related to the σ_p value of the substituent. The lack of deviation from the normal σ_p correlation, particularly on the part of the dimethylamino and methoxy substituents, argues against any enhanced resonance interaction between the substituents and the positive phosphorus center, and therefore the drift of charge would be through the P–aryl σ bond. On the other hand, the ability of the trivalent phosphorus to effect significant stabilization of the radical cation, produced by ionization from the aryl π orbitals, appears to be quite limited.

It should be noted that any correlation between phosphorus lone pair IP's and substituent σ_p values assumes no significant difference in hybridization at the phosphorus among the para-substituted aryl$_3$P. Thus the effects discussed above are not extended here to a comparison between the aryl$_3$P and other phosphines. For instance the lone-pair IP's for PH_3, $(CH_3)_3P$, and $(C_6H_5)_3P$ are 9.9,[9] 8.6,[16] and 7.9 eV, respectively, and this difference appears to reflect the difference in bond angles at the phosphorus (94°,[17] 99°,[18] and 103°,[19] respectively).[20]

Experimental Section

The spectra were obtained with a Perkin-Elmer Model PS-18 photoelectron spectrometer, using the He(I) resonance line (21.22 eV). Since elevated temperatures were necessary for proper sample vapor pressures, a direct inlet probe was used for all samples. Temperatures generally in the range of 60–130° were used in order to obtain proper count rates, but 150° was necessary for the p-$(CH_3)_3C$ and p-$(CH_3)_3Si$ derivatives, and 240° was necessary for the p-$(CH_3)_2N$ compound. The spectra were calibrated with Ar (15.759- and 15.937-eV lines) and Xe (12.130-eV line), used as internal standards. The values listed for IP$_1$ (Table I) are the band maxima. In order to obtain a comparison between the phenyl IP values for aryl$_3$P and the corresponding monosubstituted benzenes, the values of IP$_2$ and IP$_3$ (Table I) were obtained as often as possible in accordance with the method of obtaining the vertical IP's for the corresponding monosubstituted benzene (Table II).

The phosphine samples were prepared by the Grignard method.[21]

Acknowledgment. We are grateful to Dr. A. W. Yankowsky, Mr. H. A. Zunger, and Mr. B. Marien for preparation of most of the aryl phosphines. S.O.G. also thanks the National Science Foundation for partial support of this work under Grant No. GP 30703. We thank Professor N. McKelvie for his helpful advice.

Registry No.—**1**, 13406-29-6; **2**, 1159-54-2; **3**, 18437-78-0; **4**, 603-35-0; **5**, 18848-96-9; **6**, 1038-95-9; **7**, 29949-82-4; **8**, 54409-77-7; **9**, 855-38-9; **10**, 1104-21-8; **11**, 25688-42-0; **12**, 6163-58-2; **13**, 4731-65-1; **14**, 23039-94-3; **15**, 6224-63-1; **16**, 29949-84-6.

Supplementary Material Available. Photoelectron spectra of 1–16 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JOC-75-1292.

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Stereochemistry of Dihydrothiophene Formation from Vinylphosphonium Salts[1a]

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Received November 4, 1974

Evidence is presented which shows that the *cis*-2,5-dialkyl-2,5-dihydrothiophenes are formed in preference to the trans isomers in the reaction between vinylphosphonium salts and α-mercaptocarbonyl compounds. Substituent trends suggest a steric basis for this effect. The implications of the results for stereoselective conjugated diene preparation are discussed. Seven new examples of the synthesis of the dihydrothiophenes are reported.

One of the most active areas in organic synthesis in the past decade has been the development of methods for the construction of unsaturated compounds in stereoselective and stereospecific ways. Whereas the preparation of 1,5-dienes is an active field,[2] work on the stereoselective synthesis of 1,4- and 1,3-dienes has been limited. As we have pointed out,[3] this has greatly restricted the application of the Diels–Alder reaction to stereospecific organic synthesis.

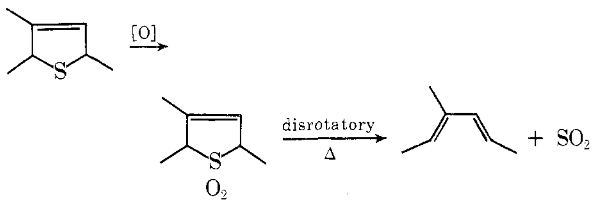
One method of 1,3-diene synthesis which has been shown to be stereospecific is the thermal decomposition of 2,5-

Table I
Products and Yields of 2,5-Dihydrothiophenes[a]

Carbonyl compd	Vinyl salt[b]	Product	R_1	R_2	R_3	Reaction time, hr	Yield, %
1a	**2a**	**3**[c]	Me	H	Me	18	32
1b	**2a**	**4**[d]	Et	H	Me	2	70
1b	**2c**	**5**	Et	H	*i*-Pr	3	50
1c	**2a**	**6**	Me	Me	Me	18	78
1c	**2b**	**7**	Me	Me	Et	18	60
1d	**2a**	**8**	Me	Et	Me	18	80
1d	**2b**	**9**	Me	Et	Et	18	64
1d	**2c**	**10**	Me	Et	*i*-Pr	18	64
1e	**2a**	**11**[e]	$-(CH_2)_4-$		Me	18	91
1e	**2b**	**12**	$-(CH_2)_4-$		Et	42	88

[a] Satisfactory analytical data were recorded for all new compounds in this table. [b] Prepared by in situ isomerization of the allylic isomer. [c] Reference 12. [d] Contains ca. 10% thiophene impurity. [e] Reference 3.

dihydrothiophene sulfones,[4] which occurs in a completely regiospecific and stereospecific disrotatory[5] manner. We have recently published[3,6] a new and facile preparation of 2,5-dihydrothiophenes from vinylphosphonium salts and have shown that they can be converted to conjugated dienes in high yields through the intermediacy of the corresponding sulfones (eq 1). In view of its importance for diene synthesis, we decided to investigate the stereochemistry of the dihydrothiophene formation.

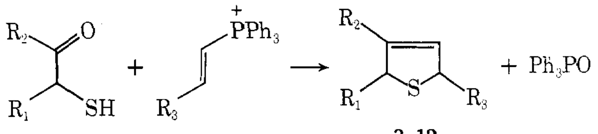


(1)

The stereochemistry of this process is important in other ways. Thus it has been shown[5c,7] that the photochemical decomposition of the sulfones occurs in the opposite stereochemical sense and therefore a stereoselective preparation of dihydrothiophenes would allow the selective formation of either of two diene isomers at will. Further, the use of the sulfones has been illustrated in the synthesis of 1,4-dienes,[8] divinyl ethers,[8] divinyl amines,[9] and cyclobutenes.[10] In each case, the stereochemistry of the sulfone determines that of the product.

Results

A. Dihydrothiophene Preparations. The dihydrothiophenes were prepared by the general method previously outlined.[3] The yields, reaction times, and spectral characteristics of new materials are collected in Tables I and II. In all cases, the allylic phosphonium salt was used as the reagent and isomerized to its vinyl isomer in situ.[3]



1 2 3-12

Several comments on this reaction are required. We have found that the use of *undistilled* α-mercaptocarbonyl compounds, especially in the case of α-mercaptoaldehydes, leads to much superior results. Distillation of these materials invariably leads to dehydration of their dimeric form and subsequent diminution of the yields of dihydrothiophenes. In addition, in several reactions using α-mercaptoaldehydes, the NMR spectrum of the chromatography product showed the presence of thiophene (δ 6.5–7.0). Since all reactions were performed under a blanket of nitrogen, air oxidation of the dihydrothiophene seem unlikely, and as no trace of the corresponding tetrahydrothiophene could be detected, disproportionation does not seem probable. At this time, we have no explanation for this result.

Table II
Indices of Refraction and NMR Spectra of New Dihydrothiophenes

Compd	nD (temp, °C)	NMR spectral data[a]
5	*b*	5.75 (s, 2), 4.4–3.9 (m, 2), 2.1–1.35 (m, 3), 1.0 (t, 3, $J = 7$ Hz), 0.97 (d, 6, $J = 7.5$ Hz)
6	1.5291 (25)	5.37 (d, 1, $J = 2$ Hz), 4.4–3.8 (m, 2), 1.8 (d, 3, $J = 0.5$ Hz), 1.46 (d, 3, $J = 7$ Hz), 1.42 (d, 3, $J = 7$ Hz)
7	1.4930 (20)	5.32 (d, 1, $J = 2$ Hz), 4.25–3.5 (m, 2), 2.0–1.5 (m, 2), 1.78 (d, 3, $J = 0.5$ Hz), 1.37 (d, 3, $J = 7.0$ Hz), 1.0 (t, 3, $J = 6.5$ Hz)
8	1.4910 (25)	5.5 (s, 1), 4.55–3.95 (m, 2), 2.6–1.8 (m, 2), 1.46 (d, 3, $J = 7.5$ Hz), 1.42 (d, 3, $J = 7.5$ Hz), 1.12 (t, 3, $J = 9.0$ Hz)
9	1.4921 (25)	5.52 (s, 1), 4.5–3.9 (m, 2), 2.5–1.6 (m, 4), 1.48 (d, 3, $J = 7.5$ Hz), 1.16 (t, 3, $J = 8.0$ Hz), 1.01 (t, 3, $J = 8.0$ Hz)
10	1.5062 (20)	5.37 (d, 1, $J = 1.5$ Hz), 4.4–3.8 (m, 2), 2.7–1.5 (m, 3), 1.39 (d, 3, $J = 7$ Hz), 1.10 (t, 3, $J = 8$ Hz), 0.96 (d, 6, $J = 8$ Hz)
12	1.5221 (20)	5.25 (d, 1, $J = 2.0$ Hz), 4.3–3.7 (m, 2), 2.80–1.15 (m, 10), 1.00 (t, 3, $J = 6$ Hz)

[a] Tabulation follows the order chemical shift (δ), multiplicity, number of protons, coupling constant. Spectra run in $CDCl_3$. [b] Sample contaminated by thiophene.

B. Separation of the Dihydrothiophenes. Initially we were unable to detect any indication of the presence of two dihydrothiophene isomers using gas chromatography. However, by utilizing a very polar column packing and low temperatures[12] we finally achieved separation of two isomers in some cases. In each case, the order of elution was *trans*- followed by *cis*-2,5-dialkyl-2,5-dihydrothiophene, as was shown by the ratios of dienes subsequently obtained (vide post). Unfortunately, in cases where the NMR spectrum showed the presence of the corresponding thiophenes as an impurity, it could not be separated and therefore the cis/trans ratio of dihydrothiophenes could not be determined directly. In Table III the cis/trans ratio derived by GLC analysis is recorded.

C. Preparation and Decomposition of the Sulfones. As already discussed, thermal elimination of sulfur dioxide is a stereospecific disrotatory process and therefore the stereochemistry of the dienes obtained faithfully reflects that of the dihydrothiophenes from which they are derived. Specifically, *cis*-1 leads to *E,E* or *Z,Z* diene whereas *trans*-1 affords *E,Z* or *Z,E* diene on oxidation and pyrolysis. Therefore isomeric analysis of the dienes also affords the cis/trans ratio of the dihydrothiophenes and gives a check on the direct GLC analysis.

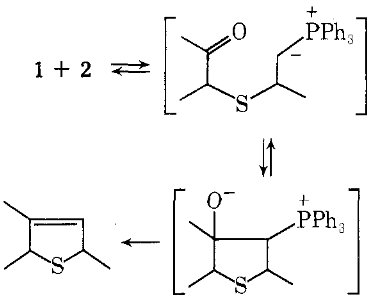
One possible problem foreseen was the rearrangement of the dienes by 1,5-hydrogen transfer.[5c,13] We chose to effect the pyrolysis of the sulfones in the injection port of a gas chromatograph to minimize the pyrolysis time and thus the chance for rearrangement. As yet we have failed to detect a rearranged diene in any of the cases studied.

The dihydrothiophenes were oxidized to the sulfones using *m*-chloroperbenzoic acid and were immediately decomposed by injection into the GLC. In every case, the only products observed were sulfur dioxide and a diene mixture. The results of the diene analysis are incorporated into Table III. Where possible, the dienes were collected separately and identified by their spectra. In several cases (**8, 9, 10**) separation on a preparative scale was not feasible and then the NMR spectrum of the diene mixture served to identify the major component and GLC analysis gave the *E,E*/*E,Z* ratio. In the case of **11**,[14] because of the extremely heavy bias of the diene mixture, authentic samples were prepared and compared to the pyrolysis products.

Inspection of Table III shows that the two methods of analysis give similar results when thiophenes are not present in the dihydrothiophene preparation. In all cases, the cis isomer is favored over the trans, but incorporation of increasingly bulky groups on the ring leads to a relative increase in the amount of trans isomer present.

Discussion

The accepted mechanism for the cyclization reaction involves[3] the conjugate addition of thiolate ion to the polarized double bond of the phosphonium salt, followed by an intramolecular Wittig reaction of the ylide so formed (eq 2). The first step of this sequence is known to be reversible.[15] Assuming irreversible betaine decomposition,[16] the product stereochemistry will be determined by structural influences on the transition state for this step. Models suggest that the ring is nearly planar at this point with substantial eclipsing of all substituents. Thus it is clear that to minimize the serious steric interactions, substituents at C-2 and C-5 (Figure 1) must be trans to the phosphorus atom, thus favoring the formation of the *cis*-2,5-dialkyl-2,5-dihydrothiophene. A result of this analysis is the prediction that this steric discrimination should decrease as the steric bulk of R,R′, and X increase. Inspection of Table III bears this out and lends support to the rationale.



(2)

The two dihydrothiophenes (**11, 12**) derived from α-mercaptocyclohexanone appear to be special cases. Here R′ and X constitute part of a six-membered ring and models suggest that cis fusion in these compounds should be by far the favored mode. Again the isomeric distribution supports this interpretation.

Table III
Isomeric Distribution of Dihydrothiophene and Diene Mixtures[a]

Dihydrothiophene	GLC analysis cis:trans (%)	Sulfone pyrolysis $(E,E + Z,Z):(E,Z + Z,E)$, %
3		92:8
4	83:17	81:19
5	*b*	75:25
6	79:21	79:21
7	67:33	69:31
8	78:22	*c*
9	78:22	*c*
10	54:46	57:43
11		96:4
12		96:4

[a] See Experimental Section for GLC conditions. [b] Direct determination impossible owing to thiophene contamination. [c] Separation of isomers not achieved.

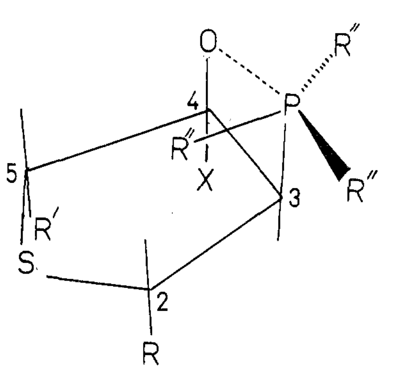


Figure 1. Stereochemical model for dihydrothiophene formation.

It is interesting to note that we have observed no case where the formation of *Z,Z* diene occurs in the sulfone pyrolyses. Apparently the well-known steric problems encountered in such a compound prevent its formation.

Conclusions

It is evident from the foregoing that the formation of dihydrothiophenes from vinylphosphonium salts is a stereoselective process, especially when the steric bulk of the substituents is not too large. Therefore the overall diene synthesis allows the regiospecific and stereoselective formation of conjugated dienes. As we have pointed out,[6b] the net effect achieved is the coupling of two vinyl moieties. This unique aspect, as well as the mildness of the conditions, the readily availability of the starting materials, and the high yields, make the method of potential use in organic synthesis.

Experimental Section

Infrared spectra were recorded on a Beckman 1R-12 in carbon disulfide solution; NMR spectra were obtained on a Jeolco C60HL spectrometer in carbon tetrachloride solution unless otherwise noted and are reported in parts per million downfield from Me$_4$Si as internal standard. Mass spectra were obtained on a Varian MATCH5-DF instrument. GLC analyses were carried out on F & M Models 720 and 5750 gas chromatographs utilizing the following columns: A, 10 ft × 0.375 in. 20% TCEP on Chromosorb P; B, 8 ft × 0.375 in. 20% SE-30 on Chromosorb W. The flow rate of helium carrier gas was 1 ml/sec. Compositions of mixtures were determined using a disc integrator and are considered to be accurate to ±3%. Unless otherwise noted, solvents were removed at reduced pressure and chromatographies were performed using Fisher acidic alumina, Brockman activity grade I. Microanalyses were performed by A. B. Gygli, Microanalysis Laboratory, Toronto, Ontario, Canada.

Preparation of Dihydrothiophenes 3–12. These were prepared using the conditions outlined previously,[3,6] reflux times and yields being indicated in Table I. GLC analyses were performed using column A at 120° and the results are shown in Table III. Compounds 11 and 12 showed no detectable separation of isomers under any conditions. Analytical samples were collected from column B.

Mercaptocarbonyl compounds **1b**,[17] **1c**,[18] and **1e**[11c] were prepared by literature methods.

2-Bromo-3-pentanone. To a mechanically stirred slurry of 110 g (1.1 mol) of calcium carbonate and 87 g (1 mol) of 3-pentanone in 1 l. of cold chloroform was added dropwise 145 g (0.9 mol) of bromine over a period of 4 hr at 0°. After addition was complete, the mixture was stirred for 3 hr and filtered and the filtrate was washed with 300 ml of saturated aqueous sodium bicarbonate solution and dried ($MgSO_4$). Removal of the solvent gave an oil which was distilled to give the bromo ketone (80 g, 55%), bp 55° (15 mm) [lit.[19] bp 48° (12 mm)].

2-Mercapto-3-pentanone (1d). A solution of 30 g of potassium hydroxide in 150 ml of water was saturated with hydrogen sulfide at 0°. With continuous addition of hydrogen sulfide, 45 g (0.27 mol) of 2-bromo-3-pentanone in 10 ml of absolute ethanol was added dropwise with stirring over a period of 2 hr. The solution was stirred for 2 hr as it warmed to room temperature and extracted with two 75-ml portions of ether. The ether extracts were washed with water, dried, and evaporated to give 25 g (78%) of pure **1d**[20] which was used without distillation: NMR δ 3.45 (q, 11, $J = 7.5$ Hz), 2.9–2.4 (d of q, 2, $J = 2, 7$ Hz), 1.4 (d, 4, $J = 7.5$ Hz), 1.1 (t, 3, $J = 7$ Hz).

2-Mercaptopropionaldehyde (1a). To a cooled mixture of 56 g of finely pulverized sodium sulfhydrate in 250 ml of ether was added 25 g (0.18 mol) of 2-bromopropanal,[21] bp 42–50° (60 mm). The slurry was stirred vigorously overnight and filtered and the solvent was removed to afford an oil which solidified on trituration with methanol: yield 1.0 g (6%); NMR δ 5.93 (d, 2, $J = 6$ Hz), 4.7 (broad d, 2, $J = 6$ Hz), 3.63 (broad q, 2, $J = 7.5$ Hz), 1.06 (d, 6, $J = 7.5$ Hz). The material exists as the dimer,[11] as no carbonyl absorption could be detected in the infrared spectrum.

3-Methyl-2-buten-1-yltriphenylphosphonium Bromide. To a solution of 7.0 g (0.02 mol) of triphenylphosphine hydrobromide[22] in 50 ml of acetonitrile was added 3.0 g of isoprene, and the solution was stirred for 15 hr. The salt was precipitated by adding 150 ml of ethyl acetate and filtered, and the residue was dried to give 8.2 g (100%) of a solid: mp 230–234° (lit.[23] mp 233–235°); NMR δ 8.0 (m, 15), 5.5–4.5 (m, 3), 1.75 (d, 3, $J = 7$ Hz), 1.35 (d, 3, $J = 4.5$ Hz).

Refluxing a solution of this salt in pyridine containing some triethylamine for 3 hr[3] caused its isomerization into salt **2c**.

(*Z*)-1-(1-Cyclohexenyl)propene. To a suspension of 7.42 g (0.02 mol) of ethyltriphenylphosphonium bromide in 100 ml of dry tetrahydrofuran was added a solution of 2.2 g (0.02 mol) of potassium *tert*-butoxide in 25 ml of the same solvent dropwise with stirring and under nitrogen. The mixture was stirred at ambient temperature for 25 min, and 2.2 g (0.02 mol) of cyclohexenecarboxaldehyde was added slowly with stirring. The milky solution was stirred overnight and added to a mixture of 100 ml of water and 100 ml of ether, and the organic layer was separated and concentrated to 20 ml. After addition of 100 ml of pentane, the mixture was filtered, concentrated, and distilled to give 1.4 g (55%) of a mixture of dienes, bp 62–65° (12 mm). GLC analysis (column A, 130°) showed the mixture to consist of 24% *E* and 76% *Z* isomer. The latter was collected: NMR δ 5.81–4.95 (m, 3), 2.40–1.85 (m, 4), 1.84–1.40 (m, 7); ir 700 (m), 720 (s), 800 (m), 920 (s), 970 cm^{-1} (w), in agreement with the literature values.[14,24] The retention time was identical with that of the minor isomer obtained from 11 via oxidation and pyrolysis.

(*E*)-1-(1-Cyclohexenyl)propene.[14] The pure *Z* isomer was dissolved in 5 ml of petroleum ether and a crystal of iodine was added. The flask was irradiated for 16 hr with a 60-W incandescent bulb. GLC analysis showed a quantitative conversion to the *E* isomer, identical in all respects with the major isomer obtained from 11 via oxidation and pyrolysis.

General Procedure for Oxidation of 3–12. Dihydrothiophene (0.01 mol) was dissolved in 50 ml of methylene chloride and cooled in an ice bath. *m*-Chloroperbenzoic acid (0.02 mol) was added in two portions and the solution was stirred for 3 hr at 0° and overnight at ambient temperature. The filtered solution was washed with 50 ml of saturated aqueous sodium carbonate, dried, and concentrated to give a quantitative yield of sulfone, which was used directly.

Sulfone Pyrolyses. The sulfone was injected into the injection port (280°) of the gas chromatograph fitted with column A. The dienes were eluted after sulfur dioxide and were collected, individually where possible, for spectral analysis, and were compared to authentic samples where required.

2,4-Hexadiene, obtained from **5**, was separated into the *E,Z* and the *E,E* isomers, which were identified by comparison of spectra and retention times with those of authentic samples.[25]

2,4-Heptadiene,[26] obtained from **4**, was separated into the 2*E*,4*Z* isomer [NMR δ 6.41–5.05 (m, 4), 2.08 (q, 2, $J = 7.5$ Hz), 1.70 (d, 3, $J = 6$ Hz), 1.00 (t, 3, $J = 7.5$ Hz); ir 715 (s), 765 (m), 780 (m), 840 (m), 900 (w), 950 (s), 985 cm^{-1} (s)] and the *E,E* isomer [NMR δ 6.07–5.01 (m, 4), 2.02 (q, 2, $J = 7.5$ Hz), 1.65 (d, 3, $J = 6$ Hz), 1.00 (t, 3, $J = 7.5$ Hz); ir 820 (w), 895 (m), 930 (m), 950 (m), 985 cm^{-1} (vs)].

2-Methyl-3,5-octadiene, obtained from **5**, was separated into two isomers. The major one [NMR (CS_2) δ 6.0–5.12 (4, m), 2.45–1.76 (3, m), 0.96 (d, 6, $J = 6.5$ Hz), 0.98 (t, 3, $J = 7.5$ Hz); ir 700 (w), 860 (m), 900 (w), 990 cm^{-1} (s)] was identified as the 3*E*,5*E* isomer. The other isomer showed NMR δ 6.20–5.05 (m, 4), 2.37–1.78 (m, 3), 1.02 (d, 6, $J = 7.0$ Hz), 0.98 (t, 3, $J = 7.5$ Hz); ir 700 (m), 861 (s), 950 (m), 985 cm^{-1} (m). Although the 3*Z*,5*E* isomer cannot be excluded by these data, we favor 2-methyl-3*E*,5*Z*-octadiene for this compound.

Anal. Calcd for C_9H_{16}: *m/e* 124.12520 Found: *m/e* 124.12582.

3-Methyl-2,4-hexadiene[27] was obtained from **6**. The major isomer was obtained pure and its spectra showed it to be the 2*E*,4*E* isomer [NMR δ 6.07–5.05 (m, 3) which contained the low-field half of an AB quartet centered at 5.95, $J_{AB} = 15$ Hz, 1.86–1.55 (m, 9); ir 772 (s), 840 (m), 927 (m), 970 (vs), 1030 cm^{-1} (m)]. Not enough of the minor isomer could be obtained for NMR, but its ir spectrum [825 (m), 927 (w), 964 cm^{-1} (s)] suggested that no cis-disubstituted double bond was present and a mixture of the two isomers enriched in the minor one showed a very complex absorption at δ 5.66–5.05, strongly reminiscent of (2*E*,4*Z*)-hexadiene. On this basis we assign it the structure 3-methyl-(2*Z*,4*E*)-hexadiene.

3-Methyl-2,4-heptadiene was obtained from **7**. The major component was separated and identified as the 2*E*,4*E* isomer [NMR δ 6.06–5.01 (m, 3), 1.90 (q, 2, $J = 7$ Hz), 1.74–1.48 (m, 6), 0.97 (t, 3, $J = 7$ Hz); ir 700 (w), 795 (m), 810 (w), 860 (s), 965 cm^{-1} (s)]. Not enough of the minor isomer could be obtained pure for NMR analysis but on the basis of the infrared spectrum [700 (m), 760 (w), 865 (vs), 967 cm^{-1} (s)] we believe that the majority of the material must possess a trans-disubstituted double bond and therefore we designate it as the 2*Z*,4*E* isomer. Contamination of this material with the 2*E*,4*Z* isomer cannot be excluded.

Anal. Calcd for C_8H_{14}: *m/e* 110.10955. Found: *m/e* 110.10969.

3-Ethyl-2,4-hexadiene[28] was obtained from **9**. It could not be separated into its isomeric components, but analysis of the spectra of the mixture was done as follows. The NMR absorption for the three vinyl protons occurred between δ 6.36 and 5.00 and included the low-field half of an AB quartet ($J_{AB} = 15$ Hz), the intensity of which suggested that all the material contained a trans-disubstituted double bond. The absence of a strong infrared absorption below 800 cm^{-1} confirmed this. The remainder of the NMR spectrum showed δ 2.38–1.92 (q, 2, $J = 7$ Hz), 1.90–1.55 (m, 6), and two overlapping triplets, $J = 7.5$ Hz, centered at δ 1.01 and 0.98 whose relative intensities were 25:75. This is consistent with a mixture of 75% 3-ethyl-(2*E*,4*E*)-hexadiene and 25% of the 2*Z*,4*E* isomer, in good agreement with results of GLC analysis of **8**. The ir spectrum of the mixture showed 780 (w), 825 (w), 930 (w), 965 cm^{-1} (s).

3-Ethyl-2,4-heptadiene was obtained from **9**. It could not be separated into its components under any conditions. The mixture of isomers showed NMR δ 6.45–5.05 [m, 3, which contained the low-field portion of an AB quartet centered at 5.91 ($J_{AB} = 15$ Hz)], 2.48–1.88 (m, 4), 1.67 (d, 3, $J = 6$ Hz), 1.01 (t, 3, $J = 7.2$ Hz), 0.97 (t, 3, $J = 7.2$ Hz); ir 760 (w), 800 (w), 900 (w), 960 cm^{-1} (vs).

Anal. Calcd for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 86.89; H, 12.84.

3-Ethyl-6-methyl-2,4-heptadiene was obtained from **10** and was separated into the 2*E*,4*E* isomer [NMR δ 5.87–5.07 (m, 3), 2.45–1.92 (m, 3), 1.61 (d, 3, $J = 7$ Hz), 0.97 (d, 6, $J = 6$ Hz), 0.96 (t, 3, $J = 6$ Hz); ir 810 (m), 860 (w), 950 (m), 975 cm^{-1} (vs)] and the 2*Z*,4*E* isomer [NMR δ 6.37–5.02 (m, 3), 2.55–1.82 (m, 3), 1.66 (d, 3, $J = 7$ Hz), 1.03 (d, 6, $J = 6$ Hz), 1.00 (t, 3, $J = 7.5$ Hz); ir 800 (m), 945 (m), 968 cm^{-1} (s)]. This latter assignment of structure was based on the absence of any significant absorption below 800 cm^{-1}, which suggested the absence of a cis-disubstituted double bond.

Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.70; H, 13.24.

1-(1-Cyclohexenyl)propene[14] was obtained from **11**. The major and minor isomers were identical with the authentic samples of the *E* and *Z* isomers, respectively.[24]

1-(1-Cyclohexenyl)butene[14] was obtained from **12**. The vinyl region of the NMR spectrum was very similar to that of the *E* isomer obtained from **11** and on that basis was assigned the same configuration: NMR δ 6.11–5.20 (m, 3, which contained the low-field half of an AB quartet, J_{AB} = 15 Hz), 2.34–1.33 (m, 10), 1.00 (t, 3, J = 6.5 Hz).

Acknowledgment. The financial assistance of the National Research Council of Canada in the form of a scholarship (to G.M.M.) and operating grants is gratefully acknowledged. Mr. P. Y. Lau was of great assistance in obtaining the mass spectra.

Registry No.—**1a**, 54354-14-2; **1b**, 53101-85-2; **1c**, 40789-98-8; **1d**, 17042-24-9; **1e**, 42904-05-2; **2a**, 7301-94-2; **2b**, 54354-15-3; **2c**, 54354-16-4; *cis*-**3**, 33765-35-4; *trans*-**3**, 33765-34-3; *cis*-**4**, 54354-17-5; *trans*-**4**, 54354-18-6; *cis*-**5**, 54354-19-7; *trans*-**5**, 54354-20-0; *cis*-**6**, 54354-21-1; *trans*-**6**, 54354-22-2; *cis*-**7**, 54354-23-3; *trans*-**7**, 54354-24-4; *cis*-**8**, 54354-25-5; *trans*-**8**, 54354-26-6; *cis*-**9**, 54354-27-7; *trans*-**9**, 54354-28-8; *cis*-**10**, 54354-29-9; *trans*-**10**, 54354-30-2; *cis*-**11**, 54354-31-3; *trans*-**11**, 54354-32-4; *cis*-**12**, 54354-33-5; *trans*-**12**, 54354-34-6; 2-bromo-3-pentanone, 815-52-1; 3-pentanone, 96-22-0; 2-bromopropanal, 19967-57-8; 3-methyl-2-buten-1-yltriphenylphosphonium bromide, 1530-34-3; triphenylphosphine hydrobromide, 6399-81-1; isoprene, 78-79-5; (*Z*)-1-(1-cyclohexenyl)propene, 5680-41-1; (*E*)-1-(1-cyclohexenyl)propene, 54354-35-7; ethyltriphenylphosphonium bromide, 1530-32-1; cyclohexenecarboxaldehyde, 30326-86-4; (*E*,*Z*)-2,4-hexadiene, 5194-50-3; (*E*,*E*)-2,4-hexadiene, 5194-51-4; (2*E*,4*Z*)-heptadiene, 54354-36-8; (*E*,*E*)-2,4-heptadiene, 2384-94-3; 2-methyl-(3*E*,5*E*)-octadiene, 54354-37-9; 2-methyl-(3*E*,5*Z*)-octadiene, 54354-38-0; 3-methyl-(2*E*,4*E*)-hexadiene, 54354-39-1; 3-methyl-(2*Z*,4*E*)-hexadiene, 54354-40-4; 3-methyl-(2*E*,4*E*)-heptadiene, 54354-41-5; 3-methyl-(2*Z*,4*E*)-heptadiene, 54354-42-6; 3-ethyl-(2*E*,4*E*)-hexadiene, 54354-43-7; 3-ethyl-(2*Z*,4*E*)-hexadiene, 54354-44-8; 3-ethyl-2,4-heptadiene, 54354-45-9; 3-ethyl-6-methyl-(2*E*,4*E*)-heptadiene, 54354-46-0; 3-ethyl-6-methyl-(2*Z*,4*E*)-heptadiene, 54354-47-1.

References and Notes

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Stable Rotamers of 9,9′:9′,9″-Terfluorenyls at Room Temperature[1]

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Received October 11, 1974

The reactions and spatial structures for the stereoisomers $C_{39}H_{26}$, mp 293° dec (A) and mp 257° dec (B), which are stable at room temperature in solution were investigated. It is proposed from NMR spectra that these are conformational isomers, namely *s-cis,s-cis-* and *s-cis,s-trans*-9,9′:9′,9″-terfluorenyls occurring as the result of restricted rotation about the sp^3–sp^3 carbon–carbon single bonds. A isomerized to B by treatment with Raney nickel. Rotamers A and B were obtained simultaneously by the Michael addition of fluorene to 9,9′-bifluorenylidene.

During investigation on the self-condensation of fluorene (**1**) by treating with various bases, we have obtained 9,9′:9′,9″-terfluorenyl, mp 257° dec (B),[2] by reaction of **1** with sodamide. Pinck and Hilbert also obtained this compound but with mp 293° dec (A)[3] by the Michael addition of **1** to 9,9′-bifluorenylidene (**2**) (Scheme I).

A was isomerized to B, followed by thermolysis of the resulting B to give 9,9′-bifluorenyl (**3**) and **2**,[2] as established by ESR.[4] Isomers A and B were isolated simultaneously by reaction of 9-bromofluorene with methanolic potassium hydroxide in acetone or from other reactions.[5] Both compounds are stable at room temperature in solution, and give fluorenone by oxidation and **1** by reduction.[2,6] Previously we suggested that A and B could be rotational isomers around the C_9–$C_{9'}$–$C_{9''}$ carbon–carbon single bonds.[7]

In the preliminary communication,[8] we reported the conformations and conformational isomerizations of A and B. The present investigation gives further details on the spectral basis of the previous assignments, and is concerned with the Michael addition of **1** to **2**.

Conformations of 9,9′:9′,9″-Terfluorenyl Isomers. Mass spectra of A and B are virtually identical: the parent peak appears at *m/e* 494; the base peak at *m/e* 329 (9,9′-bifluorenyl cation) and *m/e* 165 (9-fluorenyl cation) are fragments whose origin can be interpreted by simple cleavage of $C_{9-9'}$ or $C_{9'-9''}$ bonds from the parent ion.

The ir spectra show absorption bands due to the methine hydrogen C–H stretching frequencies at 2899 cm^{-1} for **3** (9-CH, 9′-CH) and 2917 cm^{-1} for A (9-CH, 9″-CH), whereas two bands at 2883 and 2918 cm^{-1} are observed for B (9-