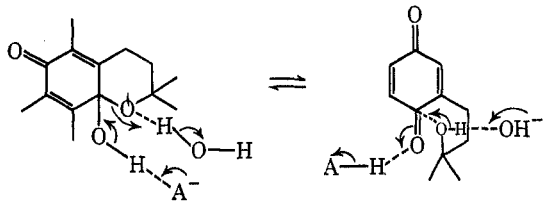
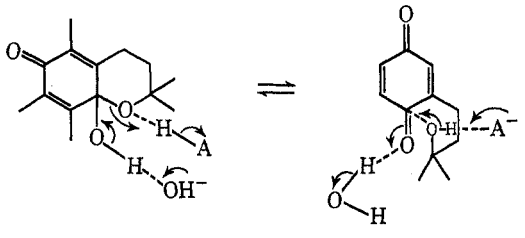
suggested to be important in the acid-catalyzed hydrolysis of a formamidium compound,[20] reaction by this pathway would lead to the prediction that the rate of the ring-opening reaction would decrease significantly with an increase in inert salt concentration.[19] Since this prediction is contradictory to the experimental results, this mechanism cannot be important here.

Little or no effect of salt is predicted and observed (Table II, expt 9 and 10) for the reaction catalyzed by monobasic anions. According to mechanism 15, a



(15)

proton is removed from the hydroxy group by the negatively charged general base, A^-, while a molecule of water functions as the acid. In mechanism 16, a



(16)

proton is transferred from the general acid to the oxygen in the 1 position, while a proton is removed from the hydroxy group in the 8a position by hydroxide ion. This reaction, which proceeds by specific base and general acid catalysis mechanistically, will behave kinetically as catalyzed by general base.

A distinction between the two pathways on the basis of salt effects should be feasible if the general base were unchanged. A change from a negatively to a neutrally charged base leads to the predictions that with an increase in the inert salt concentration the rate constant should increase if the reaction proceeds by mechanism 15 and decrease if the reaction proceeds by mechanism 16. As seen by the results of expt 11 and 12 (Table II), addition of inert salt (sodium perchlorate) to a pyridinium perchlorate–pyridine buffer system results in a marked increase in the experimental rate constant. We conclude from this result that general base catalysis for pyridine proceeds *via* mechanism 15 and suggest that catalysis by carboxylic anions occurs by this reaction pathway also.

It is of final interest to compare the stability of IIIb to that of IIIa.[21] The latter intermediate was reported to exhibit a bell-shaped pH–rate profile with maximum stability at pH 5.5. While maximum stability for IIIb is also noted in this study near this pH, the rate law for the decomposition of IIIb is first order in both hydrogen and hydroxide ions. The apparent difference in the two rate laws probably arises from the different methods used for the preparation of the two intermediates (IIIa,b). In the work of Dürckheimer and Cohen,[21] IIIa was prepared by the chemical oxidation of Ia using N-bromosuccimide as the oxidant. A change in the rate-determining step from the decomposition of IIIa to the oxidation of Ia would satisfactorily account for the observed differences in the rate law.

Registry No.—Ib, 950-99-2; IIIb, 24165-02-4.

Acknowledgment.—These studies were supported by the U. S. Public Health Service Research Grant No. 1 RO1 AM 13258-01.

(20) D. R. Robinson and W. P. Jencks, *J. Amer. Chem. Soc.*, **89**, 7088 (1967). For a complete discussion of carbonyl addition reactions, see ref 11, pp 63–128.

(21) W. Dürckheimer and L. A. Cohen, *ibid.*, **86**, 4388 (1964).

Axially Dissymmetric Molecules. Characterization of the Four 1-Carbethoxy-4-methylspiropentanes

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In order to map the energy surface of various reactions of substituted spiropentanes, the four diastereomers of 1-carbethoxy-4-methylspiropentane were synthesized by methylene addition to *syn*- and *anti*-1-carbethoxy-2-ethylidenecyclopropane. The relative stereochemical configurations of the spiropentane esters were determined by their conversion into the dimethylspiropentanes which were, in turn, synthesized from the spiropentane-1,4-dimethanols, whose configurations were determined by ir hydrogen bonding and nmr studies.

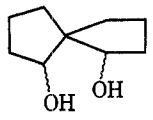
Axially dissymmetric molecules such as allenes and spirans are of historical interest because their synthesis and optical resolution provide experimental confirmation of the predicted geometry of bonds emanating from carbon centers.[1] Spirans with substituents or heteroatoms in each ring having nonsuperimposable mirror images have, in addition, the possibility of existing as diastereomers depending on the nature and point of attachment of the substituents. A few examples of this situation have been reported;[1] however, to our knowledge, the only cases where all possible diastereomers of a disubstituted spiran were separated and characterized are due to Cram[2] and to Applequist[3]

(1) For reviews, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 12.

(2) E. Hardegger, E. Maeder, M. Semarne, and D. J. Cram, *J. Amer. Chem. Soc.*, **81**, 2729 (1959).

(3) D. E. Applequist and E. G. Alley, *J. Org. Chem.*, **33**, 2741 (1968).

who identified all three diastereomers of spiro[4.4]-nonane-1,6-diol (1) and of 1,4-dichlorospiropentane (2), respectively.[4] These molecules each have two



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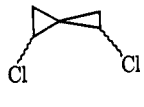
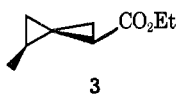


2

dissymmetric centers as well as an axis of dissymmetry; thus, four diastereomeric *dl* pairs of each are possible. Examination of the molecules reveals, however, that one of the *dl* pairs is equivalent to another in each case by virtue of the equivalent substitution in the two rings.

We wish to report the preparation, characterization, and spectroscopic properties of all four diastereomers of 1-carbethoxy-4-methylspiropentane, **3**–**6**, not simply to provide more examples of axially dissymmetric molecules but because it has proven possible to utilize these materials in providing a partial geographic survey of the energy surface associated with the thermal isomerization of isopropenylspiropentane.[5] Furthermore, these materials are well suited as stereochemically labeled materials for investigation of the possible multiple cyclopropylcarbinyl-type rearrangements of the spiropentylcarbinyl charged and uncharged species.



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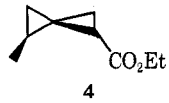

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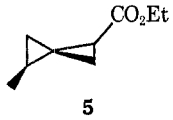

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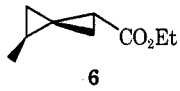
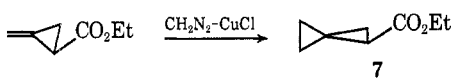


6

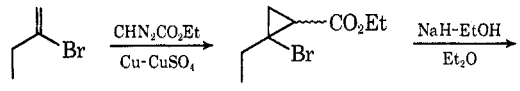
Results

Synthesis of the Four 1-Carbethoxy-4-methylspiropentanes.—Synthetic entry into the substituted spiropentane system is best accomplished by carbene addition to allenes or to methylenecyclopropanes. For instance, carbethoxyspiropentane (**7**) was prepared by treating 1-carbethoxy-2-methylenecyclopropane with the Simmons–Smith reagent.[6] Since relatively large quantities of materials were desired, the Gaspar–Roth cyclopropanation procedure[7] involving cuprous chloride catalyzed addition of methylene from diazomethane was attempted and found to be superior to the previously reported synthesis of **7**.

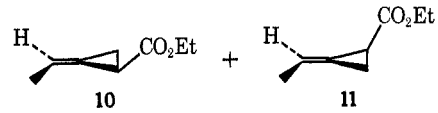


7

The syntheses of **3**, **4**, **5**, and **6** followed that for production of **7**.[6] Thus, the *cis*- and *trans*-2-bromo-2-ethyl-1-carbethoxycyclopropanes (**8** and **9**) were prepared by copper-catalyzed addition of ethyl diazoacetate to 2-bromo-1-butene and were subjected to sodium ethoxide in diethyl ether according to the procedure reported by Ullman to give a mixture of *syn*- and *anti*-1-carbethoxy-2-ethylidenecyclopropane (**10** and **11**), respectively. This mixture (1:4 ratio of two compounds by capillary vpc) was separated by preparative vpc. However, assignment of stereochemistry was not attempted at this point because of the near-identical spectroscopic properties of **10** and **11**.



8 and 9



10 : 11

1 : 4

Each ethylidene derivative was cyclopropanated using the Gaspar–Roth procedure which is known to preserve the stereochemistry about the double bond attacked (ref 7 and references contained therein). In these cases, two isomers were expected from each ethylidene derivative because there are two possible orientations for methylene addition, *syn* or *anti*, to the carbethoxy group. Indeed, two and only two 1-carbethoxy-4-methylspiropentanes were produced from reaction with one of the ethylidene substrates, and two different 1-carbethoxy-4-methylspiropentanes were formed using the other ethylidene material. These conclusions derive from the analysis and spectroscopic properties of vpc purified materials. At this point, it was still not possible to assign the stereochemistry of the precursors, **10** or **11**, or of the product spiropentanes, **3**, **4**, **5**, and **6**. Yet already relationships between the diastereomers were established since two of the four possible compounds were produced in a known stereospecific synthesis from one precursor while the other two possible isomers were derived from the other precursor.

Relative Configurations of the Four 1-Carbethoxy-4-methylspiropentanes.—Examination of Figure 1 reveals that stereospecific addition of methylene to (*R*),-1(*R*)-*syn*-1-carbethoxy-2-ethylidenecyclopropane (**10**) should give (*R*),1(*R*),4(*S*)- and (*S*),1(*R*),4(*R*)-1-carbethoxy-4-methylspiropentane (**3** and **4**), respectively, while (*R*),1(*S*)-*anti*-1-carbethoxy-2-ethylidenecyclopropane, (**11**) should give (*S*),1(*S*),4(*S*)- and (*R*),1(*S*),4(*R*)-1-carbethoxy-4-methylspiropentane (**5** and **6**), respectively. Throughout, however, racemic starting materials were utilized, and the two sets of *dl* pairs derived from racemic **10** are merely epimeric at C-1. Similarly, the two *dl* pairs derived from racemic **11** are epimeric at C-1. To distinguish between these isomers, it was convenient to utilize a system of trivial stereochemical designations. The terms *proximal*, *medial*, and *distal* refer to the relative distances (on a line) between the substituents in the four compounds. The two *medial* compounds can further be distinguished by the terms *syn* and *anti* which refer to the relative positions of substituents using as the plane of reference the plane of the ring bearing the higher priority sub-

(4) Mention should be made of the elegant work of G. E. McCasland and S. Proskow [*J. Amer. Chem. Soc.*, **76**, 4688 (1955)], who prepared the four diastereomers of 3,4,3′,4′-tetramethylspiro[1,1′]bipyrrolidinium *p*-toluenesulfonate and verified that one of the *trans,trans* compounds which had neither a plane nor a center of symmetry was optically inactive by virtue of a fourfold alternating axis of symmetry.

(5) J. J. Gajewski, *ibid.*, **92**, 3688 (1970).

(6) E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961).

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

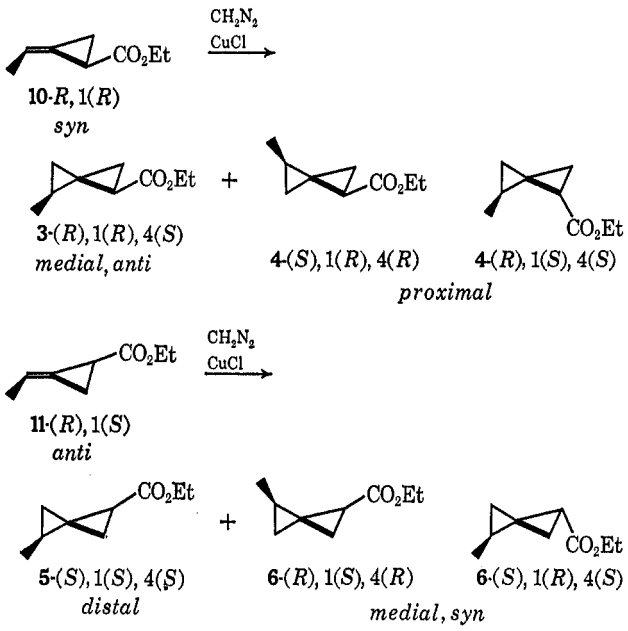
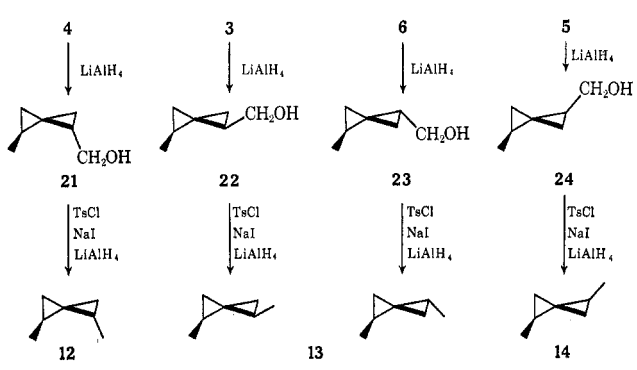


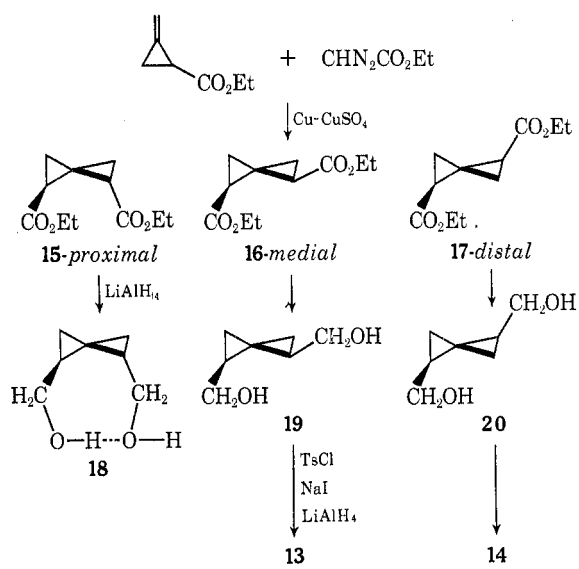
Figure 1.—Cuprous chloride catalyzed addition of diazomethane *syn*- and *anti*-1-carbethoxy-2-ethylidenecyclopropane (10 and 11).

stituent. Thus, **3** is *medial,anti;* **4** is *proximal;* **5** is *distal;* and **6** is *medial,syn.*

A reduction of the stereochemical problem was possible by virtue of the fact that the two different *medial*-1-carbethoxy-4-methylspiropentanes could be made to be identical if the substituents of the two isomers could be made equivalent. Thus, the four carbethoxy derivatives were converted by a reduction, tosylation, iodide displacement, hydride displacement sequence to the 1,4-dimethylspiropentane isomers. As expected, one ester from each of the pairs of spiropentane esters from the ethylidene compounds gave a common hydrocarbon, namely, *medial*-1,4-dimethylspiropentane (**13**), so it was clear that **3** and **6** were *medial* derivatives, but complete assignment of stereochemistry was not yet possible. However, merely determining which hydrocarbon was *proximal*, **12**, or, alternatively, which was *distal*, would serve to establish the configurations of **3**, **4**, **5**, and **6** as well as their precursors, **10** and **11**. This was accomplished by direct synthesis of *distal*-1,4-dimethylspiropentane (**14**), from precursors whose stereochemistry was assigned by chemical and spectroscopic studies.



Syntheses and Relative Configurations of the Symmetrically 1,4-Disubstituted Spiropentanes.—Copper-catalyzed addition of ethyl diazoacetate to 1-carbethoxy-2-methylenecyclopropane gave a mixture of three isomeric 1,4-dicarbethoxyspiropentanes, **15**, **16**, and **17**, in the ratio 1:4:2, respectively, which were separated by preparative vpc. The major product was easily identified as the *medial* compound because its pmr spectrum indicated the presence of two different ethoxy groups and two different sets of ABX ring proton resonances. The *medial* compound, **16**, has no symmetry elements, while the *proximal* and *distal* materials each have a C_2 axis passing through the central carbon. Thus, a single ethoxy group and an ABX ring proton resonance pattern were expected and found for the other two isomers. The *proximal* and *distal* isomers were further distinguished by reduction to the dimethanols, **18** and **20**, the latter of which (*distal*) showed no evidence for intramolecular hydrogen bonding in the ir in carbon disulfide solvent, while the former (*proximal*) had a sharp, third absorption at 3480 cm^{-1} (see Table I). *medial*-Dimethanol (**10**) showed no evidence of intramolecular hydrogen bonding. The *distal*-1,4-spiropentanedimethanol was then converted by the tosylation, iodide displacement, hydride displacement route to the same 1,4-dimethylspiropentane derived from **5**. Finally, the *medial*-1,4-spiropentanedimethanol (**19**) was converted to the same 1,4-dimethylspiropentane derived from both **3** and **6**.



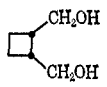
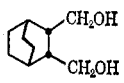
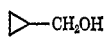
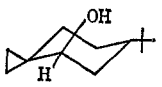
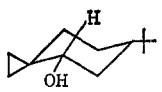
Thus, the relative configurations of the following compounds were assigned: all three 1,4-dicarbethoxyspiropentanes, all three 1,4-spiropentanedimethanols, all three 1,4-dimethylspiropentanes, all four 4-methyl-1-carbethoxyspiropentanes, and, therefore, the two 1-carbethoxy-2-ethylidenecyclopropanes.

Discussion

Assignment of Configuration. Hydrogen-Bonding Studies.—The stereochemical assignment of all the compounds described results ultimately on the distinction between the diols **18**, **19**, and **20**. Since **19** was clearly the *medial* diol on the basis of its nmr spectrum, the problem was reduced to characterization of **18** and **20** by infrared hydrogen bonding studies using the carbon disulfide solvent.[8] The data of Table

(8) For an extensive study of intramolecular OH–O bonding, see L. P. Kuhn, P. von R. Schleyer, W. F. Battinger, Jr., and L. Eberson, *J. Amer. Chem. Soc.*, **86**, 650 (1964).

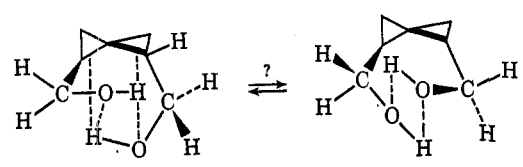
TABLE I
IR O–H STRETCHING ABSORPTIONS OF 18, 19, 20, AND COMPARISON COMPOUNDS

		ν, cm^{-1}
	18[a]	3620 (1),[b] 3480 (2)[b]
	19[a]	3640, 3610[c]
	20[a]	3640, 3610[c]
	25[d]	3634 (1.2), 3507 (1.0)
	26[a]	3623 (0.9), 3490 (1.0)
	27[e]	3633 (1.0), 3615 (1.1)
	28[e]	3621 (0.3), 3612 (1.0)
	29[e]	3636 (1.0), 3625 (0.4)

[a] Very dilute solutions in CS_2. [b] Numbers in parentheses denote relative intensities. [c] Low-intensity shoulders. [d] Dilute solutions in CCl_4 (ref 8). [e] Dilute solutions in CCl_4 (ref 9).

I are most revealing in this respect, indicating that **18** is, indeed, the *proximal* diol. Thus, the frequency shift between the free and the bonded O–H stretching absorptions of **18** is very similar to that of the dimethanols **25** and **26**. While the relative intensities of the two absorptions in **18** and the model compounds are not the same, they are of the same order of magnitude and indicate that hydrogen bonding occurs to a greater degree in **18** relative to **25** or **26**.[8] This latter observation may be consistent with other data included in Table I; *i.e.*, the position of the "free" O–H stretches in **18** is shifted about 20 cm^{-1} from that of **19** and **20**. Furthermore, both **19** and **20** have low-intensity shoulders around 3610 cm^{-1}. This is reminiscent of OH to cyclopropane interactions studied by Joris, Schleyer, and Gleiter,[9] *e.g.*, **27**, **28**, and **29** of Table I.

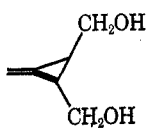
A reasonable explanation for these facts recalls that OH to cyclopropane bonding occurs most efficiently to the "edge" of the cyclopropane ring rather than from above the plane of the ring; *cf.* **28** and **29**. In **19** and **20** both OH groups can bond either to the cyclopropane ring bearing them or to the other ring. However, in one conformation of **18** (**18a** below) the OH groups can easily be disposed toward bonding with each other as well as to the edge of the other ring. (That **18a** and **18b** are the two conformations to consider here derives from the fact that at closest approach the O···O distance is about 0.6 Å in **18** which is much too close for efficient OH···OH hydrogen bonding.) Thus, the shift to lower frequencies of the "free" OH in **18** appears reasonable and is analogous to the shift seen for **28** relative to its model, **29**. A qualitative comparison of



18a **18b**

the solubilities of **18**, **19**, and **20** reinforces the conclusions based on the ir studies. The *proximal* diol, **18**, was much more soluble in CS_2 solvent than **19** or **20**. Thus, a saturated solution of **18** in CS_2 had a broad bonded OH absorption in the ir at 3260, while saturated CS_2 solutions of **19** or **20** showed no intermolecularly bonded OH groups.

A final interesting point along these lines is the nmr chemical shift difference between the carbinol hydrogens of **18**, 0.7 ppm in $CDCl_3$, a relatively good hydrogen bonding solvent.[10] On the other hand, the chemical shift difference in **20** is practically zero, and in **19** a narrow multiplet is observed. Whether or not this can be related to a conformational preference in **18** due to hydrogen bonding is not yet clear. Similar effects have been noted in instances where intramolecular hydrogen bonding is not possible; for instance, 3-methylenecyclopropane-*trans*-1,2-dimethanol (**30**) has a 0.7-ppm chemical shift difference between the carbinol hydrogens; the corresponding *cis* compound, **31**, has a carbinol hydrogen chemical shift difference of 0.63 ppm.[11]



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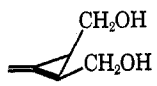

31

Experimental Section

General.—Nuclear magnetic resonance spectra were recorded on Varian A-60, HA-100, and HR-220 spectrometers. Carbon tetrachloride was used as a solvent with chloroform as an internal lock in frequency sweep mode; chemical shifts are reported as δ values in ppm relative to TMS. Infrared spectra were obtained with Perkin-Elmer Model 621, 137, and 137G spectrophotometers in the indicated solvent. Vapor phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using the indicated columns. Analyses were performed by Spang Microanalytical Laboratory.

Ethyl Spiropentanecarboxylate (7).—To a 0° stirred mixture of 3.35 g (0.0266 mol) of ethyl methylenecyclopropanecarboxylate[4] and 0.3 g of cuprous chloride in 10 ml of *n*-pentane was added gaseous diazomethane generated from 15 g (0.14 mol) of N-methyl-N-nitroso urea in the manner described by Doering and Roth.[7] The reaction mixture was filtered, concentrated by removal of the solvent through a Vigreux column at atmospheric pressure, and separated by repeated 300-μl injections on a 10 ft × $^3/_8$ in. XF1150 column operated at 135° and 200 ml/min helium flow rate. In addition to 1 g of starting ester, 2 g of ethyl spiropentanecarboxylate[6] was collected: ir of **7** (neat) 3030, 1730, and 1180 cm^{-1}; nmr (60 MHz) δ 0.88 (broad singlet, 4 H), 1.08–1.48 (multiplet, 5 H), 1.87 (doublet of doublets, J = 8.0 and 4.0 Hz, 1 H), 4.05 (quartet, J = 7.5 Hz, 2 H).

***cis*- and *trans*-1-Carbethoxy-2-bromo-2-ethylcyclopropanes (8 and 9).**—To a stirred refluxing mixture of 500 ml of 90% pure 2-bromo-1-butene (Columbia Organic), 3 g of anhydrous cupric sulfate, and 3 g of electrolytic copper dust was added 140 g (1.23 mol) of ethyl diazoacetate dropwise over a period of 12 hr. After the mixture was allowed to stir at reflux for 10 hr more, it was cooled, then filtered. Distillation of the filtrate through a large Vigreux column at atmospheric pressure gave 300 ml of starting bromo olefin. Rapid vacuum distillation of the residue gave 150 ml of light brown oil, bp 25–110° (15 Torr). Redistillation of the distillate at 11 Torr through a 15-in. spiral wire column gave 33 g of forerun; 59 g of fraction I, bp 86–90°; 5 g of fraction II, bp 90–97°; and 22 g of fraction III, bp 97.0–98.3°. Fraction I was a single isomer of 1-carbethoxy-2-bromo-2-ethylcyclopropane (**8** or **9**), from its analysis and nmr spectrum at 60 MHz: nmr δ 0.9–2.43 (multiplet, 11 H) and 4.13 (quartet, J = 7 Hz, 2 H).

(9) L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968).

(10) A. Allerhand and P. von R. Schleyer, *ibid.*, **85**, 1715 (1963).

(11) J. J. Gajewski, unpublished observations.

Anal. Calcd for $C_8H_{13}BrO_2$: C, 43.44; H, 5.98; Br, 36.16. Found: C, 43.48; H, 5.86; Br, 36.16.

Fraction III appeared to be the other isomer of 1-carbethoxy-2-bromo-2-ethylcyclopropane (**8** or **9**) contaminated with about 15% of diethyl fumarate: nmr (60 MHz) of fraction III δ 0.9–2.0 (complex multiplet, relative area 3.5), 4.14 (center of two nearly superimposed quartets, relative area 7.9), and 6.77 (singlet, relative area 1). Fraction II was a mixture of fractions I and III.

Subsequent experiments indicated that fractions I, II, and III could be dehydrobrominated to the same 1:4 mixture of the *syn*- and *anti*-2-ethylidene-1-carbethoxycyclopropanes, **10** and **11**.

***syn*- and *anti*-2-Ethylene-1-carbethoxycyclopropanes (10 and 11).**—To a rapidly stirred, refluxing slurry of 17.5 g (0.738 mol) of sodium hydride and 30.0 g (0.136 mol) of **8** and/or **9** (fractions I, II, or III) in 300 ml of diethyl ether under nitrogen was added 2.0 ml of ethanol.[12] Refluxing with stirring was continued for 80 min; then the reaction mixture was allowed to cool. The sodium hydride was decomposed by careful addition of excess acetic acid; then water was added. This treatment resulted in a clear, two-layer solution. The layers were separated and the aqueous layer was extracted with ether. The combined ether layers were washed with a 10% sodium bicarbonate solution until washings were basic. After being washed with saturated brine and dried over anhydrous sodium sulfate, the ethereal solution was concentrated by removal of the solvent through a Vigreux column at atmospheric pressure giving 27 g of a brown residue which was distilled at aspirator vacuum. A total of 5.2 g of a clear distillate, bp 74–82° (25 Torr), was collected. The pot residue consisted of starting bromide and materials containing alkylethoxy groups by nmr. The distillate contained two materials in the ratio of 1:4. The mixture was separated by repeated 100-μl injections on a 20 ft × $^3/_8$ in. UCON 50HB2000 vpc column operated at 125° and 200-ml/min helium flow. The minor product which, in addition, had the shorter retention time of the two was later shown to be *syn*-2-ethylidene-1-carbethoxycyclopropane (**10**). The major product was later found to be *anti*-2-ethylidene-1-carbethoxycyclopropane (**11**).

Properties of *syn*-1-carbethoxy-2-ethylidenecyclopropane (**10**): ir (neat) 2995, 1735, 1160, 1090, 1075, 1050, 1030 (sh), 990, 945, 915, 860 (w), 825, 785 (w), and 755 (w) cm^{-1}; nmr (100 MHz) δ 1.23 (triplet, 3 H, J = 7.0 Hz), 1.37–1.73 (multiplet, 2 H), 1.73–1.87 (complex multiplet centered at δ 1.77, 3 H), 2.00–2.20 (symmetrical multiplet centered at δ 2.10, 1 H), 4.08 (quartet, J = 7.0 Hz, 2 H), and 5.55–6.0 (symmetrical multiplet centered at δ 5.78, 1 H); nmr (220 MHz) δ 1.25 (triplet, J = 7 Hz, 3 H), δ 1.54 (triplet with fine structure, J = 7 Hz, 1 H), 1.7 (multiplet, 1 H), 1.78 (doublet of quartets, J = 7 and 2 Hz, 3 H), 2.1 (multiplet, 1 H), 3.98 (quartet, J = 7 Hz, 2 H), and 5.70 (multiplet, 1 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.57; H, 8.54.

Properties of *anti*-1-carbethoxy-2-ethylidenecyclopropane (**11**): ir (neat) 2995, 1735, 1160, 1090, 1075, 1045, 1025, 960 (sh), 940, 855 (w), 830 (w), and 750 (w) cm^{-1}; nmr (100 MHz) δ 1.25 (triplet, J = 7.0 Hz, 3 H), 1.35–1.75 (multiplet, 2 H), 1.87 (doublet of quartets, J = 6.5 and 1.8 Hz, 3 H), 2.00–2.20 (symmetrical multiplet of 11 lines each separated by 1.8 Hz, centered at δ 2.10 1 H), 4.12 (quartet, J = 7.0 Hz, 2 H), and 5.60–6.10 (symmetrical multiplet, centered at δ 5.85, 1 H); nmr (220 MHz) δ 1.25 (triplet, J = 7 Hz 3 H), 1.47 (triplet with fine structure, J = 8 Hz, 1 H); 1.63 (multiplet, 1 H), 1.85 (doublet of quartets, J = 7.5 and 2 Hz, 3 H), 2.11 (multiplet, 1 H), 3.97 (quartet, J = 7 Hz, 2 H), and 5.75 (multiplet, 1 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.68; H, 8.62.

Cyclopropanation of 10. *medial,anti*- and *proximal*-1-Carbethoxy-4-methylspiropentanes (3 and 4).—gaseous diazomethane generated from 40 g (0.39 mol) of N-methyl-N-nitrosourea was bubbled into a solution of 1.87 g (0.0135 mol) of **10** in 5 ml of *n*-pentane containing 0.2 g of cuprous chloride at 0°, according to the Gaspar–Roth recipe.[7] After filtration and bulb-to-bulb distillation under vacuum, 1.45 g of colorless liquid was obtained. Vpc analysis revealed the presence of three peaks in the ratio 0.4:0.8:1 (in order of increasing retention time) with the minor component being unreacted starting material. Preparative vpc on a 20 ft × $^3/_8$ in. UCON 50HB2000 column operated at 148° and 75-ml/min helium flow gave 0.40 g of 99+% homogeneous **3**, subsequently identified as *medial,anti*-1-carbethoxy-4-methylspiropentane, and 0.56 g of 99+% homogeneous **4** which was subsequently identified as *proximal*-1-carbethoxy-4-methylspiropentane.

Properties of *medial,anti*-1-carbethoxy-4-methylspiropentane, **3**: ir (CCl_4) 3080, etc., 1730, 1450, 1360, 1340, 1255, 1170, 1135, 1125, 1090, 1065, 1040, 1005, and 925 cm^{-1}; nmr (60 MHZ) δ 0.42 (broad singlet, 1 H), 0.9–1.55 (multiplet, 10 H), 1.78 (doublet of doublets, J = 7.5 and 4 Hz, 1 H), and 4.06 quartet, J = 7.5 Hz).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.39; H, 9.27.

Properties of *proximal*-1-carbethoxy-4-methylspiropentane, **4**: ir (CCl_4) 3060, etc., 1725, 1450, 1360, 1340, 1300, 1260, 1160, 1120, 1070, 1035, 1010, 940, and 895 cm^{-1}; nmr (60 MHz) δ 0.46 (triplet, J = 4 Hz, 1 H), 0.7–1.58 (complex multiplet, 10 H), 1.82 (doublet of doublets, J = 7 and 4 Hz, 1 H), and 4.08 (quartet, J = 7 Hz, 2 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.81; H, 9.01.

Cyclopropanation of 11. *distal*- and *medial,syn*-1-Carbethoxy-4-methylspiropentanes (5 and 6).—As described above for production of **3** and **4**, a total of 2.38 g (0.017 mol) of **11** was treated with a total of 51 g (0.49 mol) of N-methyl-N-nitrosourea. Vpc analysis revealed the presence of three components in the ratio 4:1:2 in order of retention times on a 20 ft × $^3/_8$ in. UCON 50-HB2000 preparative vpc column with the minor (middle) component being starting material. Vpc separation under the same conditions described for **3** and **4** allowed isolation of 0.76 g of 99% pure **6** which was later identified as *medial,syn*-1-carbethoxy-4-methylspiropentane and 0.43 g of 99+% pure **5** which was subsequently identified as *distal*-1-carbethoxy-4-methylspiropentane.

Properties of *medial,syn*-1-carbethoxy-4-methylspiropentane (**6**): ir (neat) 3080, etc., 1730, 1450, 1375, 1345, 1325, 1265, 1185, 1130, 1070, 1040, 890 (broad weak), 845, and 775 cm^{-1}; nmr (60 MHz) δ 0.49 (broad singlet, 1 H), 0.8–1.50 (multiplet, 10 H), 1.85 (doublet of doublets, J = 7 and 4 Hz, 1 H), and 4.05 (quartet, J = 7.5 Hz, 2 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.18; H, 9.15.

Properties of *distal*-1-carbethoxy-4-methylspiropentane (**5**): ir (neat) 3075, etc., 1730, 1450, 1410, 1390, 1380, 1350, 1320, 1270, 1180, 1160, 1120, 1090, 1070, 1030, 980, 945, 925, 880, 855, and 750 cm^{-1}; nmr (60 MHz) δ 0.58 (center of multiplet, 1 H), 0.75–1.45 (multiplet, 10 H), 1.83 (doublet of doublets, J = 7 and 4 Hz, 1 H), and 4.08 (quartet, J = 7 Hz, 2 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.23; H, 9.12.

1,4-Dicarbethoxyspiropentanes (15, 16, and 17).—Ethyl diazoacetate (4.6 g, 0.040 mol) dissolved in 30 ml of *n*-octane was added over a period of 24 hr to a refluxing solution of 2.6 g (0.021 mol) of methylenecarbethoxycyclopropane in 10 ml of *n*-octane containing 0.03 g of copper bronze and 0.07 g of anhydrous cupric sulfate. After addition the mixture was cooled and filtered, and the solvent was removed by distillation. Vacuum distillation of the residue gave 3.62 g (87%) of material boiling at 84–88° (0.5 Torr). Vpc analysis (5 ft × $^1/_4$ in. SE-30 column) of the mixture showed three peaks in a ratio of about 1:4:2. The mixture was separated using an 18 ft × $^3/_8$ in. 25% SE-30 column at 150°.

Fraction I. *proximal*-1,4-Dicarbethoxyspiropentane (15).—About 0.1 g of the first fraction was recovered after repassing through the 18-ft SE-30 column. The material was subsequently shown to be *proximal*-1,4-dicarbethoxyspiropentane, **15**: ir ($CHCl_3$) 2984, 2935, 2909, 1725, 1378, 1349, 1323, 1274, 1165, 1121, 1098, 1071, and 1019 cm^{-1}; nmr (100 MHz) (CCl_4) δ 1.03 (triplet, J = 7 Hz) superimposed on a multiplet between 0.95 and 1.25 (total of 10 H), 1.89 (doublet of doublets, J = 7.5 and 5 Hz, 2 H), and 3.86 (quartet, J = 7 Hz, 4 H).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.26; H, 7.57.

Fraction II. *medial*-1,4-Dicarbethoxyspiropentane (16).—Approximately 1.4 g of the second fraction was obtained after repassing through the $^3/_8$-in. SE-30 column. This was *medial*-1,4-dicarbethoxyspiropentane (**16**): ir ($CHCl_3$) 2978, 2933, 2904, 1720, 1393, 1370, 1340, 1323, 1267, 1163, 1117, 1092, 1058, 1028, and 1015 (sh) cm^{-1}; nmr (100 MHz) (CCl_4) δ 1.13 (two nearly superimposed triplets, J = 7 Hz, 6 H), 1.33 (multiplet,

(12) J. A. Carbon, W. B. Martin, and L. R. Swett, *J. Amer. Chem. Soc.*, **80**, 1002 (1958).

4 H), 1.83 (multiplet, 2 H), and 3.92 (two nearly superimposed quartets, J = 7 Hz, 4 H).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.36; H, 7.58.

Fraction III. *distal*-**1,4-Dicarbethoxyspiropentane (17).**—Approximately 0.8 g of fraction III was recovered after repassing through the $^3/_8$-in. SE-30 column. This material was later shown to be distal-1,4-dicarbethoxyspiropentane, **17**: ir ($CHCl_3$) 2980, 2938, 2904, 1710, 1365, 1341, 1311, 1289, 1268 (sh), 1160, 1091, 1055 (sh), and 1021 cm^{-1}; nmr (100 MHz), (CCl_4) δ 1.14 (triplet, J = 7 Hz) superimposed on a multiplet between 1.04 and 1.29 (total of 8 H), 1.45 (triplet, J = 4.5 Hz, 2 H), 1.85 (doublet of doublets, J = 6 and 4.5 Hz, 2 H), and 3.92 (quartet, J = 7 Hz, 4 H).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.22; H, 7.56.

proximal-**1,4-Spiropentanedimethanol (18).**—To a suspension of 0.1 g (2.6 mmol) of lithium aluminum hydride in about 5 ml of dry ether was added 0.05 g (0.24 mmol) of **15**. After 1 hr of reflux, a freshly prepared, saturated solution of anhydrous sodium sulfate was added dropwise until a white precipitate was obtained. The solid was filtered from the ether solution and washed several times with tetrahydrofuran. The washings were combined with the original filtrate and the solvent was removed. After passing through a 5 ft × $^1/_4$ in. 20% SE-30 column at 130° twice, pure **18** was obtained: ir (CS_2) 3620, 3480, and 3260 (broad) cm^{-1}; ($CHCl_3$) 2950, 2915, 2870, 1430, 1360, 1310, 1210 (broad), and 1153 cm^{-1}; nmr (100 MHz) ($CDCl_3$) δ 0.72 (unsymmetrical triplet, J = 4.5 Hz, 2 H), 0.90 (doublet of doublets, J = 8 and 4 Hz, 2 H), 1.55 (symmetrical seven-line multiplet with 4-Hz separation between each line, 2 H), 3.42 doublet of doublets, J = 11 and 7.5 Hz, 2 H); 4.10 (doublet of doublets, J = 11 and 4 Hz, 2 H), and 4.50 (broad singlet, 2 H).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.40; H, 9.38.

medial-**1,4-Spiropentanedimethanol (19).**—Reduction of **16** by lithium aluminum hydride to give *medial*-1,4-spiropentanedimethanol (**19**) was accomplished in near-quantitative yield after vpc purification as described above for production of **18**: ir (CS_2) 3640 cm^{-1} (intermolecularly bonded hydroxyl absorption was not observed at the low concentration employed in this measurement, which was necessitated by the poor solubility of **19** in the solvent); ir ($CHCl_3$) 3610, 3360 (broad,) 1382, 1310, 1220 (broad), 1138, 1090, and 990 cm^{-1}; nmr (100 MHz) ($CDCl_3$) δ 0.60–1.06 (multiplet, 4 H), 1.10–1.60 (multiplet, 2 H), 2.63 (singlet, 2 H), and 3.64 (ten-line multiplet, 4 H).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.68; H, 9.40.

distal-**1,4-Spiropentanedimethanol (20).**—Reduction of **17** to *distal*-1,4-spiropentanedimethanol (**20**) was accomplished in good yield in the same manner as described above for reduction of **15** to give **18**: ir (CS_2) 3640 cm^{-1} (no other hydroxyl absorptions were observed at the low concentrations employed in this measurement owing to limited solubility of **20** in the solvent); ir ($CHCl_3$) 2948, 2910, 2868, 1430, 1358, 1310, and 1152 cm^{-1}; nmr (100 MHz) ($CDCl_3$) δ 0.62 (unsymmetrical triplet, J = 4.5 Hz, 2 H), 1.06 (doublet of doublets, J = 8.0 and 4.5 Hz, 2 H), 1.46 (doublet of quartets, J = 6.5 and 4.5 Hz, 2 H), 1.92 (singlet, 2 H), and 3.58 (doublet, J = 6.5 Hz, 4 H).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.71; H, 9.48.

distal-**1,4-Dimethylspiropentane (14).**—The diol **20** (0.37 g, 0.0029 mol) was dissolved in 0.1 ml of pyridine; the solution was cooled to 0° and added dropwise to a solution of 1.25 g (0.0066 mol) of *p*-toluenesulfonyl chloride dissolved in about 3 ml of pyridine also cooled to 0°. After stirring at 0° for 2.5 hr, the reaction mixture was taken up in ether and washed twice with 50-ml portions of ice-cold 5% hydrochloric acid, once with 50 ml of cold water, and once with saturated sodium bicarbonate solution. Drying over anhydrous magnesium sulfate and removal of the ether gave 0.91 g (71%) of a clear oil: nmr (60 MHz) ($CDCl_3$) 0.58 (triplet, J = 5 Hz, 2 H), 0.90–1.50 (multiplet, 4 H), 2.43 (singlet, 6 H), 3.95 (symmetrical five-line pattern with 6-Hz separation between lines, 4 H), 7.33 (unsymmetrical doublet, J = 8 Hz, 4 H), and 7.70 (unsymmetrical doublet, J = 8 Hz, 4 H).

This ditosylate (0.91 g, 0.021 mol) was dissolved in acetone, added to an acetone solution of 0.80 g (0.0053 mol) of sodium iodide, and refluxed for 1.5 hr. After this time the mixture was filtered, the acetone was distilled from the filtrate, and the residue was dissolved in ether. The ether solution was washed with saturated sodium sulfite and dried over anhydrous magnesium sulfate. Upon distillation of the ether at atmospheric pressure, there remained 0.65 g (89%) of a yellow oil: nmr (60 MHz) (CCl_4) δ 0.58 (triplet, 2 H), 1.13–2.13 (multiplet, 4 H), and 3.16 (doublet of doublets, 4 H).

This diiodide was added dropwise to a large excess of lithium aluminum hydride suspended in diethoxydiethylene glycol at 80° and 185 Torr. The hydrocarbon, *distal*-1,4-dimethylspiropentane (**32**), was trapped in a U tube cooled by liquid nitrogen; about 90 μl of material was obtained. The compound was purified by vpc using a 5 ft × $^1/_4$ in. 20% SE-30 column at room temperature and 25-ml/min helium flow rate (50–60 μl recovered): ir (CCl_4) 3045, 2987, 2946, 2863, etc., 1380, 1078, 1029, 999, 957, and 850 cm^{-1}; nmr (100 MHz) δ 0.22 (broad singlet with fine structure, 2 H) and 1.02 (doublet, J = 2 Hz) superimposed on a multiplet 0.74–1.12 (total of 10 H).

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.49; H, 12.60.

medial-**1,4-Dimethylspiropentane (13).**—*medial*-1,4-Dimethylspiropentane (**13**) was prepared from **19** in the same manner as described for production of **14** from **20**: ir (CCl_4) 3050, etc., 1378, 1305, 1089, 1045, 1030, 999, and 848 cm^{-1}; nmr (100 MHz) (CCl_4) δ 0.33 (unsymmetrical multiplet, 2 H) and 1.03 (broad doublet) superimposed on a multiplet between 0.70 and 1.14 (total of 10 H).

Anal. Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.33; H, 12.54.

medial,syn-**4-Methyl-1-spiropentanemethanol (23).**—Reduction of **6** to *medial,syn*-4-methyl-1-spiropentane-methanol (**23**) was accomplished as described above for reduction of **17** to **20**: ir of (CCl_4) 3614, 3350 (broad), 3050, etc., 1380, and 1055 cm^{-1}; nmr (100 MHz) (CCl_4) δ 0.30 (unsymmetrical triplet, J = 3.5 Hz), 0.48 (unsymmetrical triplet, J = 4 Hz, 1 H), 1.00 (doublet, J = 2 Hz) superimposed on a multiplet from 0.70 to 1.40 (total of 7 H), 2.56 (broad singlet, 1 H), and 3.39 (doublet, J = 7 Hz, 2 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 75.05; H, 10.75.

medial-**1,4-Dimethylspiropentane (13) from 23.**—The alcohol **23** was converted to *medial*-1,4-dimethylspiropentane (**13**) in the same manner as described for conversion of **20** to **14**. The spectral properties and vpc retention time on a 250-ft UCON 50-HB2000 capillary column of vpc purified hydrocarbon were identical with those of the hydrocarbon prepared from **19**.

proximal-**4-Methyl-1-spiropentanemethanol (21).**—Reduction of **4** to *proximal*-4-methyl-1-spiropentane-methanol (**21**) was accomplished as described above for reduction of **17** to **20**: ir (CCl_4) 3614, 3360 (broad), 3050, etc., 1377, and 995 cm^{-1}; nmr (100 MHz) (CCl_4) δ 0.35 (broad singlet, 1 H), 0.53 (unsymmetrical triplet, J = 4.5 Hz, 1 H), 0.82 (doublet of doublets, J = 7 and 4 Hz, 2 H), 1.08 (doublet, J = 1.5 Hz, 4 H), 1.40 (multiplet, 1 H), 2.30 (broad singlet, 1 H), 3.31 (unsymmetrical triplet with 7-Hz separation between lines, 1 H), and 3.63 (broad singlet, 1 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 75.06; H, 11.04.

proximal-**1,4-Dimethylspiropentane (12).**—The alcohol **21** was converted to *proximal*-1,4-dimethylspiropentane (**12**) in the same manner as described for conversion of **20** to **14** ir of vpc-purified **12** (CCl_4) 3050, 1505, 1381, 1373, 1183, 1093, 1043, 998, and 850 cm^{-1}; nmr (100 MHz) (CCl_4) δ 0.33 (broad singlet, 2 H), 0.80 (broad singlet, 2 H), and 1.00–1.10 (doublet, J = 1 Hz, superimposed on a multiplet, total of 8 H). The capillary vpc retention time of this material was similar to but not the same as that of **13** or of **14**. Because of the limited amounts of starting material and losses on vpc purification, it was not possible to obtain an elemental analysis of this hydrocarbon.

medial,anti-**4-Methyl-1-spiropentanemethanol (22).**—Reduction of **3** to *medial,anti*-4-methyl-1-spiropentanemethanol (**22**) was accomplished as described above for reduction of **17** to **20**: ir (CCl_4) 3618, 3400 (broad), 3053, etc., 1379, and 999 cm^{-1}; nmr (100 MHz) (CCl_4) δ 0.38 (broad singlet, 1 H), 0.59 (unsymmetrical triplet, J = 3.5 Hz, 1 H), 1.01 (broad singlet) superimposed on a multiplet between 0.77 and 1.39 (total of 7 H), 1.99 (broad singlet, 1 H), and 3.47 (doublet, J = 7 Hz, 2 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.90; H, 10.71.

medial-**1,4-Dimethylspiropentane (13) from 22.**—The alcohol **22** was converted to *medial*-1,4-dimethylspiropentane (**13**) in the

same manner as described for conversion of **20** to **14**. The spectral and vpc retention time on a 250-ft UCON 50HB2000 capillary column of vpc-purified material were identical with those of the hydrocarbon prepared from **19**.

distal-**4-Methyl-1-spiropentanemethanol** (**24**).—Reduction of **5** to *distal*-4-methyl-1-spiropentanemethanol (**24**) was accomplished as described above for reduction of **17** to **20**: ir (CCl_4) 3620, 3370 (broad), 3050, etc., 1380, and 1022 cm^{-1}; nmr (100 MHz) (CCl_4) δ 0.23 (broad singlet, 1 H), 0.44 (unsymmetrical triplet, 1 H), 1.01 (broad singlet) superimposed on a multiplet between 0.75 and 1.44 (total of 7 H), 2.53 (broad singlet, 1 H), and 3.40 (doublet, J = 7 Hz 2 H).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.79. Found: C, 74.84; H, 10.61.

distal-**1,4-Dimethylspiropentane** (**14**) **from 24**.—The alcohol **24** was converted to *distal*-1,4-dimethylspiropentane (**14**) in the same manner as described for conversion of **20** to **14**. The spectral properties and vpc retention time on a 250-ft UCON 50-HB2000 capillary column of vpc purified hydrocarbon were identical with those of the hydrocarbon prepared from **30**.

Registry No.—**3**, 24298-73-5; **4**, 24298-74-6; **5**, 24298-75-7; **6**, 24299-28-3; **7**, 6142-68-3; **8**, 24299-29-4; **9**, 24299-30-1; **10**, 24299-31-8; **11**, 24299-32-9; **12**, 24299-33-0; **13**, *medial*, 24299-34-1; **14**, 24299-35-2; **15**, 24299-36-3; **16**, 24299-37-4; **17a**, 24375-89-1; **18**, 24299-39-6; **19**, 24299-40-9; **20**, 24343-79-1; **21**, 24299-41-0; **22**, 24299-42-1; **23**, 24343-80-4; **24**, 24299-43-2.

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The *ortho* Claisen Rearrangement. VIII. Solvent Effects[1,2]

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The rates of rearrangement of allyl *p*-tolyl ether in the gas phase and in 17 solvents of different polarities have been determined. The rates varied over a 300-fold range, indicating a considerable solvent effect. The normal rearrangement product was formed in every case. The results cannot be explained solely on the basis of the hydrogen-bonding ability of the solvent and it is necessary to invoke other solvent properties to account for the findings.

The Claisen rearrangement has often been cited as a reaction insensitive to solvent effects, in spite of the fact that early studies[3] indicated that this was probably not so. A couple of more recent investigations[1a,4] have also indicated that the reaction is influenced by the nature of the medium. A more complete evaluation of solvent effects and their origin was attempted in this investigation.

Results

The rates of rearrangement of allyl *p*-tolyl ether in the gas phase and in 17 solvents of differing polarities were determined. The specific rate constant was measured in one of three different ways, depending on the nature of the solvent. If the solvent had negligible absorption in the ultraviolet–visible range, aliquots of the reaction mixture were dissolved in aqueous or alcoholic base and the formation of product was followed through the absorption of the 2-allyl-4-methylphenoxide ion. The reaction in solvents that have significant absorption in the ultraviolet–visible region was monitored by observing the change in a band at 12.91 μ that appears in the infrared spectrum of allyl *p*-tolyl ether. In the gas phase runs, samples of the ether were sealed in evacuated tubes and thermostated for various intervals. The sample size was such that all of the reactant and/or product was in the gas phase at the reaction temperature. The extent of reaction was determined from the ultraviolet spectrum of a solution of the partially reacted sample in alcoholic sodium hydroxide solution. The absence of a wall effect in the gas phase reaction was obvious from the constancy of per cent reaction in normal tubes and in tubes packed with glass wool. The rate constants obtained by these methods are listed in Table I. These values were used to obtain rate constants at 170° by extrapolation or interpolation (Table II).

The reaction product in all of the solvents was shown to be 2-allyl-4-methylphenol by isotope dilution analysis. A solution of allyl-C^{14} *p*-tolyl ether in the solvent under study was rearranged; *n*-2-allyl-4-methylphenol was mixed in and then was converted into the 3,5-dinitrobenzoate for isolation and purification. The per cent yield of 2-allyl-4-methylphenol was calculated from the specific activity of the purified product. The yields in the various solvents are shown in Table III. The expected product, 2-allyl-4-methylphenol, was formed in greater than 80% yields in all of the solvents except 2-aminoethanol, 2-octanol, propylene carbonate, sulfolane, and *p*-chlorophenol. Because of the possibility for decomposition of the product during the long reaction period, the rearrangement in these five solvents was carried out for a shorter period. In all cases, the yields were improved indicating that the product was being destroyed by prolonged heating.

Discussion

As is evident from the data listed in Table II, the rate of the *ortho* Claisen rearrangement is significantly

(1) Previous papers in this series: (a) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. K. Fife, *J. Amer. Chem. Soc.*, **80**, 3271 (1958); (b) W. N. White and B. E. Norcross, *ibid.*, **83**, 1968 (1961); (c) W. N. White and B. E. Norcross, *ibid.*, **83**, 3265 (1961); (d) W. N. White and W. K. Fife, *ibid.*, **83**, 3846 (1961); (e) W. N. White and C. D. Slater, *J. Org. Chem.*, **26**, 3631 (1961); (f) W. N. White and C. D. Slater, *ibid.*, **27**, 2908 (1962); (g) W. N. White and E. F. Wolfarth, *ibid.*, **26**, 3509 (1961); (h) W. N. White, C. D. Slater, and W. K. Fife, *ibid.*, **26**, 627 (1961).

(2) This investigation was supported by Grants G-7345 and GP-1970 from the National Science Foundation.

(3) J. F. Kincaid and D. S. Tarbell, *J. Amer. Chem. Soc.*, **61**, 3085 (1939), found that the rate of rearrangement of allyl *p*-tolyl ether in the absence of solvent increased about fourfold as the reaction progressed implying that the reaction occurred faster in the phenolic product than in the original ether.

(4) H. L. Goering and R. R. Jacobsen, *ibid.*, **80**, 3277 (1958).