a multiplet from 0.96 to 1.07 (8 H).

***cis*-2-Methyl-*medial*,*syn*- and -*distal*-4-methylcarbethoxyspiropentane (17 and 18).** In the same manner as described above, 0.5 g (3.2 mmol) of *cis*-2-methyl-*anti*-3-ethylidenecarbethoxycyclopropane (**10**) was allowed to react with diazomethane generated from 10 g (97 mmol) of *N*-methyl-*N*-nitrosourea to give a mixture which contained two minor components and one major component. The mixture was separated using the UCON column (120°, 150 ml/min). One of the minor components (about 10% of the mixture) was unreacted starting material.

The second minor component was assumed to be *cis*-2-methyl-*distal*-4-methylcarbethoxyspiropentane (**18**): ir 3057, 2980, etc., 1725, 1450, 1420, 1380, 1365, 1345, 1337, 1300, 1260, 1165, 1140, 1120, 1100, 1050, 1040, 950, 920, 895, and 842 cm^{-1}; nmr (220 MHz) δ 0.46 (t, J = 4 Hz, 1 H), 1.01 (d, J = 7 Hz, 3 H), 1.15 (d, J = 6 Hz), and 1.24 (t, J = 7 Hz) superimposed on a multiplet, total of 8 H, 1.59 (m, 1 H), 1.85 (d, J = 8 Hz, 1 H), and 4.02 (d of q, J = 7 Hz, 2 H); *m/e* 168.1142 (calcd for $C_{10}H_{16}O_2$, 168.1150).

The major component was assumed to be *cis*-2-methyl-*medial*,*syn*-4-methylcarbethoxyspiropentane (**17**): ir 3055, 2985, etc., 1715, 1445, 1365, 1295, 1255, 1160, 1130, 1108, 1090, 1030, 1010, 945, 887, 860, and 835 cm^{-1}; nmr (220 MHz) δ 0.43 (t, J = 4 Hz, 1 H), 0.94 (d of d, J = 7 and 4 Hz, 1 H), 1.16 (d, J = 6 Hz), 1.20 (d, J = 6 Hz), 1.23 (t, J = 7 Hz) superimposed on a multiplet extending to 1.40, total of 10 H, 1.65–1.85 (m, 2 H), 4.03 (d of q, J = 7 Hz, 2 H); *m/e* 168.1146 (calcd for $C_{10}H_{16}O_2$, 168.1150).

***cis*-2-Methyl-*proximal*- and -*medial*,*anti*-4-methylcarbethoxyspiropentane (19 and 20).** In the same manner as described above, 70 mg (0.4 mmol) of *cis*-2-methyl-*syn*-3-ethylidenecarbethoxycyclopropane (**8**) was allowed to react with diazomethane from 6 g (58 mmol) of *N*-methyl-*N*-nitrosourea. Glpc (UCON capillary) indicated two barely separable compounds in a ratio of 4:1. The compounds were inseparable by preparative glpc: ir of the mixture 3055, 2980, etc., 1730, 1450, 1422, 1380, 1368, 1348, 1338, 1295, 1260, 1170, 1140, 1110, 1090, 1032, 950, 890, 860, and 840 cm^{-1}; nmr (220 MHz) (signals assignable to the major component are given with approximate proton ratios) δ 0.41 (t, J = 4 Hz, 1 H), 0.80 (d of d, J = 8 and 4 Hz, 1 H), 1.08 (d, J = 6 Hz, 3 H), 1.19 (d, J = 6 Hz, 3 H), 1.23 (t, J = 7 Hz, 3 H), 1.85 (d, J = 8 Hz, 1 H), and 4.02 (m, 2 H). Two signals could be assigned to the minor isomer, a doublet at 1.13 and a multiplet at 1.77. The *m/e* value was determined as 168.11479 (calcd for $C_{10}H_{16}O_2$, 168.1150).

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