Organic and Biological Chemistry

Reactions of Carbon Vapor. II. Reactions of Ground-State (^3P) Atomic Carbon with Olefins[1,2]

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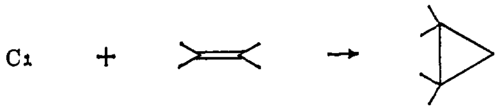
Abstract: Atomic carbon has been produced in a low-intensity carbon arc under high vacuum. This method produces a mixture of ground- and excited-state species of atomic carbon. When allowed to age on an inert matrix at −196°, all species decay to the triplet ground state (^3P). The chemistry of this species in reactions with olefins has been studied. A carbon atom (^3P) reacts with two molecules of olefin to form a spiropentane. With *cis*-2-butene and *trans*-2-butene, the initial addition is stereospecific and the second addition is nonstereospecific, in accordance with the triplet nature of ground-state carbon atoms.

It has long been known that the carbon arc is a source of atomic carbon.[4-7] However, before the present work, this method of producing atomic carbon has not been used for studying the chemistry of the species in reactions with organic molecules.

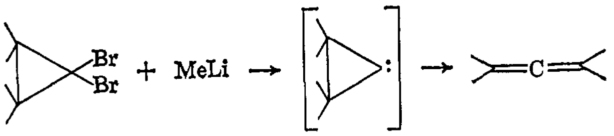
By the use of spectroscopic methods, the electronic states of atomic carbon have been thoroughly investigated and are well understood.[8] The carbon atom is known to have a triplet ground state (^3P) with two long-lived metastable singlet states, the ^1D state 1.3 ev above the ground state and the ^1S state 2.7 ev above the ground state.

Previously, the reactions of atomic carbon have been studied mainly by the use of carbon atoms formed in nuclear processes.[9-13] Owing to the high energies of the reacting species and resultant intermediates in these systems, however, skeletal fragmentation and rearrangement occur which cloud the basic mechanisms. A hallmark of this work is the high yields of acetylene, C_2H_2, from the lower molecular weight organic substrates (C_6 and less). Only a small portion of the studies using carbon atoms produced in nuclear processes have used olefins as trapping agents,[14-16] and in these cases the high energy of the carbon atoms and the further reactions of hot primary products preclude definitive assignments of mechanisms.

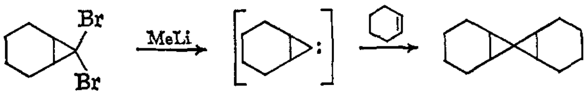
The reactions of olefins with carbon atoms produced in a carbon arc would be expected, by analogy with other carbene reagents, to lead to a cyclopropylidene intermediate.



The formation of allenic products seems to be a major reaction pathway for cyclopropylidenes prepared in solution.[17-20]



Morecver, the additions of cyclopropylidene derivatives to olefins have been observed.[21,22]



It is doubtful, however, that the intermediate cyclopropylidenes in these cases were "free carbenes." These carbenes were generated in the presence of strong Lewis bases in the reaction media and probably were complexed by these bases.[23,24]

Nuclear transformation atomic carbon has been reported to react with ethylene to produce acetylene, allene, cyclopropane, methylacetylene, vinylacetylene,

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(1) For the first paper in the series, see P. S. Skell, L. D. Wescott, Jr., J.-P. Golstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965).

(2) Preliminary communications have appeared: (a) P. S. Skell and R. R. Engel, *ibid.*, **87**, 1135 (1965); (b) *ibid.*, **87**, 2493 (1965).

(3) National Science Foundation Cooperative Graduate Fellow, 1963-1966.

(4) I. S. Bowers, *Phys. Rev.*, **29**, 231 (1927).

(5) J. W. Ryde, *Proc. Roy. Soc.* (London), **A117**, 16A (1928).

(6) A. Fowler and E. W. H. Selwyn, *ibid.*, **A118**, 34 (1928).

(7) W. T. Gray, *Phys. Rev.*, **48**, 474 (1935).

(8) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944, p 142.

(9) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 202 (1964).

(10) C. MacKay, P. Polack, H. E. Rosenberg, and R. Wolfgang, *J. Am. Chem. Soc.*, **84**, 308 (1962).

(11) J. E. Nicholas, C. MacKay, and R. Wolfgang, *ibid.*, **87**, 3008 (1965).

(12) A. F. Voigt, D. E. Clark, and F. G. Mesich, *Chem. Effects Nucl. Transformations, Proc. Symp., Vienna*, **1**, 385 (1965).

(13) J. L. Sprung, S. Winstein, and W. F. Libby [*J. Am. Chem. Soc.*, **87**, 1812 (1965)] have published a preliminary communication where carbon atoms produced by heating a carbon rod were studied in reaction with benzene.

(14) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 959 (1964).

(15) M. Marshall, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4741 (1964).

(16) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

(17) W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

(18) L. Skattebøl, *Tetrahedron Letters*, **5**, 167 (1961).

(19) T. L. Logan, *ibid.*, **5**, 173 (1961).

(20) L. Skattebøl, *Acta Chem. Scand.*, **17** (6), 1683 (1963).

(21) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(22) L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

(23) P. S. Skell and L. D. Wescott, Jr., *J. Am. Chem. Soc.*, **87**, 1721 (1965).

(24) P. S. Skell, M. S. Cholod, and L. D. Wescott, Jr., *ibid.*, in press.

as well as C_4 and C_5 products; spiropentane, if present, was too small to detect.[14]

In the carbon-vapor studies the condensed-phase reactions of ground state (^3P) and two metastable states (^1D and ^1S) with olefins have been reported in preliminary form;[2,25] *acetylene is not a product.* This paper describes the reactions of ^3P carbon atoms with olefins; the sole products are spiropentanes. The properties of ^1D and ^1S carbon atoms will be described elsewhere.

Method

An earlier publication[1] dealing with the reactions ot C_3 and olefins described the carbon arc and molecular flow system employed to ensure that reaction takes place in the condensed phase on the liquid nitrogen cooled walls. An identical system was used in this work.

Reactions were carried out in the following manner: the system was pumped out to an initial pressure of $<5 \times 10^{-6}$ torr and cooled with liquid nitrogen. The substrate flow was started at a rate of ~1 g/min, and the olefin solidified on the liquid nitrogen cooled walls. The arc was struck as substrate was deposited and operated continuously for usually 0.5 hr, being adjusted manually. In this time, an average of 90 mg of carbon would be vaporized using a 16-v (ac) arc. The pressure during the arcing remained $<10^{-4}$ torr. At the end of this time, arcing and substrate flow were stopped.

The mixture of substrate and product was then distilled *in vacuo* through cold traps which would retain products but not excess substrate. In the reactions discussed here a $-78°$ trap was usually used since it efficiently stopped all C_1 + 2-olefin products but not the substrate. The product mixture could then be removed from the trap with or without solvent.

This product mixture was then treated with alkaline aqueous sodium permanganate which resulted in oxidation of all unsaturated products; the resistant hydrocarbons were readily pumped from the oxidation mixture and proved to be spiropentanes. The isolated spiropentanes were identified by their resistance to oxidation[26,27] and infrared[28] and mass spectra.

For the main part the syntheses of spiropentanes employed a 16 v (ac) arc which produces a mixture of ground-state (^3P) and metastable (^1S, ^1D) carbon atoms. To limit the study to ground-state carbon atoms it was necessary to eliminate the metastable species. This was accomplished by depositing less than a monomolecular layer of carbon vapor on a neopentane surface held at $-196°$. Neopentane, at $-196°$, is resistant to attack by ^3P, ^1D, and ^1S carbon atoms.[29] Since the half-life of the ^1S atom is ~2 sec and the ^1D ~15 sec,[25] after 2 min the metastable states have essentially all decayed, so that only ^3P carbon atoms and ground-state C_3 remain. Addition of substrate after this delay ensures that products are obtained from these species only Additions of olefins to "aged" carbon yield *only* spiropentanes and bisethanoallenes.

In practice, the walls of the container (~625 cm²) were cooled to $-196°$ and ~1 g of degassed neopentane was condensed while maintaining the pressure at $<10^{-5}$ torr. After complete condensation of the neopentane the arc was operated for approximately 10 sec, depositing on the neopentane surface ~0.3 mg of molecular carbon,[29] estimated from the rate of carbon vaporization in continuous arcing reactions. After aging for at least 2 min, ~5 g of olefin was added rapidly, usually causing momentary liquefaction of the system. This process was then repeated 12 to 15 times. The products were again separated from the excess substrate by distillation *in vacuo* through a $-78°$ trap and collected in a solvent decalin or 2-octanol. This solution was then analyzed by gas chromatography, identification being made with the retention times previously established in the synthetic runs.

The gas chromatographic columns used were 100-ft long 10-mil i.d. stainless steel capillary columns coated with dioctyl phthalate or squalene. With these columns, the retention times were lengthened by the use of a large amount of solvent since no split was used. Retention times were compared under the same solvent conditions.

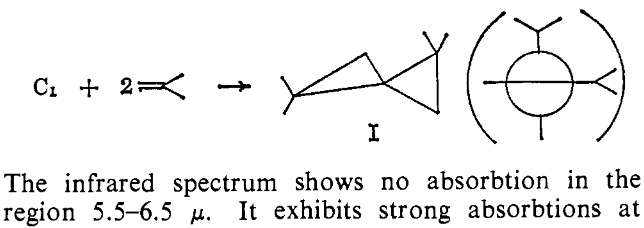
Competition reactions were carried out in the same manner as described for the time-delay studies (*vide supra*) using an equilibrated mixture of olefins and were also analyzed by comparison of gas chromatographic retention times with those of the previously prepared compounds.

In the reactions using continuous deposition of substrate with continuous arcing, the C_1 and C_3 products found accounted for 75–85% of the carbon vaporized. For the time-delay reactions 80–90% of the carbon vaporized is accounted for by C_1 and C_3 products. The remainder of the carbon is presumably lost by deposition where there is little or no substrate (on the upper part of the flask) and in the formation of a small amount of polymeric material.

Results and Discussion

A. Reaction of Atomic Carbon with Isobutene. The reaction of atomic carbon with isobutene yielded a mixture of products which was treated with an alkaline aqueous solution of sodium permanganate. In this way all materials were oxidized except the saturated hydrocarbon I which exhibited a single sharp peak on the capillary column gas chromatograph and was assigned the structure of 1,1,1′,1′-tetramethylspiropentane on the basis of its infrared and mass spectra and isomer number.

Stereochemical considerations predict only one pair of enantiomorphs for 1,1,1′,1′-tetramethylspiropentane.



I

The infrared spectrum shows no absorbtion in the region 5.5–6.5 μ. It exhibits strong absorbtions at 3.40, 6.85, 7.25, and 10.2 μ. Mass spectrometry con-

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(25) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).

(26) W. M. Jones, *ibid.*, **82**, 6200 (1960).

(27) All spiropentanes resisted oxidation except those formed in the 1,3-butadiene reaction.

(28) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p 28. The infrared and mass spectra of these compounds are tabulated in Appendix I.

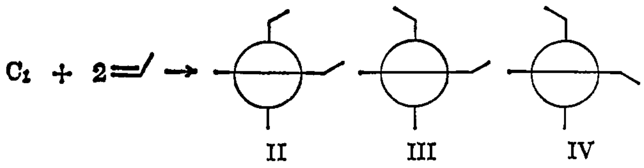
(29) If the system is warmed, the matrix darkens perceptibly, suggesting condensation to higher molecular weight carbon molecules is occurring. Addition of reactive substrate precludes this darkening: P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, in press.

firmed the assignment with a parent peak at *m/e* 124 corresponding to a composition of C_9H_{16}.

When only ^{3}P carbon atoms were available for reaction, using "aged" carbon atoms, the only product from the reaction of atomic carbon was the 1,1,1′,1′-tetramethylspiropentane (I). This was identified by its retention time on the capillary gas chromatograph, capable of resolving all the reaction products from ^{1}D and ^{1}S carbon atoms.

B. Reaction of Atomic Carbon with Propylene. The reaction of atomic carbon with propylene also yielded a mixture of products which was treated with an alkaline aqueous sodium permanganate solution. The only materials to survive this oxidation were the saturated hydrocarbons II, III, and IV, present in the ratio 0.6:2.0:1.0, which were well separated by capillary column gas chromatography. These were assigned the structures of the diastereoisomeric 1,1′-dimethylspiropentanes on the basis of their infrared and mass spectra, isomer number, and relative amounts of each formed.

Random stepwise addition of a carbon atom to two molecules of propylene leads to the prediction of three diastereoisomeric forms of 1,1′-dimethylspiropentane, II, III, and IV, to be formed in the ratio 1:2:1.[1] However, as can easily be seen with molecular models, in II there is significant interaction of the two methyl groups which would cause its rate of formation to be decreased relative to the rate of formation of III and IV. On this basis, the diastereoisomer present in the smallest amount was assigned structure II and the most abundant structure III. By contrast in the reaction of propylene with C_3, where sites of cyclopropane formation are far apart, the ratio of corresponding diastereoisomers is 1:2:1.[1]

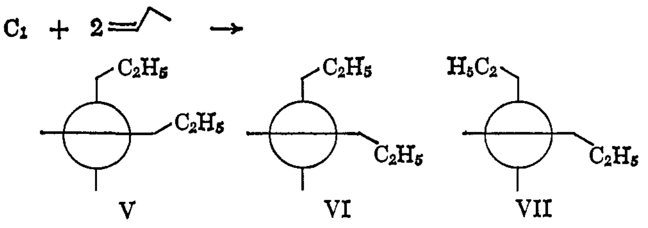


The infrared spectrum of a mixture of the three diastereoisomers shows no absorbtion in the region 5.5–6.5 μ. Strong bands are observed at 3.45, 6.85, 10.1, and 10.9 μ. The mass spectrum shows a parent peak at *m/e* 96 corresponding to a composition of C_7H_{12}.

In the "aged" carbon reactions where only ^{3}P carbon atoms were available for reaction, the only products from the reaction of atomic carbon with propylene were the diastereoisomeric 1,1′-dimethylspiropentanes (II, III, and IV). They were identified by their retention times on the capillary gas chromatograph. The ratio of II:III:IV was within experimental error the same in the "aged" carbon reaction as in the preparative reaction discussed above.

C. Reaction of Atomic Carbon with 1-Butene. A mixture of products was obtained from the reaction of atomic carbon with 1-butene. This mixture was treated with an alkaline aqueous solution of sodium permanganate. This resulted in oxidation of all materials except the saturated hydrocarbons V, VI, and VII, present in the ratio 0.5:2.0:1.3, separated by capillary column gas chromatography. These were assigned the structures of the diastereoisomeric 1,1′-diethylspiropentanes on the basis of their infrared and mass spectra, isomer number, and relative amounts of each formed.

Here, as in the propylene case, random stepwise addition of a carbon atom to two molecules of 1-butene leads to the prediction of three diastereoisomeric forms of 1,1′-diethylspiropentane (V, VI, and VII) to be formed in the ratio 1:2:1.[1] But again, as in the propylene case, there is repulsive interaction of the two opposing ethyl groups in V which would cause its rate of formation to be decreased relative to the rate of formation of VI and VII. Also, there appears to be a factor decreasing the rate of formation of VI relative to that of VII. On this basis, the diastereoisomer present in the smallest amount was assigned structure V and the most abundant structure VI.

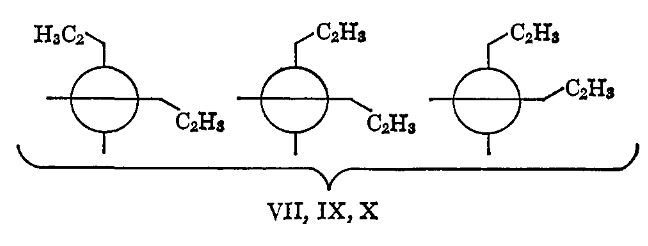


The infrared spectrum of a mixture of the three diastereoisomers shows no absorbtion in the region 5.5–6.5 μ. Strong bands are observed at 3.38, 6.78, 7.17, and 10.85 μ. The mass spectrum shows a parent peak at *m/e* 124 corresponding to a composition of C_9H_{16}.

Using "aged" carbon atoms, the only products formed from the reaction of atomic carbon were the three diastereoisomeric 1,1′-diethylspiropentanes (V, VI, and VII). They were identified by their retention times on the capillary gas chromatograph. The ratio of V:VI:VII was within experimental error the same as in the preparative reaction mentioned above.

D. Reaction of Atomic Carbon with 1,3-Butadiene. The reaction of atomic carbon with 1,3-butadiene also gave a mixture of products. However, owing to the presence of olefinic bonds in the expected spiropentanes, the diastereoisomeric 1,1′-diethenylspiropentanes, it could not be treated with permanganate to isolate these spiropentanes.

In the reaction of 1,3-butadiene with "aged" carbon atoms, most of the products were no longer present. Under the best of capillary gas chromatographic conditions this reaction product mixture showed three poorly resolved peaks. (As with propylene and 1-butene, random stepwise addition of carbon atoms to 1,3-butadiene predicts the formation of three diastereoisomeric 1,1′-diethenylspiropentanes (VIII, IX, and X).)



The materials in the synthetic reaction corresponding, by retention time, to that formed in the time-delay reaction were isolated from the other reaction products by preparative gas chromatography.

The material thus isolated showed the three poorly resolved peaks on the capillary gas chromatograph. These were assigned the structures of the three diastereoisomeric 1,1′-diethenylspiropentanes (VIII, IX, and X).

The infrared spectrum of the mixture of diastereoisomers shows only a single, very sharp absorbtion in the unsaturated region at 6.09 μ. Strong absorbtions were present also at 3.26, 3.42, 6.91, 10.10, 10.30, and 10.89 μ.

The mass spectrum does not show the expected parent peak at m/e 120 but does show moderately strong peaks at m/e 93 and 66 corresponding to loss of $CH_2{=}CH$ and $2(CH_2{=}CH)$, respectively, from C_9H_{12}. The 1,1′-diethenylspiropentanes are quite easily cleaved in the mass spectrometer.

E. Reaction of Atomic Carbon with *cis*- and *trans*-2-Butenes. The reaction of atomic carbon with *cis*-2-butene yielded a mixture of products which was treated with an alkaline aqueous solution of sodium permanganate. The only materials to survive this oxidation were the saturated hydrocarbons XI and XII, present in the ratio of 1.0:0.3, which were separated by capillary gas chromatography.

The reaction of *trans*-2-butene with atomic carbon gave a mixture of products which upon treatment with alkaline aqueous sodium permanganate gave three saturated hydrocarbons, *one of them identical with XII formed in the cis-2-butene reaction*, XII, XIII, and XIV, in the ratio 0.49:1.0:0.43, easily separated by capillary gas chromatography.

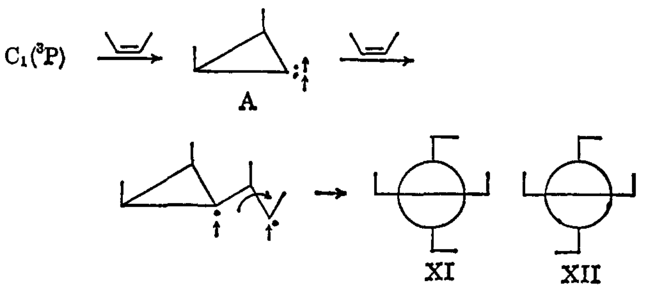
In the reaction of "aged" carbon atoms with *cis*-2-butene, XI and XII are the only products, here being formed in the ratio 1:1.

The reaction of *trans*-2-butene with "aged" carbon atoms shows XII, XIII, and XIV as the only products, now in the ratio 1.0:1.0:0.7.

The mixtures of diastereoisomers from reaction of both *cis*-2-butene and *trans*-2-butene show infrared spectra free of absorbtions in the region 5.5–6.5 μ. Mass spectra on the same mixtures show peaks at m/e 124, corresponding to C_9H_{16} compositions, and essentially identical cracking patterns.

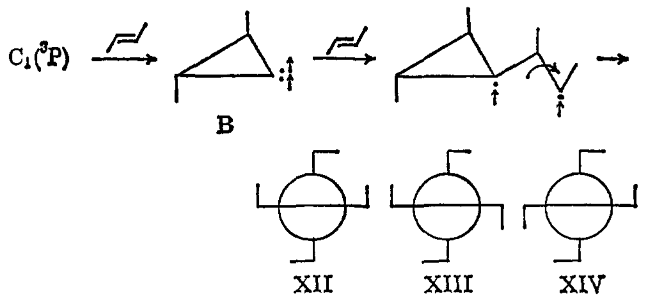
On the basis of the above data, noting the triplet nature of the ground-state carbon atom and the infrared and mass spectra, we can assign to XI, XII, XIII, and XIV the structures of the diastereoisomeric 1,2,1′,2′-tetramethylspiropentanes; these four are the only structures possible.

The data for spiropentane formation may now be interpreted on the basis of the triplet nature of ground-state carbon atoms. The initial reaction of a ground-state carbon atom is postulated to be a stereospecific[30–32] addition leading to the *cis*-dimethylcyclopropylidene, a triplet species. Triplet *cis*-2,3-dimethylcyclopropylidene (A) then adds to *cis*-2-butene in a nonstereospecific manner giving XI and XII.

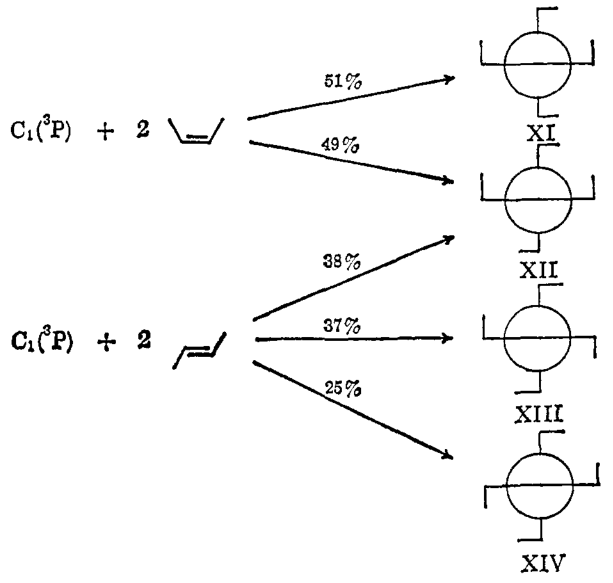


The structure shown for XII is assigned to the product which is formed in the reactions of both *cis*-2-butene and *trans*-2-butene and the assigned structure is the only spiropentane possible from both these substrates; XII increases, until equal to XI, with increasing "aging" of the carbon atom (^1D decays to ^3P during aging).[25]

The case with *trans*-2-butene is analogous. Initial reaction with *trans*-2-butene is stereospecific, leading to the triplet-state *trans*-dimethylcyclopropylidene (B) which reacts further with *trans*-2-butene in a nonstereospecific manner giving XII, XIII, and XIV[1]; from ^1D carbon atoms and *trans*-2-butene only XIII and XIV are produced.[25] The all-*cis* product XI is the only spiropentane obtained from reaction of ^1D carbon atoms with *cis*-2-butene,[25] and is not produced in the reaction of ^3P carbon atoms with *trans*-2-butene.



The structures are assigned to XIII and XIV on the basis of the relative amounts of each formed, the least abundant diastereoisomer being assigned the most hindered structure and the most abundant the least hindered.



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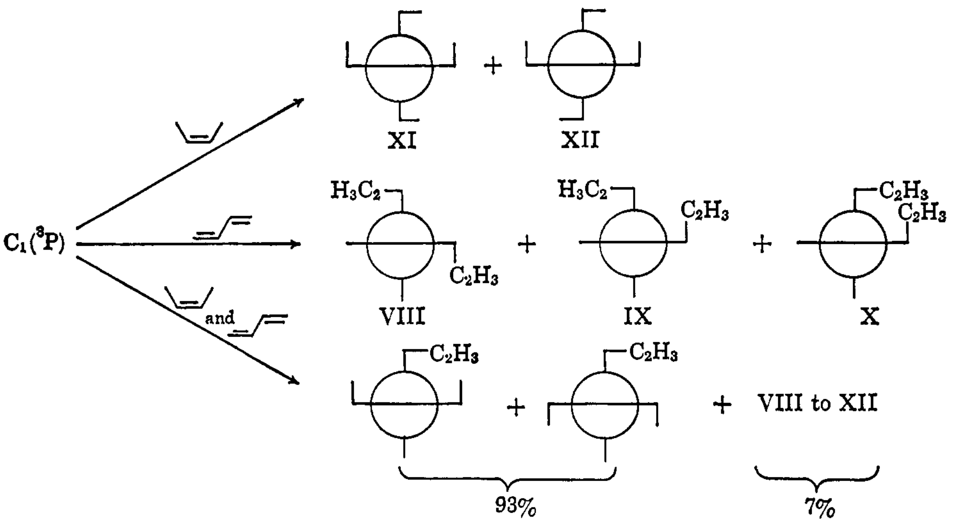
(30) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(31) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(32) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

Scheme



The sequence of addition steps, stereospecific followed by nonstereospecific, is also supported by the observed inequality

$$[XII/XI]_{cis} \neq [(XII + XIV)/XII]_{trans}$$

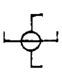
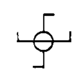
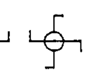
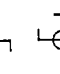
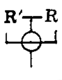
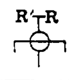
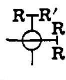
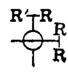
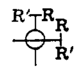
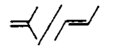
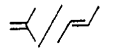
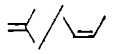
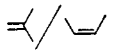
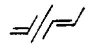
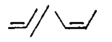
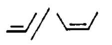
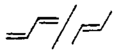
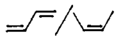
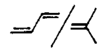
For the reverse sequence of steps, stereospecific step following the nonstereospecific, these ratios would be identical since each olefin would yield the same mixture of *cis* and *trans* singlet-state dimethylcyclopropylidenes. This sequence is also supported by the 1,3-butadiene scavenging data given below which indicates complete scavenging of A and **B** by butadiene, giving cross-adducts with the same stereochemistry as the 2-butene used.

F. Relative Reactivities of Some Olefins toward Ground-State Carbon Atoms (^3P). Relative reactivities of olefins toward $C_1(^3P)$ were determined by competition reactions, mixtures of olefins being added to aged C_1, the carbon atoms being in the triplet ground state.

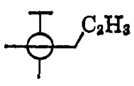
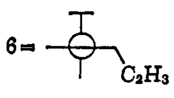
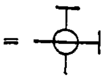
The homoadducts in all reactions were identified by comparison of capillary column gas chromatography retention times with those of the compounds as formed in the synthesis reactions.

The crossover products were not isolated but were assigned structures on the following bases: (1) the experience with the single olefins being that the only products from $C_1(^3P)$ were spiropentanes, it was rea-

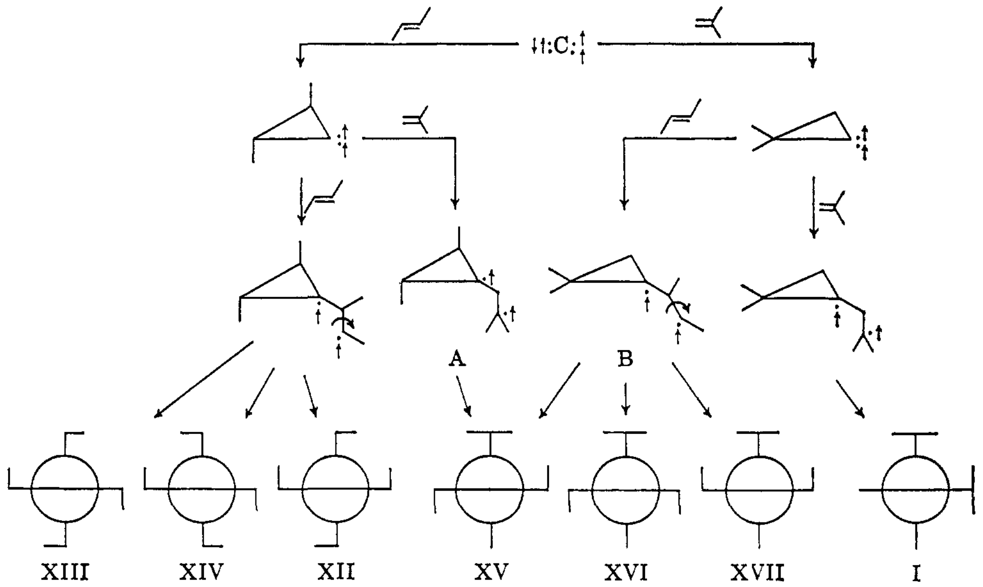
Table I

Olefin mixture ratio (A/B)		1 	2 	3 	4 	5 	6 	7 	8 	9 	10 	11 	k_A/k_B for ⇉:C:	k_A/k_B for 
	4.71[a]	...	4.9	4.8	2.6	4.9	7.3	26.8	...	48.8	...	...	0.59	0.25
	4.70[a]	...	8.1	6.5	4.3	4.9	5.4	22.4	...	48.4	...	...	0.48	0.13
	2.54[a]	10.2	10.2	...	...	16.9	20.3	25.4	...	16.9	...	...	0.83	0.23
	0.99[a]	25.5	21.8	...	...	7.2	19.9	9.2	...	17.5	...	...	0.56	0.38
	4.70[b]	...	6.1	5.2	4.3	6.1	7.0	30.0	10.4	7.8	15.7	7.0	0.28	0.37
	4.01[b]	6.6	6.2	...	...	(—57.0—)		11.8	8.3	2.9	5.2	2.0	0.25	0.72
	2.25[b]	21.1	19.5	...	...	11.7	13.7	7.0	5.9	5.9	10.9	4.7	0.42	0.14
	0.88[c]	...	2	2	1	...		(—92—)		(———3———)			0.04	25
	1.01[c]	0.9	0.9	...	...	(—93.1—)		...	...	1.3	2.8	1.0	0.05	40
	1.00[d]	...	...	...	...	(—97.5—)		1.5	...	0.3	0.5	0.2	...	...

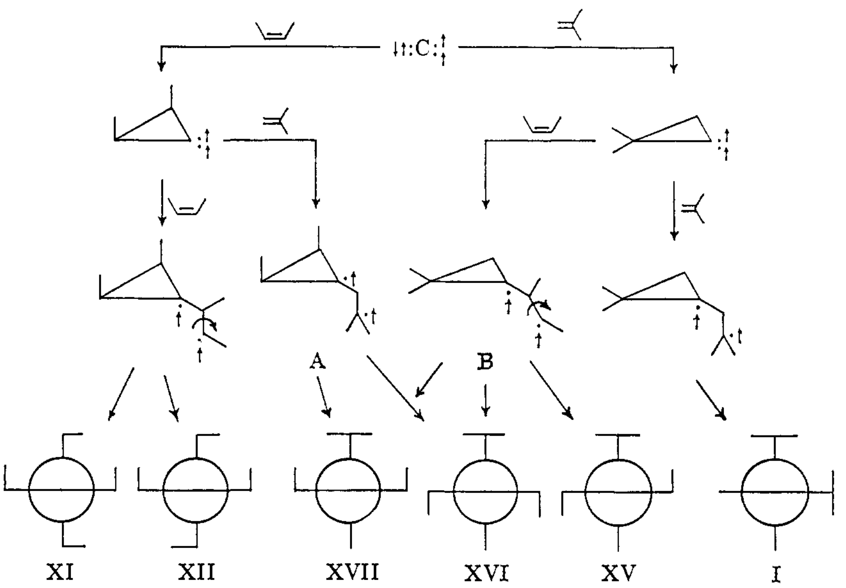
[a] R = R′ = CH_3. [b] R = CH_3; R′ = H. [c] R = C_2H_3; R′ = H. [d] R = C_2H_3; R′ = H except for

5 = , 6 = , 7 = 

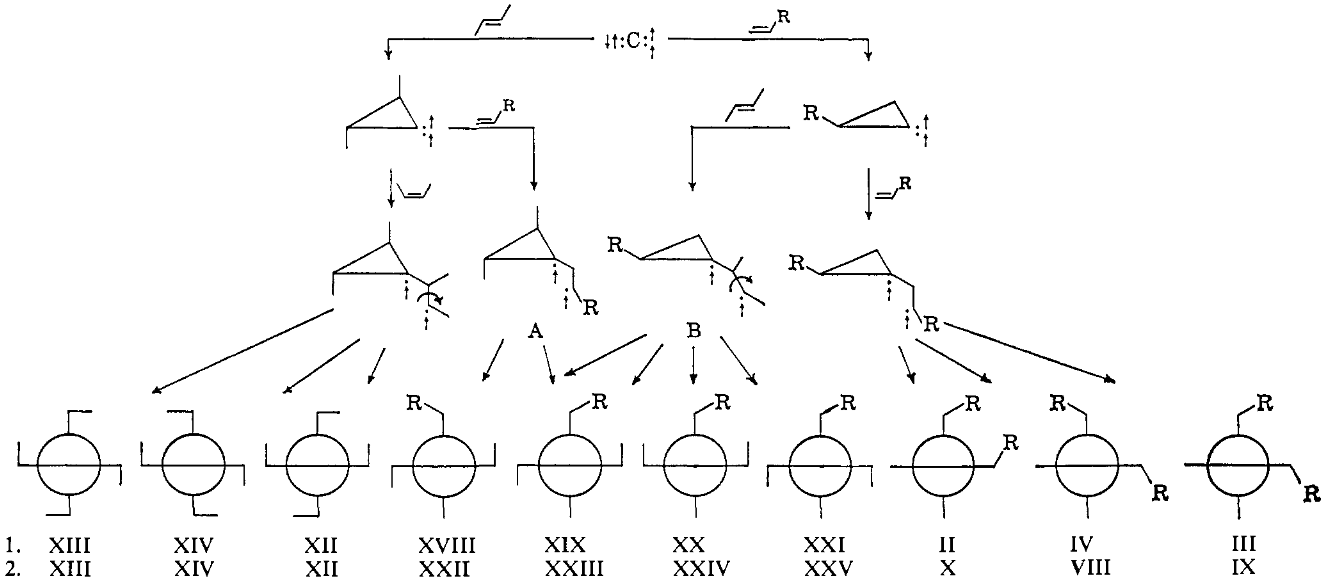
Scheme II



Scheme III

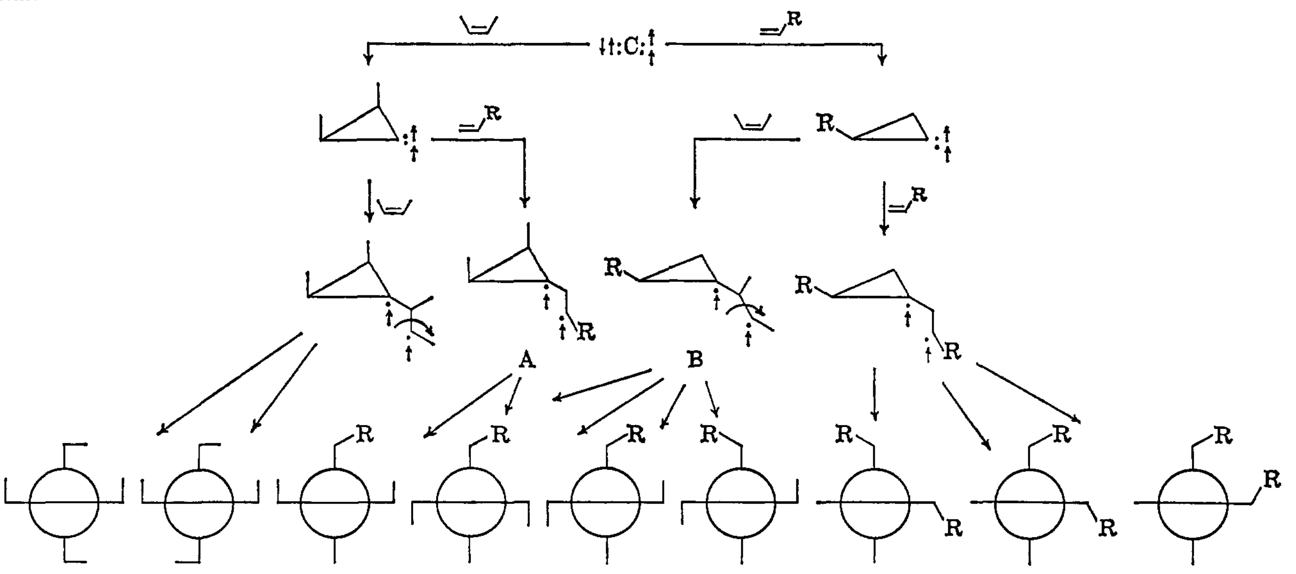


Scheme IV



line 1, R = CH_3; line 2, R = C_2H_5

Scheme V



1. XI XII XX XXI XIX XVIII IV III II
2. XI XII XXIV XXV XXIII XXII VIII IX X

line 1, R = CH_3; line 2, R = C_2H_3

sonable to assume that the new products found were spiropentanes arising from reaction of one molecule of each of the competing olefins, *i.e.*, crossover products; (2) in all cases the number of new products found was equal to the number of diastereoisomeric crossover spiropentanes possible; (3) the assignments were checked by greatly varying the relative amounts of the competing olefins and noting the changes in the amounts of crossover products.

The most striking result of these competition reactions is to be found when 1,3-butadiene is used to compete with monoolefins. In these cases it was found that the crossover products arising from addition of one molecule of monoolefin and one molecule of 1,3-butadiene were by far the most important (>90%) (Scheme I).

From a mixture of 1,3-butadiene and *cis*-2-butene, two crossover products are obtained. In the corresponding *trans*-2-butene experiment two new crossover products are produced. There is no intercontamination by these products. *Thus the crossover products are obtained in stereospecific reactions of the 2-butenes.*

One might expect 1,3-butadiene, being a triplet "scavenger," to dominate the "triplet reaction," addition to the cyclopropylidene, and addition of the monoolefin, the monoolefin being the more reactive with singlet species, to be the preferred reactant for the "singlet reaction."[33,34] The results confirm this expectation and support the proposed mechanism, initial stereospecific addition to a singlet species to produce a triplet cyclopropylidene.

The competitions of the monoolefins, propylene, *cis*-2-butene, and *trans*-2-butene, were somewhat more difficult to analyze because the multiplicity of routes available to the intermediates made separation of the data into partial rates difficult. However, in the reactions using *cis*- or *trans*-2-butene with other monoolefins, separations of partial rates were made possible using the assumption that *cis* and *trans* closure were equally probable in reactions in which cyclopropylidene intermediates add to the 2-butenes, although this is not rigorously true. Thus data sufficient for deriving a reactivity sequence was available. The experimental data are shown in Table I.

The reaction schemes for the competition reactions of *trans*-2-butene and isobutylene, *cis*-2-butene and isobutylene, *trans*-2-butene and the 1-olefins, and *cis*-2-butene and the 1-olefins are shown in Schemes II–V respectively. The equations used in calculating the relative rates are given in Chart I. This indicates a reactivity series as shown in Table II. This sequence is in accord with the proposed mechanism, initial addition of a carbon atom in a singlet reaction forming the triplet cyclopropylidene. Especially to be noted here is the extremely low reactivity of 1,3-butadiene in the first step, a singlet carbene-type reaction with the

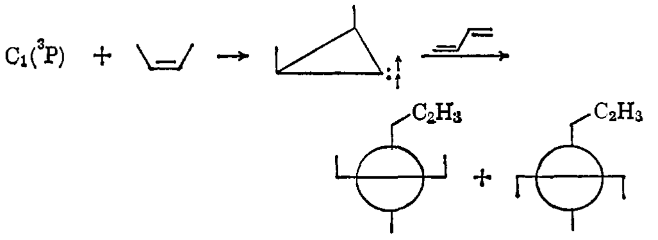
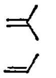
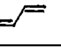


Table II. Relative Rates of Olefin Additions

Olefin	$\uparrow\cdot C: \uparrow\downarrow$	
	1.0	1.0
	0.8	0.7
	0.5	0.2
	0.3	0.4
	0.04	25

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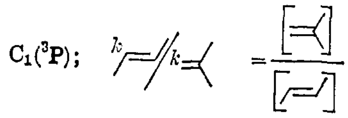
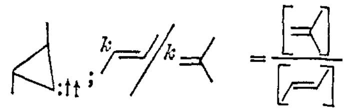
(33) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

(34) As pointed out earlier,[1] the stereospecific step is expected first since two bonds are being made in the transition state leading to the cyclopropylidene while an initial nonstereospecific step would lead to an intermediate with one new bond.

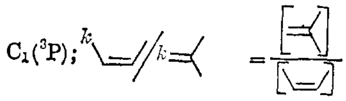
Chart I

For 

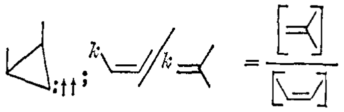
$\frac{(\mathrm{XII} + \mathrm{XIII} + \mathrm{XIV} + \mathrm{XV}_{via(A)})}{(\mathrm{I} + \mathrm{XVI} + \mathrm{XVII} + \mathrm{XV}_{via(B)})}$

For 

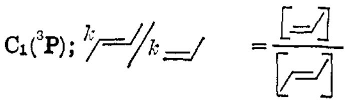
$\frac{(\mathrm{XII} + \mathrm{XIII} + \mathrm{XIV})}{(\mathrm{XV}_{via(A)})}$

For 

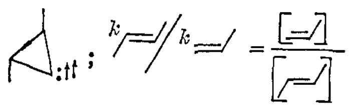
$\frac{(\mathrm{XI} + \mathrm{XII} + \mathrm{XVII}_{via(A)} + \mathrm{XVI}_{via(A)})}{(\mathrm{I} + \mathrm{XV} + \mathrm{XVII}_{via(B)} + \mathrm{XVI}_{via(B)})}$

For 

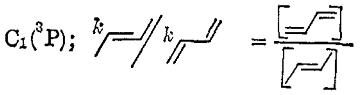
$\frac{(\mathrm{XI} + \mathrm{XII})}{(\mathrm{XVII}_{via(A)} + \mathrm{XVI}_{via(A)})}$

For 

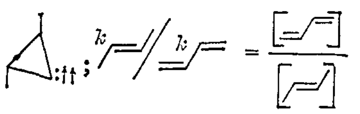
$\frac{(\mathrm{XIII} + \mathrm{XIV} + \mathrm{XII} + \mathrm{XVIII}_{via(A)} + \mathrm{XIX}_{via(A)})}{(\mathrm{IV} + \mathrm{III} + \mathrm{II} + \mathrm{XVIII}_{via(B)} + \mathrm{XIX}_{via(B)} + \mathrm{XX} + \mathrm{XXI})}$

For 

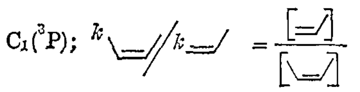
$\frac{(\mathrm{XIII} + \mathrm{XIV} + \mathrm{XII})}{(\mathrm{XVIII}_{via(A)} + \mathrm{XXII}_{via(A)})}$

For 

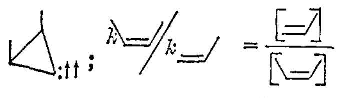
$\frac{(\mathrm{XIII} + \mathrm{XIV} + \mathrm{XII} + \mathrm{XXII}_{via(A)} + \mathrm{XXIII}_{via(A)})}{(\mathrm{XIII} + \mathrm{IX} + \mathrm{X} + \mathrm{XXII}_{via(B)} + \mathrm{XXIII}_{via(B)} + \mathrm{XXIV} + \mathrm{XXV})}$

For 

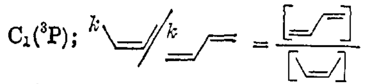
$\frac{(\mathrm{XIII} + \mathrm{XIV} + \mathrm{XII})}{(\mathrm{XXII}_{via(A)} + \mathrm{XXIII}_{via(A)})}$

For 

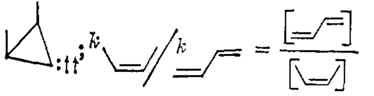
$\frac{(\mathrm{XI} + \mathrm{XII} + \mathrm{XX}_{via(A)} + \mathrm{XXI}_{via(A)})}{(\mathrm{IV} + \mathrm{III} + \mathrm{II} + \mathrm{XX}_{via(B)} + \mathrm{XXI}_{via(B)} + \mathrm{XIX} + \mathrm{XVIII})}$

For 

$\frac{(\mathrm{XI} + \mathrm{XII})}{(\mathrm{XX}_{via(A)} + \mathrm{XXI}_{via(A)})}$

For 

$\frac{(\mathrm{XI} + \mathrm{XII} + \mathrm{XXIV}_{via(A)} + \mathrm{XXV}_{via(A)})}{(\mathrm{VIII} + \mathrm{IX} + \mathrm{X} + \mathrm{XXIV}_{via(B)} + \mathrm{XXV}_{via(B)} + \mathrm{XXII} + \mathrm{XVIII})}$

For 

$\frac{(\mathrm{XI} + \mathrm{XII})}{(\mathrm{XXIV}_{via(A)} + \mathrm{XXV}_{via(A)})}$

carbon atom, *i.e.*, with an electrophilic-type reagent,[35] and the high reactivity of 1,3-butadiene in the second step, a triplet methylene-type reaction with the cyclopropylidene, *i.e.*, with a radical type reagent. We have no explanation for the relatively small reactivity differences between monoolefins.

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research and the Army Research Office (Durham).

Appendix I. Infrared Spectra of Substituted Spiropentanes and Bis(ethanoallenes)

Infrared spectra were measured on a Beckman IR-5. Intensity abbreviations are: s = strong; m = medium; w = weak; sh = shoulder. Wavelengths are in microns.

A. 1,1,1',1'-Tetramethylspiropentane: 3.40 (s), 3.51 (sh), 6.85 (s), 7.25 (s) 10.20 (s), 10.70 (m), 11.15 (m).

B. 1,1'-Dimethylspiropentane: 3.28 (w), 3.41 (sh), 3.45 (s), 6.85 (m), 7.21 (m), 10.10 (m), 10.90 (s).

C. 1,1'-Diethylspiropentane: 3.28 (w), 3.38 (s), 3.43 (sh), 3.51 (sh), 6.78 (s), 7.17 (m), 10.03 (m), 10.30 (m), 10.85 (s), 11.77 (m).

D. 1.1'-Diethenylspiropentane: 3.26 (m), 3.42 (s), 3.47 (sh), 3.53 (sh), 6.09 (s), 6.91 (s), 7.23 (w), 10.10 (m, sh), 10.30 (s), 10.89 (s).

E. 1,2,1',2'-Tetramethylspiropentane: 3.40 (s), 3.50 (sh), 6.71 (m), 7.24 (m), 10.30 (s), 10.69 (s). The mass spectrum from the spiropentanes of the *cis*-2-butene reaction (XI and XII) were virtually identical with that from the *trans*-2-butene reaction (XII, XIII, and XIV) at 12-v source potential.

F. 1,1,1'1'-Tetramethylbis(ethanoallene): 3.28 (sh), 3.40 (s), 3.48 (sh), 4.90 (s), 6.86 (m), 6.99 (sh), 7.28 (m), 8.04 (w), 8.92 (s), 9.59 (sh), 9.71 (sh), 9.85 (s), 10.21 (w), 10.65 (m), 11.00 (m), 12.52 (m), 14.20 (m). Spectra for the bis(ethanolallenes) are taken from the Ph.D. Thesis of L. D. Wescott, Jr., The Pennsylvania State University, June 1963.

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[35] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

Appendix I (*Continued*)

G. 1,1′-Dimethylbis(ethanolallene): 3.29 (sh), 3.38 (s), 3.41 (sh), 3.49 (sh), 4.88 (s), 6.85 (m), 7.01 (m), 7.24 (m), 7.45 (w), 8.62 (w), 9.09 (m), 9.46 (m), 9.80 (m), 10.21 (w), 10.90 (m), 11.42 (w), 11.64 (w), 12.02 (w), 13.10 (s).

H. 1.1′-Diethylbis(ethanoallene): 3.29 (sh), 3.38 (s), 3.42 (sh), 3.49 (sh), 4.87 (s), 6.82 (m), 7.01 (w), 7.22 (w), 7.63 (m), 7.94 (w), 8.58 (w), 9.84 (m), 10.98 (m), 11.85 (m).

I. 1,1′-Diethynylbis(ethanoallene): 3.24 (m), 3.37 (s), 4.86 (s), 6.10 (s), 7.04 (m), 8.41 (s), 9.76 (m), 10.12 (s), 11.05 (s), 11.84 (s), 12.97 (s).

J. *trans*-1,2-*trans*-1′,2′-Bis(ethanoallene): 3.18 (w), 3.44 (s), 3.66 (w), 4.91 (s), 6.89 (s), 7.27 (s), 7.71 (m), 8.60 (m), 8.74 (m), 9.24 (s), 9.48 (m), 10.62.

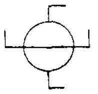
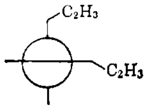
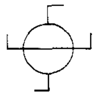
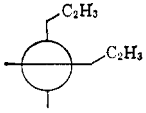
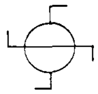
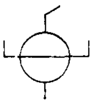
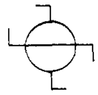
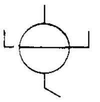
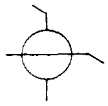
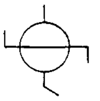
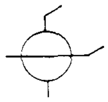
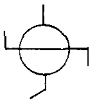
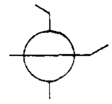
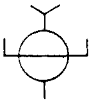
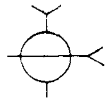
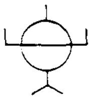
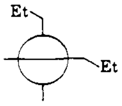
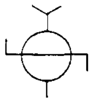
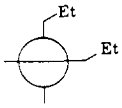
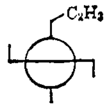
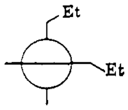
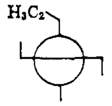
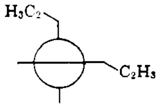
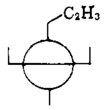
K. *cis*-1,2-*trans*-1′,2′-Tetramethylbis(ethanoallene): 3.37 (s), 3.41 (sh), 3.49 (sh), 4.90 (s), 6.86 (m), 7.25 (m), 8.49 (w), 8.67 (w), 9.21 (s), 10.60 (w), 12.22 (w), 13.58 (m).

L. *cis*-1,2-*cis*-1′,2′-Tetramethylbis(ethanoallene): 3.35 (s), 3.42 (s), 3.50 (sh), 4.93 (s), 6.83 (sh), 6.90 (m), 7.22 (m), 7.31 (m), 7.90 (w), 8.41 (m), 8.78 (m), 9.28 (s).

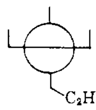
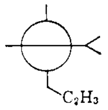
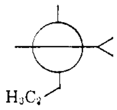
Appendix II. Gas Chromatographic Retention Times for Substituted Spiropentanes and Bis(ethanoallenes)

A. Substituted Spiropentanes

Column A: 100 ft, 10-mil i.d. capillary, silicone oil, 68°, 20 psig. Column B: 100-ft, 10-mil i.d. capillary, dioctyl phthalate, 67°, 30 psig. Column C: 5-ft, $^3/_{16}$-in. i.d., 15% squalene on Gas Chrom Z, 68°, 25 cc/min. Column D: 100-ft, 10-mil i.d. capillary, Fluorosilicone, 73°, 10 psig.

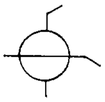
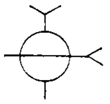
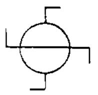
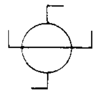
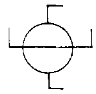
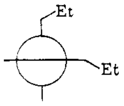
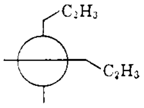
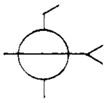
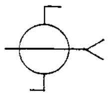
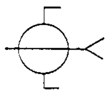
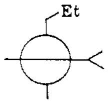
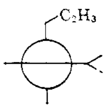
	Relative retention times					Relative retention times			
Compound	Col A	Col B	Col C	Col D	Compound	Col A	Col B	Col C	Col D
	1.00	...	1.00	...		...	2.19	2.89	...
	1.31	1.14	1.14	...		...	2.19	3.35	...
	1.04	1.00	1.07	...		...	...	1.61	. .
	1.44	1.27	1.19	...		...	...	1.64	...
	...	...	1.21	1.41		...	...	2.50	...
	...	...	1.08	1.07		...	...	2.36	...
	...	...	1.44	1.83		1.80	...	...	...
	1.09	...	1.02	...		1.63	...	...	...
	...	...	...	1.93		1.93	...	...	...
	...	...	...	1.00		...	2.02	1.73	...
	...	...	...	1.35		...	2.02	1.73	...
	...	2.19	2.46	...		...	...	1.57	...

Appendix II (*Continued*)

Compound	Relative retention times Col A	Col B	Col C	Col D
	...	...	1.57	...
	...	...	1.68	...
	...	...	1.68	...

B. Substituted Bis(ethanoallenes)

Column A: 5-ft, 0.25-in. i.d., 20% fluorosilicone on Gas Chrom Z, 60°, 106 cc/min. Column B: 10-ft, 0.25-in. i.d., 10% 1,2,3-tris(2-cyanoethoxy)propane on Gas Chrom Z, 90°, 60 cc/min. Column C: 100-ft, 10-mil i.d. capillary, silicone grease, 70°, 20 psig. Column D: 5-ft, 0.5-in. i.d., 20% fluorosilicone on Gas Chrom Z, 70°, 200 cc/min.

Compound	Col A	Col B	Col C	Col D
 (3)	1.00	2.64	1.00, 1.03, 1.09	1.36
	1.11	1.00	1.07	1.27
 (2)	...	1.74, 1.93	...	1.00, 1.09
	...	2.58	...	3.28
	2.67	...	...	4.55
 (3)	3.00, 3.56	3.42, 3.81, 4.26	...	...
 (3)	3.28	...	2.11, 2.17, 2.34	5.55
 (2)	...	1.61	...	...
	...	1.55	...	...
 (2)	1.67, 1.83	...	...	...
 (2)	1.72, 1.89	...	...	...
 (2)	...	...	...	2.54