Spiro Compound Formation. II. The Formation of Spiro Compounds and Its Mechanistic Aspects by the Acetolysis of 1-(Δ^4-Pentenyl)cyclohexanol and 1-(Δ^4-Pentenyl)cyclopentanol[1]

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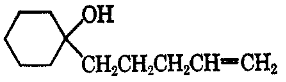
The acetolysis of 1-(Δ^4-pentenyl)cyclohexanol (I) and 1-(Δ^4-pentenyl)cyclopentanol (VII) in the presence of *p*-toluenesulfonic acid or perchloric acid gave spiro[5.5]undecan-2-ol (VI) and spiro[4.5]decan-7-ol (IX), respectively, in good yield. In the absence of catalyst, I gave 1-(Δ^4-pentenyl)cyclohexyl acetate (II). At the same time, alcohol I was in equilibrium with acetate II in the molar ratio of 40:60. In the presence of *p*-toluenesulfonic acid the disappearance of 1-(Δ^4-pentenyl)cyclohexene (III), which was formed at the initial stage of the reaction, followed pseudo-first-order kinetics. Alcohol I, in the presence of perchloric acid, was consumed very rapidly, but the olefin (III) could not be detected. Spiro[5.5]undecyl acetate (V) was in equilibrium with spiro[5.5]undecene (IV) in a molar ratio of 95.5:4.5. A possible mechanism for formation of the spiro compounds has been presented.

In recent years closing of five- and six-membered rings through participation of olefinic bonds has been investigated energetically by Bartlett,[2] Johnson,[3] and others.[4] The activity of the carbon–carbon double bond as an internal nucleophilic reagent varies enormously with its geometry, substitution, and position in the molecule. For example, Bartlett[2] indicated that the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate in the presence of 1.6 equiv of sodium acetate gave a cyclized material in 16.3% yield in contrast to 4-pentenyl *p*-nitrobenzenesulfonate which gave no cyclization product. Zelinskiĭ and Elagina[5] investigated the reaction of 1-(Δ^4-pentenyl)cyclohexanol with phosphoric acid and obtained a 73.9% yield of spiro[5.5]undecene. Furthermore, the reaction of 1-(Δ^3-butenyl)cyclohexanol with formic acid was investigated by Johnson and Owyang,[6] and they obtained 25% of *cis*-2-decalol.

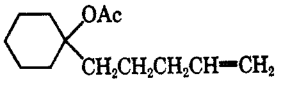
With the above in mind, we examined the acetolyses of 1-(Δ^4-pentenyl)cyclohexanol (I) and 1-(Δ^4-pentenyl)cyclopentanol (VI) under the three reaction conditions, *i.e.*, in the presence of (i) *p*-toluenesulfonic acid, (ii) perchloric acid, and (iii) no catalyst, in order to prepare cyclization products and to investigate the effects of the difference among these three conditions on the processes and products.

Results

A. 1-(Δ^4-Pentenyl)cyclohexanol System.—The acetolysis of 1-(Δ^4-pentenyl)cyclohexanol (I) was performed in the presence of 2 mol equiv of Ac_2O to I at 75° under the foregoing reaction conditions i, ii, and iii. Products obtained were analyzed by vpc and characterized by infrared and nmr spectroscopy.



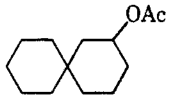
I



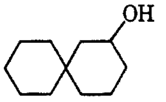
II

III

IV



V



VI

In the presence of *p*-toluenesulfonic acid, the products were found to be only 1-(Δ^4-pentenyl)cyclohexene (III), spiro[5.5]undecene (IV) (the position of the double bond was not ascertained), and spiro[5.5]undecyl acetate (V). Unexpectedly, the product formed from solvent addition across the terminal double bond could not be detected.[7] This is probably due to the predominant formation of the stable tertiary carbonium ion by attack of a proton on the double bond of a cyclohexene ring.

The data summarized in Table I show that the disappearance of I and the formation of III in the presence of *p*-toluenesulfonic acid was very rapid (in 30 min, most of I was consumed and a 97.3% yield of III was obtained) and that III rearranged to spiro compounds IV and V after a prolonged reaction time. Furthermore, the plot of the log of the concentration of the olefin III at the time *t*/the initial concentration of the olefin III *vs.* time was linear with a slope of 0.016/hr (Figure 1) indicating that the disappearance of III followed pseudo-first-order kinetics. The data in Table I also show that the ratio of IV:V was kept constant during the reaction (the molar ratio of IV:V was 15:85).

In Table II the results obtained from the reaction of I in the presence of perchloric acid are summarized and the data indicate the drastic difference from those obtained under the former reaction conditions. First, in the presence of perchloric acid, the olefin III was not detected and the products obtained were only the spiro compounds IV and V. This distinctly different result suggests that perchloric acid is the stronger acid and works more effectively, and is probably the catalyst of choice from a synthetic view point. Second, in the reaction of I in the presence of *p*-toluenesulfonic acid, the molar ratio of IV and V was constant but in the present reaction conditions the molar ratio of IV:V varied from 14.3:85.7 after 30 min to a constant value of 4.5:95.5

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[1] Part I: M. Nojima, T. Nagai, and N. Tokura, *J. Org. Chem.*, **31**, 3966 (1966).

[2] P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *J. Amer. Chem. Soc.*, **87**, 1308 (1965).

[3] W. S. Johnson and R. Owyang, *ibid.*, **86**, 5593 (1964).

[4] W. S. Trahanovsky and M. P. Doyle, *ibid.*, **89**, 4867 (1967), and its references.

[5] N. D. Zelinskiĭ and N. V. Elagina, *Dokl. Akad. Nauk SSSR*, **87**, 755 (1952); *Chem. Abstr.*, **48**, 542 (1954).

[6] W. S. Johnson and J. K. Crandall, *J. Org. Chem.*, **30**, 1785 (1965).

[7] Bartlett[2] reported that when the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate was carried out at reflux in the absence of sodium acetate a considerable amount of solvent addition to the olefinic bond occurred.

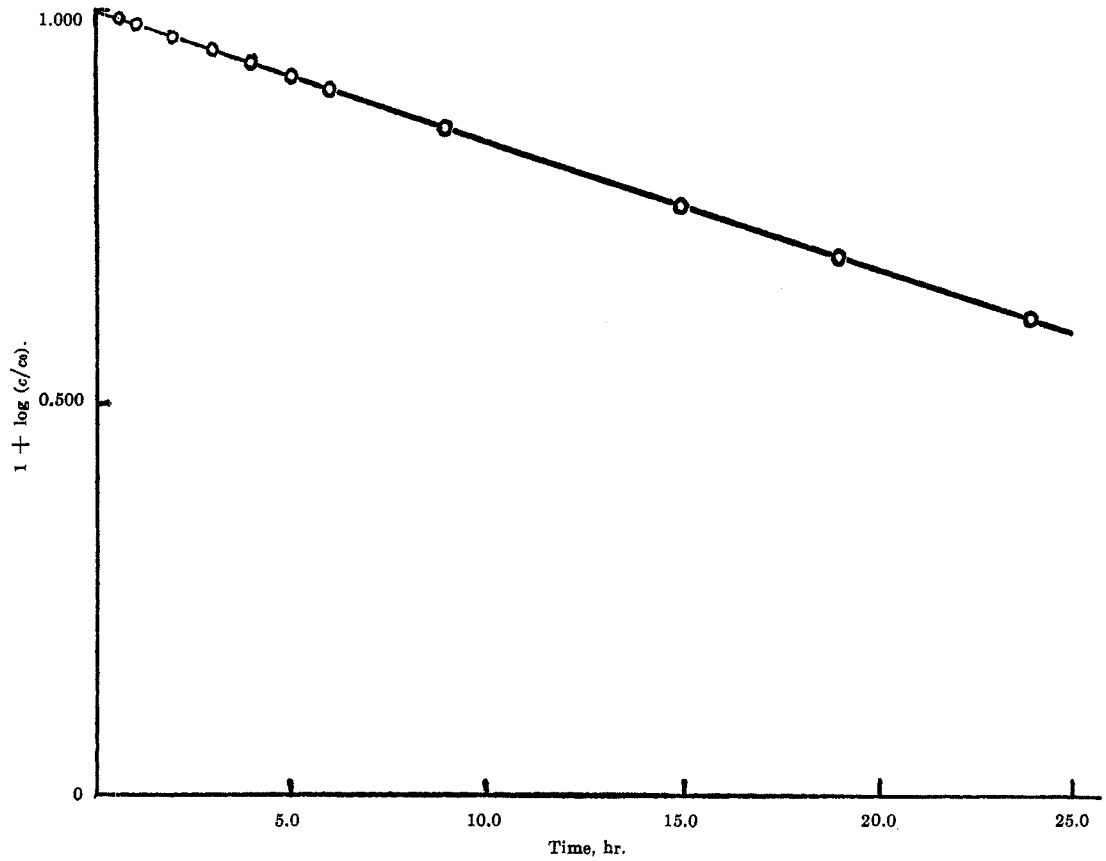


Figure 1.—First-order plot for the disappearance of 1-(Δ^4-pentenyl)cyclohexene (III) in the presence of p-toluenesulfonic acid (the reaction conditions are shown in Table I).

TABLE I

THE ACETOLYSIS OF 1-(Δ^4-PENTENYL)CYCLOHEXANOL (I) IN THE PRESENCE OF p-TOLUENESULFONIC ACID[a]

	Yield, %			
Time, hr	1-(Δ^4-Pentenyl)-cyclohexene (III)	Spiro[5.5]-undecene (IV)	Spiro[5.5]undecyl acetate (V)	V/(IV + V)
0.5	97.3	0.4	2.3	0.852
1	95.8	0.6	3.6	0.857
2	94.0	0.9	5.1	0.850
3	88.0	1.9	10.1	0.842
4	83.8	2.4	13.8	0.851
5	80.8	3.0	16.2	0.843
6	78.4	3.2	18.4	0.851
9	70.5	4.9	24.5	0.845
12	65.3	5.5	29.2	0.841
15	60.5	6.9	35.0	0.850
19	49.1	8.4	42.5	0.845
24	40.5	9.8	49.7	0.850

[a] 0.44 M 1-(Δ^4-Pentenyl)cyclohexanol (I), 0.024 M p-toluenesulfonic acid, and 0.88 M Ac_2O in AcOH at 75°.

TABLE II

THE REACTION OF 1-(Δ^4-PENTENYL)CYCLOHEXANOL (I) AND SPIRO[5.5]UNDECYL ACETATE (V) IN THE PRESENCE OF PERCHLORIC ACID

	Yield, %	
Time, hr	Spiro[5.5]undecene (IV)	Spiro[5.5]undecyl acetate (V)
	The Reaction of I[a]	
0.5	14.3	85.7
1	13.2	86.8
2	12.0	88.0
3	10.3	89.7
4	9.2	90.8
5	8.3	91.7
6	7.5	92.5
9	5.7	94.3
12	4.6	95.4
18	5.8	94.2
24	4.6	95.4
	The Reaction of V[b]	
5	3.5	96.5
10	3.8	96.2
15	4.4	95.6
20	4.5	95.5
25	4.5	95.5

[a] 0.29 M substrate, 0.016 M $HClO_4$, and 0.58 M Ac_2O in AcOH at 75°. [b] 0.29 M substrate, 0.016 M $HClO_4$, and 0.58 M Ac_2O in AcOH at 75°.

after 12 hr. We also examined the reaction of V with perchloric acid and obtained the following results. V changed to IV with the molar ratio of IV:V becoming constant (IV:V = 4.5:95.5) after 15 hr. This problem will be discussed later.

The acetylation of I in the absence of catalyst was also examined and the data obtained are summarized in Table III. In this case 1-(Δ^4-pentenyl)cyclohexyl acetate (II) was obtained as a major product along with a small amount of the olefin III. The cyclization products IV or V were not detected.

B. 1-(Δ^4-Pentenyl)cyclopentanol System.—The acetolysis of 1-(Δ^4-pentenyl)cyclopentanol (VII) was performed at 75° in the presence of p-toluenesulfonic acid or perchloric acid and the results obtained are summarized in Table IV. We obtained under both reaction conditions spiro[4.5]decan-7-ol (IX) which had only previously been obtained in a low yield. The product was characterized by comparing the infrared and nmr spectra with those of an authentic sample pre-

TABLE III
THE ACETYLATION[a] OF 1-(Δ^4-PENTENYL)CYCLOHEXANOL (I) IN THE ABSENCE OF CATALYST

Time, hr	Yield, % 1-(Δ^4-Pentenyl)-cyclohexanol (I)	1-(Δ^4-Pentenyl)-cyclohexyl acetate (II)	1-(Δ^4-Pentenyl)-cyclohexene (III)	I/(I + II)
0.5	39.5	60.5		0.395
1	40.0	60.0		0.400
2	41.0	59.0		0.410
5	38.4	61.6		0.384
8	40.0	57.5	2.5	0.410
16	38.4	57.4	4.2	0.401
24	36.6	57.4	6.0	0.390
32	35.0	56.7	8.3	0.382
36	38.0	52.5	9.5	0.420
48	35.0	53.8	11.2	0.395

[a] 0.44 *M* substrate and 0.88 *M* Ac_2O in AcOH at 75°.

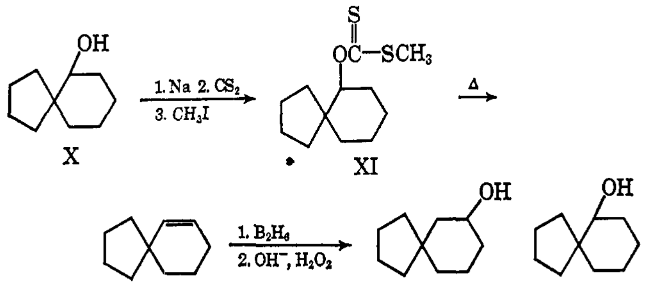
TABLE IV
THE ACETOLYSIS OF 1-(Δ^4-PENTENYL)CYCLOPENTANOL (VII) IN THE PRESENCE OF *p*-TOLUENESULFONIC ACID[a] AND PERCHLORIC ACID[b]

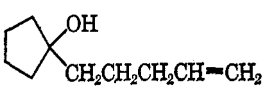
Catalyst	Time, hr	Yield, % 1-(Δ^4-Pentenyl)-cyclopentene (VIII)	Spiro[4.5]-decan-7-ol (IX)	Spiro[4.5]-decene-6 (XII)
p-Toluenesulfonic acid	24	29.9	57.8	12.3
Perchloric acid	24	0	87.0	13.0

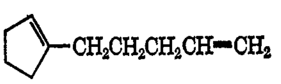
[a] 0.44 *M* substrate, 0.024 *M* *p*-toluenesulfonic acid, and 0.88 *M* Ac_2O in AcOH at 75°. [b] 0.29 *M* substrate, 0.016 *M* $HClO_4$, and 0.58 *M* Ac_2O in AcOH at 75°.

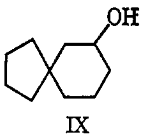
pared according to the synthetic route shown in Scheme I. The acetolysis condition for VII and the synthetic methods for IX are described in detail in the Experimental Section.

SCHEME I




VII


VIII


IX

Discussion

We obtained some interesting results from the acetolysis of 1-(Δ^4-pentenyl)cyclohexanol (I) under the three reaction conditions. From these data, Scheme II is considered to be the more plausible reaction mechanism.

When the reaction was run in the absence of catalyst, the acetate (II) was obtained in equilibrium with the alcohol (I) after 30 min in a molar ratio of 60:40. This ratio remained constant during the prolonged reaction time in spite of the slow formation of olefin (III). The fact that the disappearance of III in the presence of *p*-toluenesulfonic acid followed pseudo-first-order kinetics and the products obtained were only IV and V is very suggestive. As was mentioned previously, the olefin III was not detected after 30 min in the acetolysis of I in the presence of perchloric acid and the molar ratio of V to IV under these conditions varied with time. Furthermore, under the same conditions, V rearranged to IV in the same ratio as obtained in the above reaction (IV:V was 4.5:95.5). These results obviously indicate the existence of an equilibrium between IV and V in the presence of perchloric acid. These results are listed in Table V. It is well known[8] that perchloric acid is the strongest of the three acids employed and *p*-toluenesulfonic acid is a stronger acid than acetic acid. From the relationship among the three acids and the results obtained in the acetolysis of I (Table V), it is obvious that the differences in the acid strength decided the acetolysis reaction processes.

The fact that there exists an equilibrium between I and II, and that the olefin III was formed very slowly in the absence of catalyst is contrary to the rapid formation of III from I in the presence of *p*-toluenesulfonic acid and suggests that the intermediate of the reversible reaction between I and II is A.[9] This consideration would be probable, because acyl cation should be formed from the attack of proton to Ac_2O under this condition. As was mentioned previously, *p*-toluenesulfonic acid, which is stronger acid than acetic acid, worked effectively for the formation of III.[10] This is reasonable if III is formed by the loss of a proton from the intermediate B which is formed by protonation of I and II[11] followed by the loss of H_2O and acetic acid, respectively.

The single formation of the 2-substituted spiro compound V in the reaction of I in the presence of *p*-toluenesulfonic acid or perchloric acid supports the selective existence of the intermediate C which would be formed from B by participation of the double bond. This consideration is also consistent with the fact that the disappearance of III followed first-order kinetics.

The fact that the olefin III was not detected in the reaction in the presence of perchloric acid is very suggestive. The formation step of spiro compounds IV and V was greatly affected by the strength of the acid, *i.e.*, the stronger the acid is, the faster the rate of the cyclization step is. The variation of the molar ratio of IV:V from an initial ratio of IV:V = 14.3:85.3 to the final ratio of IV:V = 4.5:95.5 in the acetolysis of I in the presence of perchloric acid (*cf.*, Table I) is also considered to have depended on the differences in acid

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(8) R. W. Gurney, "Ionic Processes in Solution," Dover Publications, Inc., 1962, p 238; L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 261.

(9) The formation of II may also be explained by the attack of AcOH to the tighter ion pair from B, however, this mechanism can not explain the reversible path II → I, since OH^- seems not to exist in this reaction condition.

(10) The acetate II was not detected in the reaction of I in the presence of *p*-toluenesulfonic acid and so it is not clear whether III was formed through the step I → A → II → B → III or the step of I → B → III.

(11) We confirmed that the reaction of II in the presence of *p*-toluenesulfonic acid gave very similar results to those obtained from the reaction of I under the same condition.

SCHEME II

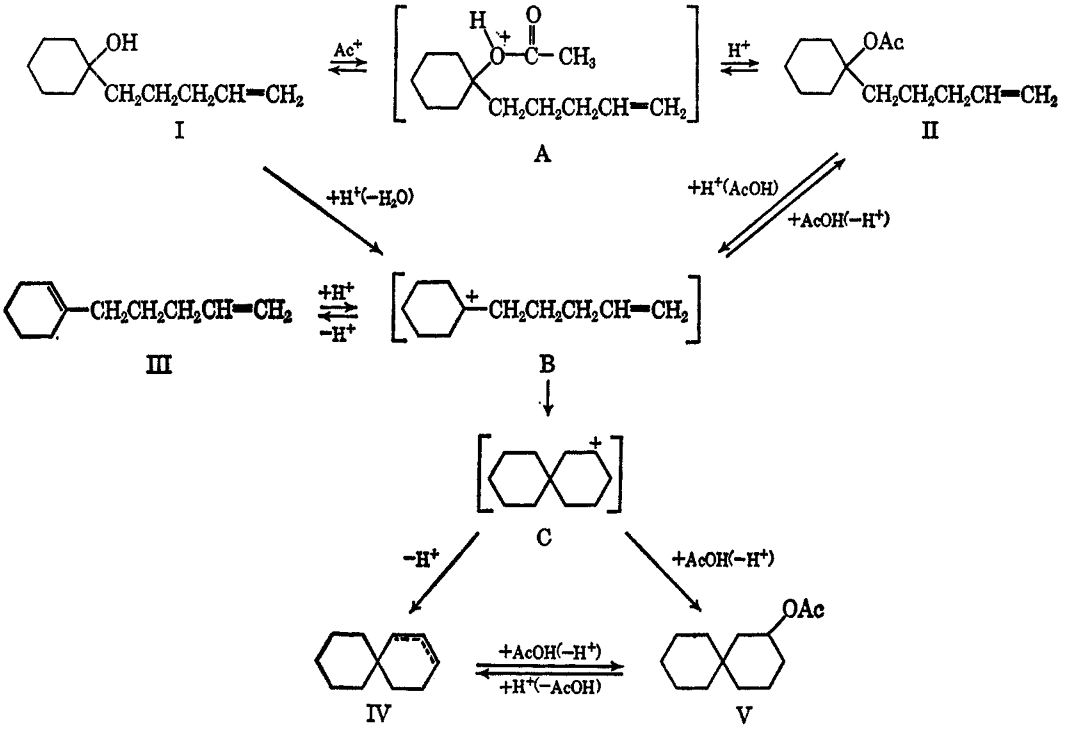

TABLE V

RESULTS OF THE REACTION[a] OF 1-(Δ^4-PENTENYL)CYCLOHEXANOL (I) UNDER VARIOUS CONDITIONS

Reaction condition	Catalyst	Formation of 1-(Δ^4-pentenyl)-cyclohexene (III)	Disappearance of 1-(Δ^4-pentenyl)-cyclohexene (III)	Variation of spiro[5.5]undecene (IV) to spiro[5.5]undecyl acetate (V)
i	None	Slow[b]	Very slow	Very slow
ii	*p*-Toluenesulfonic acid	Rapid[e]	0.16/hr[c]	Very slow
iii	Perchloric acid	Rapid[e]	Rapid[e]	0.090/hr[d]

[a] The reactions were run at 75°. [b] 11% yield of III was obtained after 48 hr. [c] The rate constant was calculated from the experimental results shown in Table I. [d] The rate constant was obtained by measuring the variation of IV to V in the reaction conditions shown in Table II. [e] The term rapid indicates that the formation of III in one case and the disappearance of III in another case were performed almost completely in 30 min of reaction time.

strength between perchloric acid and *p*-toluenesulfonic acid. Whereas the stable carbonium ion (B) was obtained from the protonation of III in the presence of either *p*-toluenesulfonic acid or perchloric acid, the protonation of IV to form the less stable secondary carbonium ion occurred only in the presence of the stronger perchloric acid.

In order to clarify the existence of the equilibrium between IV and V, log $[(A_0 - A_e)/(A - A_e)]$ *vs.* time was plotted[12] and gave a straight line as shown in Figure 2, where A_0, A_e, and A are the mole per cents of the olefin (IV) initially, at equilibrium, and at time t, respectively, and A_0 and A_e are assumed to be 15.0[13] and 4.5, respectively. This fact apparently indicates the existence of an equilibrium between IV and V in the presence of perchloric acid, the equilibrium constant being estimated as 4.5:95.5.

In conclusion, the selective formation of spiro compounds with a substituent in a special position such as spiro[5.5]undecyl 2-acetate or spiro[4.5]decanyl 7-acetate (which can readily be converted into the alcohols VI or IX as described in the Experimental Section) from the acetolyses of 1-(Δ^4-pentenyl)cyclohexanol (I) and 1-(Δ^4-pentenyl)cyclopentanol (VII) is a very attractive syntheses of six-membered spiro compounds. Further investigations are probably necessary to clarify the generality and the limitation of this preparative method.

Experimental Section

1-(Δ^4-Pentenyl)cylohexanol (I) was prepared by the method of Zelinskiĭ and Elagina.[4] From 38 g of 4-pentenyl bromide, 6.6 g of magnesium, and 21 g of cyclohexanone was obtained 15 g (25% yield based on 4-pentenyl bromide) of 1-(Δ^4-pentenyl)cyclohexanol, bp 114–116° (7 mm).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.84. Found: C, 78.50; H, 11.98.

1-(Δ^4-Pentenyl)cyclopentanol (VII) was prepared in 35% yield by the action of 4-pentenylmagnesium bromide on cyclopentanone, bp 91–93° (7 mm).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.65; H, 11.61.

1-(Δ^4-Pentenyl)cyclohexene (III) was prepared from 1-(Δ^4-pentenyl)cyclohexanol with oxalic acid according to the method of Linstead,[14] bp 105–106° (25 mm).

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[12] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," revised ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 186.

[13] In the reaction of I, the molal per cent of the olefin IV was kept constant at 15.0 during the reaction in the presence of *p*-toluenesulfonic acid. When the reaction was performed in the presence of perchloric acid, the mole per cent of IV was 14.3 after a 30-min reaction time (*cf.* Tables I and II). We assumed that the mole per cent of IV at the initial state was the same under two reaction conditions and adopted 15.0 as the initial molal per cent of IV.

[14] R. P. Linstead, A. B. L. Wang, J. H. Williams, and K. D. Frington, *J. Chem. Soc.*, 1136 (1937).

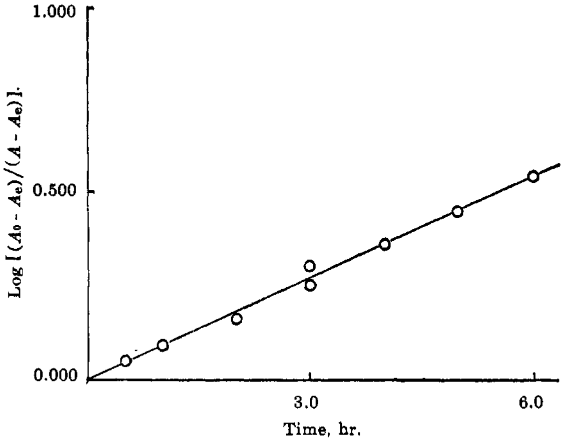

Figure 2.—First-order reversible reaction between spiro[5.5]-undecene (IV) and spiro[5.5]undecyl acetate (V) in the presence of perchloric acid (A_0, A_e, and A are, respectively, the mole per cent of the olefin (IV) at initial reaction, at equilibrium, and at time t. The reaction conditions are shown in Table II.

Anal. Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.08. Found: C, 87.97; H, 11.92.

Spiro[5.5]undecan-2-ol (VI) was prepared in three steps from spiro[5.5]undecane-2,4-dione:[15] bp 102–103° (4 mm); mp 51–52° (lit. bp 127–128° (15 mm), mp 53°); ν_{max} 3330 cm^{-1} (OH). The nmr spectrum of this compound showed absorption bands at τ (CCl_4) 6.47 (broad, 1 H), 7.05 ppm (singlet, 1 H).

1-(Δ^4-Pentenyl)cyclohexyl acetate (II) was prepared from the corresponding alcohol (I) with acetyl chloride and N,N-dimethylaniline according to the method of Nevitt and Hammond.[16] The alcohol (1.7 g) was mixed with 6 ml of N,N-dimethylaniline and the solution was cooled in an ice bath. Acetyl chloride (2.0 g) was added at room temperature over 1 hr and the mixture was then heated at 60° on an oil bath for 5 hr. After cooling, the mixture was poured into ice–water containing 10% hydrochloric acid and extracted with petroleum ether (30–60°). The yield was 30% (0.6 g): bp 104–105° (7 mm); nmr, τ ~8.07 (singlet, 3 H), 4.5 (broad, 1 H), 5.05 ppm (multiplet, 2 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.30; H, 10.65. Found: C, 74.24; H, 10.54.

1-(Δ^4-Pentenyl)cyclopentene (VIII) was prepared from 1-(Δ^4-pentenyl)cyclopentanol (VI) with iodine according to the method of Marvel and Brooks[17] in a yield of 75%: bp 172–175° (760 mm); nmr, τ ~4.4 (broad, 1 H), 4.7 (multiplet, 1 H) and 5.05 ppm (multiplet, 2 H).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.01; H, 11.95.

Spiro[4.5]decene-6.—Spiro[4.5]dec-6-yl xanthate was prepared by the reaction of sodium spiro[4.5]decan-6-oxide with carbon disulfide and methyl iodide in ether and the crude xanthate was decomposed at 210° in 3 hr according to the procedure described by Alexander and Mudrak.[18] Fractional distillation gave a 30% yield of spiro[4.5]decene-6, bp 96–97° (9 mm). Signals observed in the nmr spectrum were a singlet at τ 4.6 (one hydrogen), and a multiplet at 4.5–4.9 (one hydrogen).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.09; H, 11.91.

Spiro[4.5]decan-7-ol (IX).—To a well-stirred suspension of 0.2 g of pulverized sodium borohydride in 30 ml of tetrahydrofuran containing 0.8 g of spiro[4.5]decane-6 was added 1 ml of boron trifluoride etherate in 10 ml of tetrahydrofuran. After 1 hr at 25°, the excess hydride was decomposed with water. The organic borane was oxidized at 30–40° (water bath) by the addition of 2 ml of a 3 N solution of sodium hydroxide, followed by the dropwise addition of 2 ml of 30% hydrogen peroxide. Distillation furnished a mixture of spiro[4.5]decan-6-ol (X) and spiro[4.5]decan-7-ol (IX) in a yield of 85% (0.7 g). The ratio of the two alcohols IX:X was found to be 55:45 by vpc. The spiro[4.5]decan-7-ol (IX) was isolated on a Yanagimoto GCS-100 preparative gas chromatograph using a column coated with Carbowax 6000 at 185°. The separated sample was shown to be pure by analytical gas–liquid partition chromatography: bp 96–97° (9 mm); ν_{max} (neat) 3400 cm^{-1}; nmr, τ ~6.5 (singlet, 1 H) and 6.55 ppm (broad, 1 H).

The Acetolysis of 1-(Δ^4-Pentenyl)cyclohexanol (I) in the Presence of *p*-Toluenesulfonic Acid.—To 3.4 g of the alcohol (I), 4.08 g of acetic anhydride and 35 ml of acetic acid was added 10 ml of catalyst containing a solution which was prepared by diluting 1.0445 g of *p*-toluenesulfonic acid to 50 ml with acetic acid in a volumetric flask. The reaction temperature was maintained at 75.0 ± 0.1° and a 5-ml aliquot was withdrawn periodically. The reaction mixture was then rapidly cooled, diluted with 30 ml of water, and extracted three times with *n*-hexane. The combined organic layers were washed with saturated brine and dried over anhydrous sodium sulfate. The volume of extraction solvent was kept small so that no concentration step was necessary prior to vpc analysis.

The acetolysis products were analyzed on a Yanagimoto Model G. C. G. 5DH vpc apparatus, having a flame ionization detector, on a Carbowax 6000 column operated at 160–240°.

The Acetolysis of 1-(Δ^4-Pentenyl)cyclohexanol (I) in the Presence of Perchloric Acid.—To 1.0 g of the alcohol (I), 1.2 g of acetic anhydride, and 15 ml of acetic acid preheated to 75.0° was added 5 ml of catalyst containing a solution prepared by dissolving 0.93 g of 60% perchloric acid, (sp gr 1.55) in 100 ml of acetic acid; 2-ml samples were withdrawn at definite intervals. The reaction mixtures were treated and analyzed as was mentioned in the preceding experiment.

The Acetylation of 1-(Δ^4-Pentenyl)cyclohexanol (I) in the Absence of Catalyst.—A solution of 1-(Δ^4-pentenyl)cyclohexanol (3.4 g) was prepared in 4.08 g of acetic anhydride and 45 ml of acetic acid and allowed to react at 75.0°. Samples were removed at intervals and analyzed as previously mentioned.

The Reaction of Spiro[5.5]undecyl Acetate (V) in the Presence of Perchloric Acid.—An experiment with this substrate (V) was conducted exactly as described above for the acetylation of I in the presence of perchloric acid (1.0 g of V, 1.2 g of acetic anhydride, 5 ml of catalyst solution prepared by dissolving 0.93 g of perchloric acid in 100 ml of acetic acid, and 15 ml of acetic acid).

The Reaction of 1-(Δ^4-Pentenyl)cyclohexyl Acetate (II) in the Presence of *p*-Toluenesulfonic Acid.—A solution of 0.1 g of 1-(Δ^4-pentenyl)cyclohexyl acetate (II), 20 mg of *p*-toluenesulfonic acid, and 0.12 g of acetic anhydride in 5 ml of acetic acid was heated at 75.0° for 30 min. The products were analyzed as described above for the acetylation of I in the presence of *p*-toluenesulfonic acid. The acetate (II) could not be detected and the products were found to be 1-(Δ^4-pentenyl)cyclohexene (II) (97%) with the small amount of spiro[5.5]undecyl acetate (V).

The Acetolysis of 1-(Δ^4-Pentenyl)cyclopentanol (VI) in the Presence of *p*-Toluenesulfonic Acid.—To 5.0 g of the alcohol, 8.0 g of acetic anhydride, and 60 ml of acetic acid was added 150 mg of *p*-toluenesulfonic acid in 20 ml of acetic acid. The solution was heated at 75° for 24 hr. The reaction mixture was then treated as in the preceding experiment and analyzed by using the already mentioned vpc apparatus on a Carbowax 6000 column operated at 140–240°. The greater part of the product was reduced by lithium aluminum hydride and the product was chromatographed over silica gel (50 g). Elution with ten 50-ml portions of ether gave 2.5 g of an oil which was fractionated and the vpc in the preceding conditions indicated that the product was 99% pure, bp 96–97° (7 mm).

The infrared spectrum was identical with that of authentic spiro[4.5]decan-7-ol.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.87; H, 11.82.

The Acetolysis of 1-(Δ^4-Pentenyl)cyclopentanol (VII) in the Presence of Perchloric Acid.—An experiment with this substrate was conducted exactly as described for the acetolysis of 1-(Δ^4-pentenyl)cyclohexanol (I) in the presence of perchloric acid (1.0 g of VII, 1.2 g of acetic anhydride, 5 ml of 0.056 M perchloric acid solution, and 15 ml of acetic acid). The reaction was run at 75.0° for 24 hr and the products were analyzed by vpc.

Acetolysis Products from 1-(Δ^4-Pentenyl)cyclohexanol (I).—1-(Δ^4-Pentenyl)cyclohexanol (5.0 g), 150 mg of *p*-toluenesulfonic acid, 6.0 g of acetic anhydride in 65 ml of acetic acid were heated at 75.0° for 24 hr and extracted with *n*-hexane and dried over anhydrous sodium sulfate. The residue after removal of the solvent was chromatographed over 50 g of silica gel. Elution

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(15) W. S. G. P. Norris, *J. Chem. Soc.*, 245 (1926).

(16) T. D. Nevitt and G. S. Hammond, *J. Amer. Chem. Soc.*, **72**, 1810 (1950).

(17) C. S. Marvel and L. A. Brooks, *ibid.*, **63**, 2630 (1941).

(18) E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950).

with ten 50-ml portions of ether gave 3.0 g of an oil which was fractionated. Vpc on a 30% Carbowax 6000 column indicated that this product was 99% pure: bp 107-108° (7 mm), ν_{max} (neat) 1752 and 1242 cm^{-1}; nmr, $\tau \sim 5.25$ (broad, 1 H) and 8.04 (singlet, 3 H).

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.10; H, 10.51.

The acetate obtained was reduced by lithium aluminum hydride and the product was fractionated, and 2.1 g of the pure material (42% yield based on I) was obtained, bp 101-102° (5 mm). The mixture melting point of the product with authentic spiro[5.5]undecan-2-ol was undepressed (52-53°), and the infrared and nmr spectra were identical with those of authentic spiro[5.5]undecan-2-ol.

1-(Δ^4-Pentenyl)cyclohexene (III) was isolated from the reaction mixture by the reaction of I in the presence of *p*-toluenesulfonic acid at 75.0° for 30 min. III was found to isomerize with chromatography over silica gel to spiro[5.5]undecene and other compounds. Pure 1-(Δ^4-pentenyl)cyclohexene (III) was obtained by repeated fractional distillation in 45% yield and was confirmed to be 98% pure by vpc, bp 105-106° (25 mm). The infrared and nmr spectra were identical with those of authentic 1-(Δ^4-pentenyl)cyclohexene (III).

1-(Δ^4-Pentenyl)cyclohexyl acetate (II) and spiro[5.5]undecene (IV) were not isolated.

Registry No.—I, 16133-73-6; II, 16133-74-7; III, 16133-75-8; VI, 16133-76-9; VII, 16133-77-0; VIII, 16133-78-1; IX, 16133-79-2; XII, 697-28-9.

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The Disilylation of Conjugated Dienes. The Configuration of Diene Anion Radicals and Dianions

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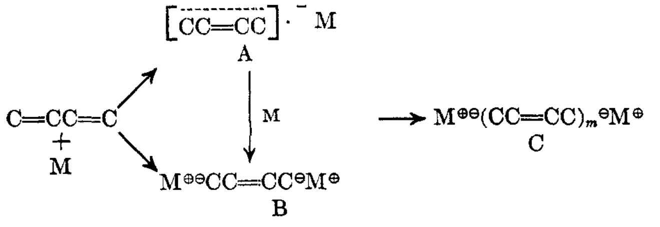
Butadiene, isoprene, and 2,3-dimethylbutadiene react rapidly with an alkali metal and trimethylchlorosilane in tetrahydrofuran (THF) at 25° to give bis(trimethylsilyl)butenes. A *cis*-1,4 addition of silyl groups is favored with sodium in THF (over 90% *cis*-1,4 addition), lithium naphthalenide in THF (65-80% *cis*), and lithium in diethyl ether (60% *cis*). A *trans*-1,4 addition of silyl groups is favored with lithium in THF. Dimethylchloromethoxysilane gave silacyclopentenes and disilylbutenes with the stereochemistry of the reaction determined by the choice of metal and solvent. Conversion of the *cis*-1,4-bis(dimethylmethoxysilyl)-2-butenes into cyclosiloxanes and the corresponding *trans* isomer to a linear polymer confirmed the structure assignments for the *cis*- and *trans*-1,4-disilyl-2-butenes. These data support the previously suggested scheme for the disilylation reaction which involves the trapping *via* reaction with a chlorosilane of short-lived organometallic reagents from the alkali metal and olefin. The stereochemistry of the reaction is apparently determined by the type of organometallic reagent being trapped by the chlorosilane. The anion radical, which in nonionizing solvents should exist in a *cis* configuration, leads to a *cis*-1,4 addition of silyl groups, whereas the organodimetallic reagent leads to a *trans*-1,4 addition of silyl groups.

Many conjugated dienes interact with alkali metals to give a variety of organoalkali reagents.[1] Butadiene and the simple alkyl-substituted butadienes in aprotic solvents give polymeric organoalkali reagents (C)[2] as shown in Scheme I.

SCHEME I



These polymerizations are similar to those observed with styrene and α-methylstyrene with the added complication provided by the choice of 1,2- and *cis*- or *trans*-1,4 addition to the diene in the initiating and propagating step. Although the stereochemistry of the propagation step has been shown to be dependent on the choice of metal and solvent, little is known about the geometry of the monomeric organoalkali reagents.

By the use of sodium dispersions at low temperatures in tetrahydrofuran (THF) solvent, Frank and Foster[3] have obtained high yields of the dimeric organodimetallic reagent, which upon carbonation gave a complex mixture of isomeric decadiendioic acids.

As in the polymerization of aryl olefins, the dimeric and polymeric organodialkali reagents are presumably reaction products of transitory and nonisolable monomeric organoalkali reagents; either the anion radical A or the dianion B in the above scheme. The trapping of these monomeric organoalkali reagents *via* protonation by some protic solvent forms the basis of the chemical reduction of dienes to give *cis*- and *trans*-alkenes.

The current study deals with the disilylation of 1,3-dienes; a reaction which involves trapping, *via* reaction with a chlorosilane, of organoalkali reagents formed from an alkali metal and a diene.[4] This reaction has provided a convenient synthesis for a variety of *cis*- and *trans*-1,4-disilyl-2-butenes and has given additional information on the factors governing the geometry of the monomeric organoalkali reagents from 1,3-dienes and an alkali metal.

Results

Butadiene, isoprene, and 2,3-dimethylbutadiene react with an alkali metal and trimethylchlorosilane in THF at 25° to yield the disilylated derivatives of the diene (Scheme II).

As in the disilylation of styrene,[4] both monomolecular derivatives containing one reduced olefin unit (I and II)

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(1) K. N. Campbell and B. K. Campbell, *Chem. Rev.*, **31**, 77 (1942).

(2) M. Szwarc, *J. Polym. Sci.*, **40**, 585 (1959).

(3) C. E. Frank and W. E. Foster, *J. Org. Chem.*, **26**, 303 (1961).

(4) For a summary of studies on the disilylation reaction, see D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *ibid.*, **30**, 4096 (1965).