shift on hydrogenation of 1 to 2 and 5 to 6 and by its conversion to a singlet—far downfield—in the spectrum of 3.

The chemical shifts of the various carbonyl carbons may be deduced from known parameters of cyclopentenones, cyclopentanones, cycloheptanones, substituted esters (or lactones), and acetates.[10] The upfield shift in the cyclopentanone carbonyl frequency of 8 relative to 6 is notable. Among the remaining nonprotonated carbon atoms, C-16 of 1 and 2 is unique; recognition is eased by its downfield shift in 3–6 and disappearance in 7 and 8. Differentiation between C-5 and C-11 of 1 and 2 is based on comparison with the spectra of 5, 6, and 8 where the upfield shift of one of the signals, that of C-11, and the relative constancy of the second, that of C-5, which moves downfield on oxidation of the neighboring carbon atom, leaves no ambiguity.

Among the methyl signals, assignment of the quartet at lowest field to C-17 is based on single-frequency off-resonance decoupling in 1 and its conversion to a triplet near 86 ppm, characteristic of vinyl ethers, in the spectra of 3 and 4. Differentiation between the remaining methyl signals is difficult because of the superposition of methyl frequencies in the proton NMR spectra. Inspection of Table I reveals a significant upfield shift of one of the methyl signals upon hydrogenation (compare 1 with 2 and 5 with 6) and an upfield shift of a second methyl signal upon opening the hemiacetal ring (compare 1 with 4 and 2 with 6). We assume that the signals affected are those of C-14 and C-15, because (a) the chemical shift of C-13 should not be affected significantly by hydrogenation, (b) conversion of 1 to 2 or 2 to 4 produces a small downfield shift of one of the methyl signals which must be that of C-13, and (c) 5–8 all exhibit at least one relatively invariant signal in the 19–20-ppm region which again must be attributed to C-13. Comparison of 3 and 4 with 2, and 6 and 8 with 5, suggests that the signal which moves upfield on hydrogenation is that of C-14, the shift probably being associated with the introduction of a hydrogen atom peri to C-14. The signal which is shifted upfield on opening of the hemiacetal ring (and downfield on conversion of 6 to 8) is therefore that of C-15, although the reasons for the upfield shift are not clear as opening of the hemiacetal ring would appear to result in removal of a gauche interaction.

Experimental Section

Spectra were recorded on a Bruker HFX-270 instrument in $CDCl_3$ (1–4, 6) and Me_2SO-d_6 (5) solution, using Fourier transform techniques.

Registry No.—**1a,** 55721-12-5; **1b,** 55780-22-8; **2a,** 55660-88-3; **2b,** 55700-79-3; **3,** 55660-89-4; **4,** 55660-90-7; **5,** 10092-04-3; **6,** 55700-80-6; **7,** 54933-23-2; **8,** 55660-91-8.

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(6) The stereochemistry shown in the formula is based on a recent X-ray analysis (private communication from Dr. P. J. Cox, University of Glasgow).
(7) Anhydrodihydrotenulin (4) can be prepared from 2 in >80% yield.[1] Consequently the unlikely (because of the H-6 and H-8 proton shifts) possibility that 1 and 2 are 4:1 mixtures of C-8 epimers (the existence of a C-6 epimer of 1 is not possible) and that purification of 3, 4, and 5 has resulted in fractionation of the more abundant isomer product can be dismissed.
(8) Reexamination of 60-MHz traces recorded 15 years ago revealed a weak doublet (H-6 of minor isomer) partially obscured by the H-6 doublet of the major isomer and two shoulders on the sharp singlets of H-13 and H-17.
(9) The downfield shift of C-9 and the upfield shifts of C-1, C-4, C-5, C-6, and C-7 on going from 1 to 5 (and 2 to 6) are due partially to changes in electron density at C-6 and partially to changes in conformation of ring B and subsequent alterations of spatial relationships on opening the hemiacetal ring.
(10) The conversion of C-6 from sp^3 to sp^2 must be responsible for the surprisingly large upfield shift of C-4 in going from 6 to 8.

Reaction of (+)-1,3-Dimethylallene with Lead Tetraacetate

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Although there has been a great deal of interest in the reaction of lead tetraacetate (LTA) with alkenes,[1] there have been few examples utilizing this reaction with allenes. An earlier study by Laforge and Acree[2] reported that the major product of the reaction of acyclic allenes with LTA was a diacetate. More specifically, the reaction of 1,3-dimethylallene with LTA in acetic acid was also assumed to afford a diacetate. In a more recent disclosure, we have shown that the electrophilic addition of LTA to (−)-1,2-cyclononadiene in acetic acid solvent afforded (+)-3-acetoxycyclononyne by a suprafacial addition.[3] This was a particularly interesting result since the dominant pathway in the oxymercuration[3] and the oxythallation[4] of 1,2-cyclononadiene has been shown to be antarafacial addition to an alkene–metal π complex. The above results of Laforge and Acree[2] with acyclic allenes and our own results[3] with a cyclic allene, which afforded an alkyne as the major product, prompted us to examine the orientation and the stereochemistry of the addition of LTA to (+)-1,3-dimethylallene (1). We now report that the electrophilic addition of LTA to 1 also proceeds principally by a suprafacial pathway affording (*S*)-(+)-4-acetoxy-2-pentyne as the major product.

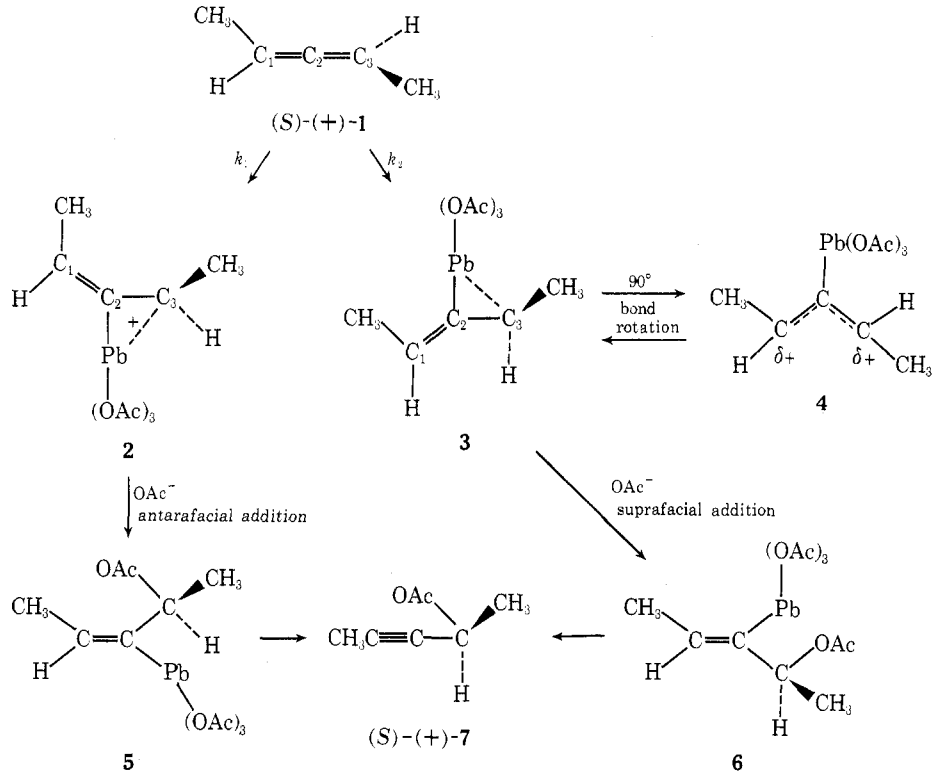
Results and Discussion

When 1,3-dimethylallene (1) was treated with LTA in acetic acid solvent, gas chromatographic analysis (GLC) showed that the major product of the reaction was 4-acetoxy-2-pentyne (7). When the reaction was carried out with optically active (*S*)-(+)-1,[5] $[\alpha]_D$ +22.4°, the product 7 had $[\alpha]_D$ +6.6° (Scheme I). The absolute configuration of 7 was established as *S* by saponification of 7 followed by catalytic hydrogenation of 4-hydroxy-2-pentyne to (*S*)-(+)-2-pentanol (8), $[\alpha]_D$ +1.4°. The stereochemistry of 7 was also established by direct hydrogenation of 7 to (+)-2-acetoxypentane (9). The absolute configuration of 9 was established by conversion of (*S*)-(+)-2-pentanol, $[\alpha]_D$ +12.2°, of known configuration to (*S*)-(+)-9, $[\alpha]_D$ +13.8°, by the action of acetyl chloride (Scheme II).

The relative stereospecificity of the addition of LTA to 1 was determined in the following manner. The rotation of optically pure (+)-2-pentanol is 18.8°.[7] Therefore, the optical purity of 2-pentanol having $[\alpha]_D$ +1.4° is approximately 7.4%. The optical purity of the allene 1, $[\alpha]_D$ +22.4°, from which 8 was derived may also be estimated to be about 13% based upon a calculated rotation for optically pure (*R*)-(−)-1 of −174° (EtOH).[6b] Thus, we may conclude that the stereospecificity of LTA addition to 1 is at least 57%. The specificity could conceivably be higher since our data cannot exclude some racemization of the allene or the acetoxypentyne under the reaction conditions.

In the reaction of 1 with LTA, there are two possible

Scheme I



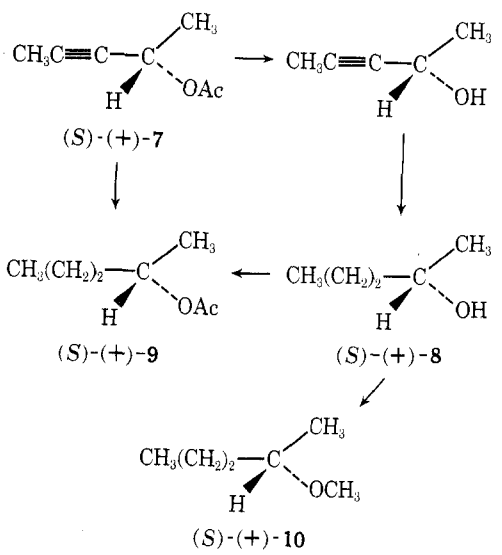
pathways for approach of the attacking electrophilic lead reagent. The stereochemistry of the formation of (+)-7- from (+)-1 can either result from antarafacial addition to 2 or suprafacial addition to 3. Because the vinyllead intermediates 5 and 6 are labile and not isolable, a definitive mechanism is not attainable. However, examination of molecular models suggest that attack of $Pb(OAc)_3^+$ from the least hindered side as in 2 results in an intermediate having a potential methyl–methyl steric interaction. Although approach of the electrophile affording 3 is hindered by the methyl substituent at the vinyl terminus, the resulting plumbonium ion 3 is less sterically crowded, having only hydrogen–methyl interactions. Any rehybridization at C_2 affording the nonlinear structures 2 and 3 will further accentuate steric repulsions in the transition state for antarafacial acetate anion addition to the π complex. The transition state for a suprafacial addition to such a π complex should require that the metal ion be unsymmetrically bonded to the double bond in order that a more nearly empty p orbital at C_3 is available. Moreover, rehybridization at C_2 makes antarafacial addition of acetate ion to 2 more difficult because of steric hindrance.

We therefore suggest that (+)-7 arises principally via suprafacial addition to intermediate 3 followed by the loss of the metal and alkyne formation. Further support for the suggested mechanism comes from the observation that suprafacial addition of LTA to 1,2-cyclononadiene has been unequivocally established.[3] The methoxymercuration[5a] of (−)-1 has also been shown to proceed by solvent attack on a π complex comparable to 3 which affords (+)-2-methoxypentane upon reduction. In the latter case, antarafacial addition was observed and the resulting vinylmercurial was sufficiently stable to be isolated. The vinylmercurials corresponding to 5 and 6 were formed in a ratio of 17:83. A steric argument was also offered in explanation of these results.[5a] A mixture of cis and trans pentenes has also been reported in the oxythallation of racemic 1.[10]

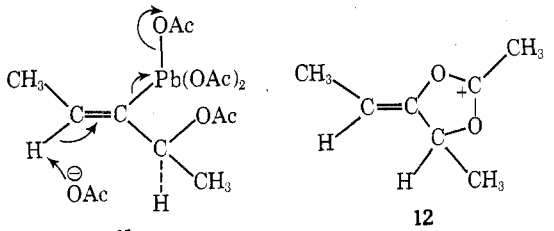
The isolation of an optically active product in this reaction precludes exclusive product formation via the planar resonance stabilized allyl cation 4, since attack by solvent on 4 would result in a racemic product. It should also be recognized that antarafacial addition to 2 or 3 will result in a reduction in stereospecificity. Our data are consistent with the formation of a π-bridged plumbonium ion intermediate that is sufficiently stabilized to prevent extensive carbon–carbon rotation affording 4. The rotational barrier in allyl cation has been calculated to be 34.8 kcal/mol.[9] However, the position of equilibrium in the present case would depend upon the relative stabilities of the bridged plumbonium ion 3 and the allyl cation 4.

The mechanism for the formation of an alkyne in this reaction is also worthy of comment. The carbon–lead bond in 6 is obviously considerably more labile than either the carbon–mercury[5] or carbon–thallium bond[4,10] in their corre-

Scheme II



sponding vinyl metal acetates. The formation of **7** from **6** may occur via anti elimination as depicted in **11**. Alternatively, ionization of the labile carbon–lead bond forming a vinyl cation may be involved. An anti elimination on the acetoxonium ion **12** will also afford **7**. Although our results



11

12

cannot distinguish between these pathways, the fact that the vinylmercury and vinylthallium derivatives are formed as discrete intermediates suggests that a similar vinyllead compound is involved that suffers ionization of the carbon–lead bond either in concert with or prior to elimination.

In conclusion, the oxyplumbation of **1** proceeds with relatively high stereospecificity by a suprafacial addition. The formation of an alkyne in these reactions appears to be general for cyclic[3] and acyclic dialkyl-substituted allenes under these reaction conditions, since 1,3-diethylallene also affords 3-acetoxy-4-heptyne as the major product upon reaction with LTA in acetic acid.

Experimental Section

Materials. Lead tetraacetate was purchased from Arapahoe Chemicals, Boulder, Colo. The nickel acetate was purchased from Allied Chemicals, Morristown, N.J. Methyllithium and 2-butene were purchased from Matheson Coleman and Bell, Norwood, Ohio. The (+)-2-pentanol was purchased from Norse Laboratories, Santa Barbara, Calif. The (+)-α-pinene was purchased from Aldrich Chemical Co., St. Paul, Minn.

Optical rotations were measured with a Perkin-Elmer Model 141 polarimeter. NMR spectra were recorded with a Varian A-60A spectrometer, and chemical shifts are reported in parts per million downfield from internal Me_4Si.

1,1-Dibromo-2,3-*cis*-dimethylcyclopropane. To 1 l. of *tert*-butyl alcohol, distilled from CaH, was added 40 g (1 mol) of potassium under argon. After 3 hr of vigorous stirring with mild heating, the potassium was consumed and 1 l. of sodium-dried heptane was added. The *tert*-butyl alcohol was removed by distillation until a head temperature of 92° was attained. The flask was equipped with a Dry Ice condenser, the thick white slurry was cooled to 0°, and 68 g (1 mol) of *cis*-2-butene was distilled into the flask. Bromoform (253 g, 1 mol) was added dropwise over a 3-hr period. After stirring overnight at 25°, the reaction was quenched by the addition of water. The aqueous layer was extracted with 3 × 50 ml of pentane and the combined organic fractions were dried ($MgSO_4$). The solution was concentrated by simple distillation and vacuum distilled to yield 180 g (80%) of dibromide, bp 40° (5 mm).

1,3-Dimethylallene (1). To 48.6 g (2 mol) of 40 mesh magnesium powder in 360 ml of dry THF was added dropwise 91.2 g (0.40 mol) of 1,1-dibromo-*cis*-2,3-dimethylcyclopropane at a rate that maintained gentle reflux. When the addition was complete, the dimethylallene was removed by flash distillation. The THF–allene mixture was fractionally distilled and the first fraction, bp 48–50°, contained 2.5 g of dimethylallene in greater than 90% purity. Succeeding fractions (contaminated with THF) yielded 3.25 g (65% pure) and 16 g (25% pure) of dimethylallene, overall GLC yield 36%. The allene had ir 3020 (s), 2970 (s), 1970 (m), 1450 (m), 1280 (m), 950 (m), 865 cm^{-1} (s); NMR (CCl_4) δ 1.62 (d, 6, J = 6 Hz), 4.92 (m, 2).

Partial Resolution of Dimethylallene (1). Using the method of Caserio,[5a] 7.0 g (~0.10 mol) of racemic dimethylallene (**1**) was treated with optically active tetraisopinocampheyldiborane, prepared from (+)-α-pinene, $[\alpha]D$ +46° (neat), at 0° for 3 hr with stirring. The reaction mixture was vacuum distilled (4 mm, 25°) until no more volatiles could be collected. Allene was collected by GLC (15 ft × 0.25 in., 10% SE-30 on Chromosorb W, injection port temperature 40° and detector 60°) and had $[\alpha]D$ +22.4° (*c* 2.09, Et_2O). Collection of the allene at higher temperatures resulted in partial racemization.

Lead Tetraacetate Oxidation of 1,3-Dimethylallene (1). To 0.34 g (0.005 mol) of dimethylallene, $[\alpha]D$ +22.44° (*c* 2.2, Et_2O), as a 30% solution in THF was added 12 ml of glacial acetic acid and 2.22 g (0.005 mol) of LTA. The flask was stoppered and allowed to stir at room temperature for 20 hr. Ether was added and a precipitate of lead diacetate was removed by filtration. The organic layer was washed with H_2O and aqueous bicarbonate. Drying ($MgSO_4$) and removal of solvent afforded 0.26 g (41.4%) of crude product consisting of 57% of 4-acetoxy-2-pentyne and two other products that were tentatively identified as diacetates. The acetylene **7** after purification by GLC had $[\alpha]D$ +6.6° (*c* 3.92, Et_2O). A duplicate experiment afforded **7** having $[\alpha]D$ +6.9° (*c* 3.95, Et_2O): ir 2275 (s), 1740 (s), 1365 (m), 1230 (s), 1170 (m), 1055 cm^{-1} (m); NMR (CCl_4) δ 1.40 (d, 3, J = 7 Hz), 1.82 (d, 3, J = 2 Hz), 1.97 (s, 3) 5.32 (m, 1); mass spectrum *m/e* (rel intensity) 125 (6), 111 (37), 84 (45), 83 (1), 69 (33), 67 (45), 66 (100), 65 (43), 55 (8), 43 (76), 42 (6), 41 (64), 40 (33).

(*S*)-(+)-2-Pentanol (8). To 0.39 g (0.3 mmol) of **7** in 1 ml of absolute ethanol was added 0.045 g of K_2CO_3. The reaction mixture was stirred for 3 hr. The solid material was removed by filtration and 0.01 g of PtO_2 and a crystal of $NaNO_2$ (to decrease hydrogenolysis) were added to the solution which was hydrogenated at atmospheric pressure until uptake of H_2 ceased. The 2-pentanol isolated by GLC had $[\alpha]D$ +1.36° (*c* 1.1, CH_2Cl_2). The infrared spectrum of **8** was identical with that of an authentic sample of racemic **8**.

(*S*)-(+)-2-Acetoxypentane (9). A. To a solution of 1.0 g (10 mmol) of (+)-2-pentanol (**8**), $[\alpha]D$ +12.2° (neat), and 5 ml of freshly distilled pyridine was added dropwise 0.85 g (12 mmol) of acetyl chloride. After complete addition, 20 ml of ether was added and the solution was washed with 2 × 25 ml of 5% HCl solution and 3 × 20 ml of water. After drying ($MgSO_4$), the solution was concentrated and afforded **9**, $[\alpha]D$ + 13.8° (*c* 2.4, CCl_4).

B. Catalytic reduction of **7**, $[\alpha]^{25}D$ +9.8° (*c* 7.87, CH_2Cl_2), using the method of Brown[11] and the procedure given by Caserio,[5a] gave a low yield of 2-acetoxypentane, $[\alpha]^{25}D$ +2.1° (*c* 0.49, $CHCl_3$), that had ir and NMR spectra identical with those of an authentic sample of **9**. The low yield was presumably due to extensive hydrogenolysis.

(*S*)-(+)-2-Methoxypentane. A solution of 1.0 g (10 mmol) of (+)-2-pentanol (**8**), $[\alpha]D$ +12.2° (neat), 3.0 g (20 mmol) of methyl iodide, 20 ml of hexane, and 1.0 g (20 mmol) of sodium hydride (57% oil dispersion) was refluxed for 4 hr. Excess sodium hydride was destroyed by adding wet ether to the mixture. The organic layer was washed with 2 × 20 ml of a saturated NaCl solution and dried ($MgSO_4$). GLC collection (10 ft × 0.25 in., 20% SE-30 on Chromosorb W, 90°) gave **10** that had $[\alpha]D$ +9.8° (*c* 5.2, CCl_4).

Lead Tetraacetate Oxidation of Diethylallene. A mixture of 1.60 g (10 mmol) of diethylallene, 6.75 g (15 mmol) of lead tetraacetate, and 75 ml of glacial acetic acid was stirred at room temperature for 16 hr. The mixture was poured into a separatory funnel and 50 ml of water and 100 ml of ether were added. The ether layer was washed with 4 × 50 ml of water, 2 × 50 ml of a saturated sodium bicarbonate solution, and 50 ml of a saturated NaCl solution. The solution was dried ($MgSO_4$) and concentrated. Upon GLC analysis and collection, the major product peak (>75%) was identified as 3-acetoxy-4-heptyne: ir 2970 (m), 2940 (m), 2240 (w), 1740 (s), 1370 (m), 1230 (s), 1020 cm^{-1} (m); NMR (CCl_4) δ 1.10 (m), 1.98 (s), 2.1 (m), 5.22 (m).

Acknowledgment. We acknowledge the National Institutes of Health for support of this work (ES 00761-03).

Registry No.—(±)-**1**, 28383-16-6; (+)-**1**, 23190-25-2; **7**, 55621-89-1; **8**, 26184-62-3; **9**, 55621-90-4; **10**, 55621-91-5; 1,1-dibromo-2,3-*cis*-dimethylcyclopropane, 3591-57-9; *cis*-2-butene, 590-18-1; bromoform, 75-25-2; tetraisopinocamphenyldiborane, 16997-72-1; lead tetraacetate, 546-67-8; acetyl chloride, 75-36-5; methyl iodide, 74-88-4; diethyl allene, 2454-31-1; 3-acetoxy-4-heptyne, 55621-92-6.

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(7) The highest observed rotation for 2-pentanol in benzene solvent is 13.7°.[6a] However, a gas chromatographic study has determined that the absolute rotation of 2-pentanol is 18.8°.[8] Optically active 2-methoxypentane (**10**) having $[\alpha]_D$ +9.9° has been estimated[5a] to be 58% optically pure. We have prepared **10** having $[\alpha]_D$ +9.8° from **8** having $[\alpha]_D$ +12.2° which was presumed to be 65% optically pure, in fair agreement with the above value.
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Thermal Rearrangements of 4,5-Diphenyl-2*H*-imidazoles

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Some time ago Weiss reported that 2,2,4,5-tetraphenyl- and 2,2-dibenzyl-4,5-diphenyl-2*H*-imidazoles (**3c, 5a**) thermally rearrange to the corresponding 1*H*-imidazoles with migration of a phenyl or benzyl group, respectively.[2] The apparent similarity of this rearrangement to the [1,5] sigmatropic shifts of geminal dimethylcyclopentadienes,[3] spirodienes,[4] and 2*H*-pyrroles[5] prompted us to investigate this reaction, particularly since Weiss had claimed that 2,2-dimethyl-4,5-diphenyl-2*H*-imidazole (**3a**) did not rearrange thermally and that 2,2-pentamethylene-4,5-diphenyl-2*H*-imidazole (**1c**) decomposed when heated.[6]

The 2*H*-imidazoles were prepared by condensing the appropriate ketone with benzil in refluxing acetic acid[2] or *N,N*-dimethylformamide containing excess ammonium acetate. Cyclobutanone yielded only rearranged product (**2a**) and cycloheptanone and cyclooctanone gave the required product together with large amounts of colored products.

We studied the rearrangement by heating samples of the 2*H*-imidazoles, with or without solvent, under nitrogen in sealed ampoules or NMR tubes in a thermostatted microtube furnace. Rate studies were generally carried out in the melt without solvent and measured by integration of the NMR signals of rearranged product relative to the signals of the aromatic protons or the unrearranged reactant. Under nitrogen the reaction showed first-order kinetics to about 5 half-lives at several temperatures. Failure to purge with nitrogen resulted in side reactions, indicated by darkening of the reaction and appearance of many additional peaks in the NMR spectra. The kinetic and activation data are presented in Table I.

Three mechanisms have been documented for the thermal rearrangements of the analogous carbocyclic geminal dialkylcyclopentadienes and spirodienes. These are (a) a diradical route involving opening of a cycloalkane ring as observed for spiro[2,4]hepta-4,6-diene;[4b,7] (b) a suprafacial and stereospecific [1,5] alkyl shift as reported for *cis*- and *trans*-6,9-dimethylspiro[4,4]nona-1,3-diene;[8] and (c) a radical chain process, observed in geminal dimethyl cyclopentadienes, which competes with b, initiated by dissociation into cyclopentadienyl and methyl radicals.[9] Analogous stepwise and concerted processes are presumably available for 2*H*-imidazoles.

Table I
Kinetic and Activation Data for the Rearrangement of 2*H*-Imidazoles

Compd	Temp, K	k, sec^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	Rel rate at 550 K
1b	510	1.11×10^{-3}	44.1	+11	1000
	524	3.49×10^{-3}			
	545	1.90×10^{-2}			
1c	573	3.59×10^{-4}	49.4	+9	4
	582	6.68×10^{-4}			
	593	1.72×10^{-3}			
	601	2.70×10^{-3}			
1d	560	3.32×10^{-4}	45.9	+4	8
	573	8.07×10^{-4}			
	587	2.20×10^{-3}			
1e	555	4.50×10^{-3}	41.9	+3	140
	574	1.57×10^{-2}			
1f	564	5.71×10^{-3}	37.6	−5	100
	581	1.53×10^{-2}			
1g	543	1.87×10^{-3}	39.7	−1	120
	560	5.69×10^{-3}			
	576	1.54×10^{-2}			
3a	588	2.20×10^{-4}	40.5	−7	1
	603	6.66×10^{-4}			
3b	560	9.81×10^{-4}	41.2	−2	25
	573	2.40×10^{-3}			
	583	4.42×10^{-3}			
5a	498	9.33×10^{-5}	39.8	0	175
	513	2.79×10^{-4}			
	528	9.17×10^{-4}			
	543	2.58×10^{-3}			
5b	545	1.52×10^{-3}			
5c	543	6.24×10^{-3}			
5d	543	3.29×10^{-2}			
5e	543	5.92×10^{-4}			

An approximate E_a for the stepwise processes of 67 kcal/mol is obtained, assuming that dissociation is rate determining, by subtracting the gain in stabilization energy in forming the delocalized imidazolyl radical (13 kcal/mol)[10] from the C–C bond dissociation energy (80 kcal/mol).[11a] Heterolytic dissociation would yield a higher value. This result is higher than the experimentally determined values for the 2*H*-imidazoles, which suggests that stepwise processes are not involved in the thermal rearrangements of these compounds. Nonetheless, significant differences in reaction rates (interpolated or extrapolated to 550 K) and activation parameters were observed as a possible consequence of ring strain differences in the polymethylene rings, delocalization and substituent effects in the migrating groups, and medium effects.

The inability of **1a** to withstand the conditions of synthesis and its consequent rearrangement to **2a** may be the result of the 27 kcal/mol strain energy of the cyclobutane ring.[12] Similarly **1b** rearranges 250 times faster than **1c** because of the 6.5 kcal/mol strain in cyclopentane compared with cyclohexane. The carbocyclic analogs show a similar effect: spiro[4,4]nona-1,3-diene rearranges 1000 times faster than spiro[4,5]deca-1,3-diene.[4c] On the other hand, the increased rearrangement rate of **1d–g** parallels the strain in the medium-sized rings. Although the strain in medium rings is generally greater than cyclopentane, the tenfold greater rate of **1b** compared to **1d–g** may be a consequence of differences in conformational rigidity in the transition states.