Reactions of Carbon Vapor. III. Reactions of Metastable Atomic Carbon (^1S) with Saturated Hydrocarbons[1,2]

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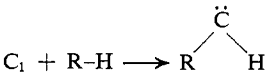
Abstract: Atomic carbon has been produced in a low-intensity carbon arc under high vacuum. The carbon atoms thus produced have been allowed to react with paraffinic substrates deposited on a liquid nitrogen cooled surface. The reactions of carbon atoms with these substrates and of the intermediates thus produced have been studied.

Atomic carbon has been thoroughly investigated through the use of spectroscopic means, and its electronic states are well understood.[4] The carbon atom has been found to have a triplet ground state (^3P) with two low-lying, 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.

A carbon arc operated under high vacuum has been found to produce atomic carbon in the ground triplet and metastable singlet states.[5–7] Prior to the work in this laboratory, this method of production had not been used to study the reactions of atomic carbon.

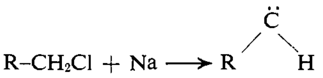
Previously, the reactions of atomic carbon with saturated hydrocarbons had been studied only in systems where the carbon atoms had been formed by nuclear processes.[8–10] The disadvantages of such systems for studying primary reaction processes of low-energy species have been discussed.[1]

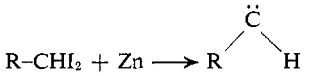
The reaction of a saturated hydrocarbon, R–H, with a carbon atom produced in a low-intensity carbon arc would be expected to lead to a monoalkylcarbene by insertion into a carbon–hydrogen bond. This species



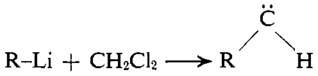
would then be expected to undergo the reactions characteristic of monoalkylcarbenes.

Numerous methods of production have been used in the study of the reactions of monoalkylcarbenes: treatment of the primary alkyl chloride with sodium or a sodium alkyl or reaction of the *gem*-diiodide with zinc or alkyllithium

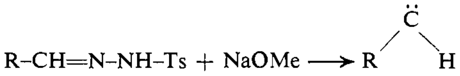


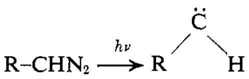


reaction of methylene chloride with the alkyllithium



treatment of the tosylhydrazone with base, or photolysis of the diazirine or diazo compound.





It should be noted that except for gas phase photolyses, all of these reactions take place in solution in the presence of good Lewis bases. Thus it would be expected that these reactions are those of a complexed species and not the free carbene.

In the present study, the reactions are carried out at liquid nitrogen temperature in hydrocarbon media, exclusive of complexing species. The fact of being a free carbene and the great temperature difference would negate detailed comparison of the results in the two types of systems.

Experimental Section

The substrate flow system and reactor design used in this study were identical with those previously described.[1] The flow system design ensured that reaction took place in the condensed phase on the liquid nitrogen cooled walls.

The substrate hydrocarbon was deposited at a steady rate (1 g/min) on the liquid nitrogen cooled surface while maintaining a high vacuum. The carbon arc was struck and maintained by manual adjustment during the substrate deposition. Under the vacuum maintained, the mean free path of the carbon species was greater than the distance to the reactor walls (5 cm).

After a suitable period of time (*ca.* 0.5 hr), the arcing and substrate flow were stopped. The reaction mixture was then distilled under vacuum through cold traps chosen to retain any $C_1 + 2$ substrate products but to allow passage of excess substrate and $C_1 + 1$ substrate products. The material passing through the first trap was collected at liquid nitrogen temperature.

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(1) For previous papers see: P. S. Skell, L. D. Wescott, Jr., J. P. Golstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965); P. S. Skell and R. R. Engel, *ibid.*, **88**, 3749 (1966).

(2) A preliminary communication has appeared: R. R. Engel and P. S. Skell, *J. Am. Chem. Soc.*, **87**, 4663 (1965).

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

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

(5) L. S. Ornstein, H. Brinkman, and A. Beunes, *Z. Physik*, **77**, 72 (1932).

(6) R. C. Mason, *Physica*, **5**, 777 (1938).

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

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

(9) C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

(10) G. Stocklin and A. P. Wolf, *ibid.*, **85**, 229 (1963).

Table I. Gas Chromatographic Retention Times on Column A[a]

Compound	Retention time, min
Propane	7.8
Propene	10.2
2-Methylpropane	13.1
Cyclopropane	17.3
n-Butane	18.8
2,2-Dimethylpropane	20.1
1-Butene	24.7
2-Methylpropene	24.7
trans-2-Butene	30.3
Methylcyclopropane	34.5
cis-2-Butene	35.2
2-Methylbutane	37.8
Allene	39.0
Cyclobutane	44.0
1,1-Dimethylcyclopropane	44.8
1,3-Butadiene	49.4
n-Pentane	50.5
Cyclobutene	51.4
trans-1,2-Dimethylcyclopropane	56.0
Methylenecyclopropane	61.4
1-Pentene	66.0
2-Methyl-1-butene	71.8
Acetylene	74.8
2,2-Dimethylbutane	75.0
1,2-Butadiene	75.5
3,3-Dimethyl-1-butene	82.0
Ethylcyclopropane	82.6
cis-1,2-Dimethylcyclopropane	85.4

[a] Description of columns: (A) 25-ft length, 0.25-in. diameter, 30% hexamethylphosphoric triamide on Fisher Columpac, 25°, 18 psig (63 cc/min); (B) 40-ft length, 0.25-in. diameter, 23% 3,3′-oxydipropionitrile on Chromosorb P, 0°, 18 psig (50 cc/min); (C) 15-ft length, 0.25-in. diameter, 20% α-chloronaphthalene on Gas Chrom Z, 42°, 10 psig (40 cc/min). [b] Relative retention times on these types of columns are given in: J. S. Lewis, "Compilation of Gas Chromatographic Data," American Society for Testing and Materials, Philadelphia, Pa., 1963.

Table II. Infrared and Mass Spectral References[a]

Compound	Mass spectrum	Infrared spectrum
Propane	API-112	API-529
Propene	API-120	API-531
2-Methylpropane	API-114	API-439
Cyclopropane	API-181	API-445
n-Butane	API-1597	API-438
2,2-Dimethylpropane	API-8	API-442
1-Butene	API-121	API-375
2-Methylpropene	API-124	API-378
trans-2-Butene	API-31	API-377
Methylcyclopropane	AS	AS
cis-2-Butene	API-30	API-376
2-Methylbutane	API-146	API-441
Allene	API-1134	AS
Cyclobutane	API-416	RPI-1158
trans-1,2-Dimethylcyclopropane	API-926	AS
1,1-Dimethylcyclopropane	AS	API-882
1,3-Butadiene	API-71	API-379
n-Pentane	API-145	API-440
Cyclobutene	AS	AS
Methylenecyclopropane	AS	AS
1-Pentene	OPI-152	API-145
2-Methyl-1-butene	API-153	API-359
Acetylene	API-72	AS
2,2-Dimethylbutane	API-150	API-656
1,2-Butadiene	API-125	API-41
3,3-Dimethyl-1-butene	API-524	API-586
Ethylcyclopropane	API-1652	API-881
cis-1,2-Dimethylcyclopropane	API-972	API-1806
1-Methyl-1-ethylcyclopropane	API-328	API-883
Isopropylcyclopropane	API-434	API-1679

[a] API refers to the American Petroleum Institute Project 44 data compilation; AS indicates that spectral comparisons were made with those of an authentic sample in this laboratory.

The material stopped in the first trap was collected in solvent and analyzed by vapor phase chromatography. The material collected at 77°K was distilled on a 3-ft packed column having a vacuum jacket. The most volatile material was taken off and analyzed for acetylene by gas phase chromatography. After removal of most of the excess substrate, the residue was further concentrated by vacuum distillation. Products in the mixture were then analyzed by gas chromatography.

In all of these reactions, a 16-v (a.c., currents up to 100 amp) arc was used. Under high vacuum, 10^{-6} torr, this produces a mixture of ground state (^{3}P) and metastable excited state (^{1}D, ^{1}S) carbon atoms. While C_3 molecules, singlet and triplet, are also produced under these conditions, no products from their reaction with substrate were found. However, the C_3 molecules could possibly react with olefinic products formed by the reaction of atomic carbon with the substrtae. There was always blackening of the colorless matrix upon warm-up which was presumably caused by condensation of unreacted carbon species.

"Delay" reactions to determine the electronic state of the carbon atoms reacting were carried out as previously described using degassed substrate. The vaporized species were deposited on a liquid nitrogen cooled matrix of neopentane. After a specified period of aging of the carbon species, a large amount of substrate was sent into the reaction system causing momentary liquefaction of the matrix. *Carbon vapor deposited on a 77°K neopentane surface contained no species reactive to alkanes after 10-sec aging.*

Analyses were carried out by gas chromatography. Details of the columns used and retention times are given in Table I. Corrections were made on peak areas for relative responses of the compounds using a thermal conductivity detector. Products were identified by comparisons of chromatographic retention times, mass spectra (Nuclide 12-90-G),[11] and infrared spectra (Beckman IR-5) with those of the known compounds. Spectral references are tabulated in Table II.

Blanks were run on the substrates by carrying them through the reaction and work-up processes, except for arcing, to determine that the products were not present in the original substrate. Substrates were used directly from the manufacturer without further purification except for the cyclopropane which contained several per cent of acetylene.

The yields in all reactions were good except for the reaction with neopentane where about $^1/_{20}$th of the yield in the other cases was obtained. The amount of $C_1({}^1S)$ produced was calculated using the C_1/C_3 ratio (3:1) and the percentage of C_1 in the ^{1}S state as determined in studies using alkenes;[7] total $C_1({}^1S)$ is 32% of carbon vaporized. In all cases at least duplicate runs were made and generally more.

Results and Discussion

A. Electronic State of Carbon Atoms Which React with Alkanes. Time-Delay Studies. As we have previously reported with olefinic substrates,[1,7] carbon atoms are deposited on an inert matrix at 77°K[12] and reactive substrate is added after a measured time interval. In this way one can observe changes in product composition with aging of the carbon atoms, thereby determining which products are coming from which electronic state and the half-lives of these electronic states. The results as previously reported with olefins were $C_1({}^1S)$, $\tau_{1/2} \cong 2$ sec; $C_1({}^1D)$, $\tau_{1/2} \cong 15$ sec.

The time-delay studies with saturated hydrocarbons show that in all cases the reacting species is $C_1({}^1S)$. In the reactions where only $C_1({}^1D)$ and $C_1({}^3P)$ were available for reaction, there were no products formed but only carbon black deposited on the flask walls upon warm-up.

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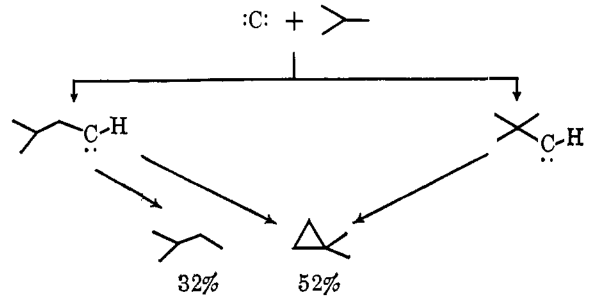
(11) The assistance of the National Science Foundation in the purchase of this instrument is gratefully acknowledged.

(12) In these studies, neopentane was used as the inert matrix. As will be seen later, neopentane is unreactive with atomic carbon at 77°.

Scheme I

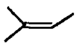
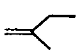
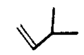
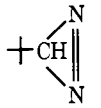


B. Reaction of Atomic Carbon with Isobutane. The reaction of atomic carbon with isobutane yielded two products in which a carbon atom had been added to isobutane, isopentane, and 1,1-dimethylcyclopropane (see Scheme I). In addition there were three products of composition C_8H_{18} identified by mass and infrared spectra. The data are shown in Table III.

Table III

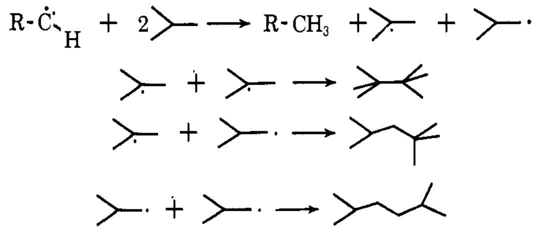
Total carbon vaporized, mg	76
Amount $C_1(^1S)$ vaporized, mg	24
Mole % $C_1(^1S)$ accounted for by product listed below	84
Isopentane	32
1,1-Dimethylcyclopropane	52
Acetylene	0
Other products present, mg	
2,2,3,3-Tetramethylbutane	8
2,5-Dimethylhexane	4
2,4,4-Trimethylpentane	3

Table IV

Method of production		Products, % 			
+CH_2Cl	+ Na[16]	100	...	...	...
+CHI_2	+ MeLi[17]	95–97	3–5	...	...
+CH_2Cl	+ C_6H_5Na[17]	96	3.5	...	...
t-BuLi	+ CH_2Cl_2[17]	69	12	18	...
+CH=NNHTs	+ NaOMe[18]	92	7	1	...
	+ $h\nu$[19]	10–38	60–72	<10	<3

Initial insertion of a carbon atom into the tertiary carbon–hydrogen bond leads to the *t*-butylcarbene which by insertion on a carbon–hydrogen bond of its methyl group leads to the 1,1-dimethylcyclopropane. Initial insertion of a carbon atom into a primary carbon–hydrogen bond gives the isobutylcarbene which by internal insertion can also lead to the 1,1-dimethylcyclopropane.

In addition, the isobutylcarbene also abstracts hydrogen atoms from the isobutane which is present in about 1000-fold excess. This scheme of hydrogen abstraction is supported by the isolation of the three isomeric octanes expected from coupling of radicals produced from isobutane.



The possibility of $:CH_2$ being an intermediate in this reaction is eliminated on several bases. First of all, it might be expected that methylene would be unselective in attack on primary and tertiary carbon–hydrogen bonds.[13,14] This would result in a significant amount of neopentane being formed, but none was found. Also, in a reaction using a 5:1 mixture of isobutane and *cis*-2-butene, no dimethylcyclopropane was formed; it would be expected if $:CH_2$ were an intermediate.

It is to be noted that *no* acetylene was produced in this reaction in contrast to the results of Wolf[8] who found 21.2% C_2H_2 in the reaction of isobutane with nuclearly produced ^{11}C in an oxygen-scavenged system.

All previously reported[15–19] methods for generation of *t*-butylcarbene produce 1,1-dimethylcyclopropane and olefin with a rearranged carbon skeleton. In sharp contrast, olefins were not observed in ^1S carbon atom addition reactions; since olefinic materials are found as products in other carbon atom reactions with alkanes (*vide infra*), it would be expected that at least a portion should have survived reaction with C_3 and C_1 if they had been formed.

C. Reaction of Atomic Carbon with Propane. The data for the reaction of atomic carbon with propane is shown in Table V. The radical coupling products were identified by infrared and mass spectra (see Scheme II).

(13) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(14) D. B. Richardson, L. R. Durrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretzky, *ibid.*, **87**, 2763 (1965).

(15) The results of previously studied systems involving the *t*-butylcarbene, probably in a complexed state, except the *t*-butyldiazirine photolysis, are summarized in Table IV.

(16) (a) F. C. Whitmore, A. H. Popkin, and J. R. Pfister, *J. Am. Chem. Soc.*, **61**, 1616 (1939); (b) F. C. Whitmore, A. H. Popkin, H. I. Berstein, and J. P. Wilkens, *ibid.*, **63**, 124 (1941); (c) F. C. Whitmore and H. D. Zook, *ibid.*, **64**, 1783 (1942).

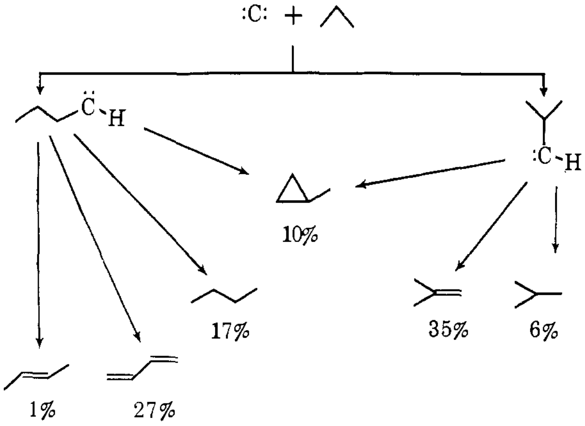
(17) W. Kirmse and B. Graf V. Wedel, *Ann.*, **666**, 1 (1963).

(18) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(19) H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 3101 (1965).

The reaction of a carbon atom with propane may take place by initial insertion into either a primary or secondary carbon–hydrogen bond. In the first case, the intermediate *n*-propylcarbene can undergo internal insertion to give methylcyclopropane or abstract hydrogen atoms from the excess propane to give *n*-butane. Again, the coupling products of propyl radicals were present to support this mechanism.

Scheme II



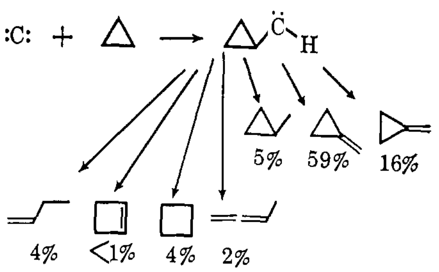
Initial insertion on the secondary carbon–hydrogen bonds gives the isopropylcarbene which by internal insertion can give methylcyclopropane; by hydrogen abstraction, the isobutane; by hydrogen migration, the isobutylene. The formation of *trans*-2-butene and 1,3-butadiene are not yet understood. Again no acetylene was formed. This is in contrast with the results of Wolf[8] who found 23.2% acetylene in the reaction of energetic ^{11}C with propane.

Table V

Total carbon vaporized, mg	84
Amount of C$_1$(^{1}S) vaporized, mg	27
Mole % C$_1$(^{1}S) accounted for by products listed below	96
Methylcyclopropane	10
Isobutene	35
Isobutane	6
n-Butane	17
1,3-Butadiene	27
trans-2-Butene	1
Acetylene	0
Other products present, mg	
2,3-Dimethylbutane	6
n-Hexane	5
2-Methylpentane	9
Trace amounts of several other materials whose chromatographic retention times indicated C$_6$ boiling range	

The results here are somewhat analogous to those found for the *n*-propyl- and isopropylcarbenes when studied in solution.[20–23] In those studies, the isopropylcarbene has been found to give methylcyclopropane, isobutene, and isobutane as well as traces of 2-butenes. In solution, the *n*-propylcarbene also gives methylcyclopropane but larger quantities of 1-butene, a material not found in our system.

Scheme III



D. Reaction of Atomic Carbon with Cyclopropane. The experimental results of the reaction of atomic carbon with cyclopropane are shown in Table VII (see also Scheme III). The reaction of a carbon atom with cyclopropane can lead to the cyclopropylcarbene by insertion into a carbon–hydrogen bond. The main product, methylenecyclopropane, can result from hydrogen migration while the methylcyclopropane can come about from hydrogen abstraction, radical coupling product being present to support the same type of mechanism as previously proposed. The isobutylene can presumably result from the cyclopropylcarbene by hydrogen migration with ring opening and hydrogen abstraction. There were small amounts of 1-butene, cyclobutane, cyclobutene, and methylallene present but there are not enough data at this time to support any one detailed mechanism.

Table VI

Method of production	Products, %				
					
n-Propylcarbene					
 CHNNHTs + NaOMe[18]	5	92	1	2	
 CH_2Cl + Na[21]	7	86	3	4	
					
Isopropylcarbene					
 CH_2Cl + Na[21,22]	35	65	...	...	...
 CHNNHTs + NaOMe[18]	45	55	...	...	...
 CHI_2 + Zn[23]	0.3	90.1	7.8	0.6	0.3

Table VII

Total carbon vaporized, mg	102
Amount C$_1$(^{1}S) vaporized, mg	33
Mole % C$_1$(^{1}S) accounted for by products listed below	90
Isobutene	16
Methylcyclopropane	5
Methylenecyclopropane	59
1-Butene	4
Cyclobutene	<1
Cyclobutane	4
1,2-Butadiene	2
Acetylene	0
Other products present, mg	
C$_6$H$_{10}$ (mass spectrum only, possibly bicyclopropyl)	10
Seven, or possibly more, compounds present in amounts too small to be isolated by analytical gas chromatography retention times indicate C$_{10}$ boiling range.	

(20) The reactions of the *n*-propyl- and isopropylcarbenes, presumably complexed species, as studied in solution are summarized in Table VI.

(21) W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960).

(22) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 492 (1961).

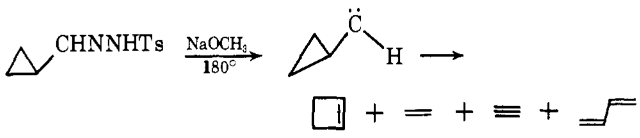
(23) R. Neuman, *Tetrahedron Letters*, 37, 2541 (1964).

Table VIII

Total carbon vaporized, mg	91
Amount $C_1(^1S)$ vaporized, mg	29
Mole % $C_1(^1S)$ accounted for by products listed below	73
Bicyclo[3.1.0]hexane	43
Cyclohexane	7
Five compounds, identified only as C_6 compounds on the basis of gas chromatographic retention times	23
Acetylene	0
Other products present, mg	
$C_{10}H_{18}$ (mass spectrum only)	5

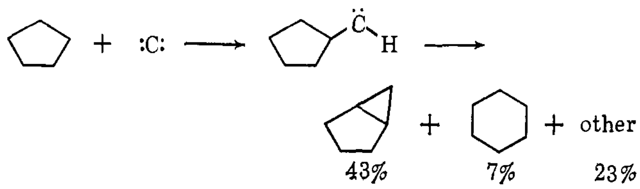
The absence of acetylene in this reaction is also in contrast with the energetic ^{11}C work of Wolf[8] who found 42.7% C_2H_2 from the reaction of cyclopropane in an oxygen-scavenged system. The formation of ethylene and acetylene from the cyclopropylcarbene would seem to be a favorable reaction requiring only a formal shift of electrons. In this system it is apparently not an important process.

These results are also in contrast with the work of Friedman and Shechter[24] who studied cyclopropylcarbene in solution and found no methylenecyclopropane



E. Reaction of Atomic Carbon with Cyclopentane. The experimental data for the reaction of atomic carbon with cyclopentane are summarized in Table VIII (see Scheme IV).

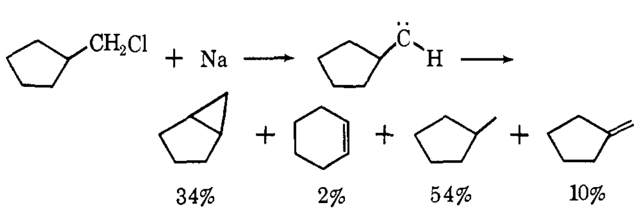
Scheme IV



Initial insertion of a carbon atom into a carbon–hydrogen bond leads to the cyclopentylcarbene. The major product from this intermediate was the result of internal insertion, the bicyclo[3.1.0]hexane. The remaining isolated material was made up of at least six other products, only one of which was completely characterized, cyclohexane.

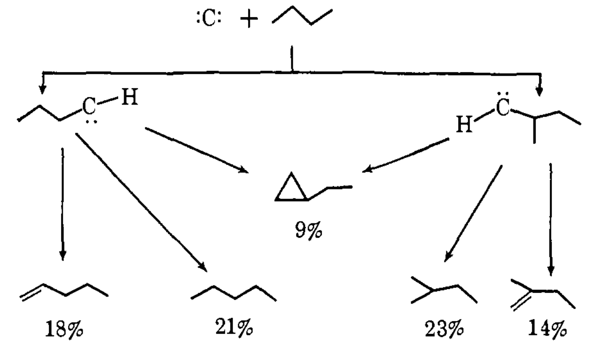
There was a trace of higher boiling material found which was shown by its mass spectrum to be of the composition $C_{10}H_{18}$. This is presumably not a carbon atom addition product but rather arises by coupling of C_5 radicals, possibly forming bicyclopentyl.

The formation of bicyclo[3.1.0]hexane is analogous to the result of Richey and Hill[25] who found it as a major product from the cyclopentylcarbene produced in solution.



F. Reaction of Atomic Carbon with *n*-Butane. Experimental data for the reaction of atomic carbon with *n*-butane is given in Table IX (see also Scheme V).

Scheme V



The reactions of carbon atoms with *n*-butane appear quite straight forward. Initial insertion may take place either on a primary or secondary carbon–hydrogen bond leading to the *n*-butylcarbene and *sec*-butylcarbene, respectively.

Table IX

Total carbon vaporized, mg	108
Amount $C_1(^1S)$ vaporized, mg	35
Mole % $C_1(^1S)$ accounted for by products listed below	85
Ethylcyclopropane	9
1-Pentene	18
n-Pentane	21
Isopentane	23
2-Methyl-1-butene	14
cis-1,2-Dimethylcyclopropane	0
trans-1,2-Dimethylcyclopropane	0
Acetylene	0
Other products present, mg	
$3C_8H_{18}$ (mass spectra only)	15
Several other materials having gas chromatographic retention times indicating a C_8 composition; insufficient for analysis	

By hydrogen migration the *sec*-butylcarbene leads to 2-methyl-1-butene and by hydrogen abstraction to isopentane. Similarly, the *n*-butylcarbene yields 1-pentene by hydrogen migration and *n*-pentane by hydrogen abstraction. The expected C_8H_{18}, identified by mass spectra, radical coupling products were also found. Both of the carbene intermediates can form the ethylcyclopropane by internal insertion.

There is a striking absence in this reaction of either *cis*- or *trans*-1,2-dimethylcyclopropane. These might be expected to result from the *sec*-butylcarbene. Doering and Kirmse,[26,27] producing the *sec*-butylcarbene by treating the alkyl chloride with sodium, found the rates of primary and secondary internal carbon–hydrogen insertion to be not very different at room temperature, the primary insertion leading to the

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(24) L. Friedman and H. Shechter [*J. Am. Chem. Soc.*, **82**, 1002 (1960)] have reported on the reaction of the *p*-tosylhydrazone of cyclopropanecarboxaldehyde with sodium methoxide in aprotic solvents to produce the cyclopropylcarbene.

(25) H. G. Richey, Jr., and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964).

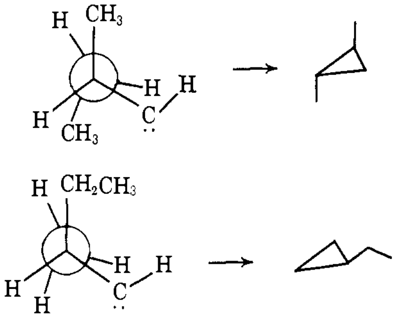
(26) W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

(27) See also W. Kirmse and G. Wachtershauser, *ibid.*, **22**, 63 (1966).

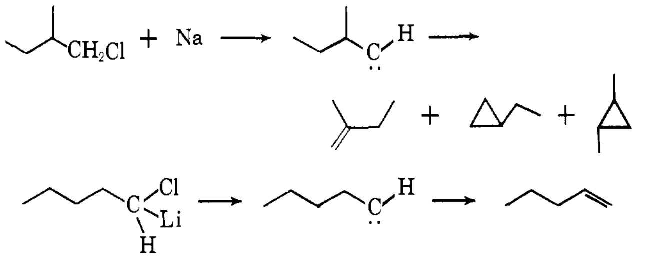
ethylcyclopropane and secondary insertion leading to the 1,2-dimethylcyclopropanes.

If the required conformations for secondary and primary carbon–hydrogen insertion in the *sec*-butylcarbene are considered, as shown in Newman projections in Scheme VI, it is seen that in the secondary insertion case there are two alkyl hydrogen oppositions while in the primary insertion case there is only one.

Scheme VI



Estimating from the internal rotational barrier in *n*-butane,[28,29] this leads to an activation energy difference for the two processes of between 2.5 and 3 kcal/mole, favoring the primary insertion case. At liquid nitrogen temperature then, using the result of Doering and Kirmse at room temperature, this leads to the primary insertion reaction being favored over the secondary insertion at 77°K by a factor of at least 10,000. Thus the absence of the 1,2-dimethylcyclopropanes can be understood. While Doering and Kirmse[29,30] found cyclopropane formation from the *sec*-butylcarbene, Closs and Closs[31] found no cyclopropane formation with the *n*-butylcarbene.



G. Reaction on Atomic Carbon with Isopentane. The experimental data for the reaction of atomic carbon with isopentane are given in Table X. The reaction of atomic carbon with isopentane by carbon–hydrogen bond insertion can lead to four possible carbene intermediates, 2-methyl-1-butylcarbene (A), 2-methyl-2-butylcarbene (**B**), 3-methyl-2-butylcarbene (C), and 3-methyl-1-butylcarbene (D). The intermediate (D) can lead to 2,2-dimethylbutane and 3,3-dimethyl-1-butene (identified by gas chromatographic retention times only) by hydrogen abstraction and hydrogen migration, respectively. The remainder of the reaction products, not fully identified except for the 3-methyl-1,2-pentadiene, presumably arise by similar routes from the other intermediates (Scheme VII).

The only cyclopropane which could possibly be formed from the 2-methyl-1-butylcarbene is 1-methyl-1-ethylcyclopropane, which can also be formed from the intermediate 2-methyl-2-butylcarbene. In the case of 3-methyl-1-butylcarbene, the only cyclopropane which could possibly be formed is isopropylcyclopropane, which can also result from the intermediate 3-methyl-2-butylcarbene.

Scheme VII

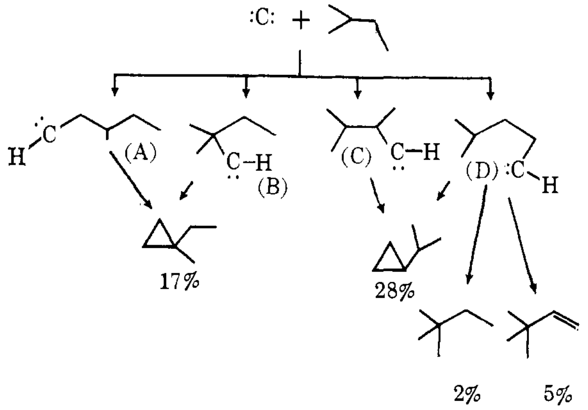
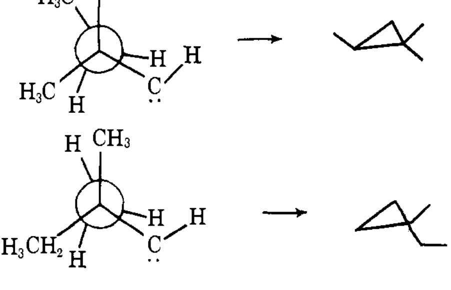


Table X.

Total carbon vaporized, mg	88
Amount $C_1(^1S)$ vaporized, mg	28
Mole % $C_1(^1S)$ accounted for by products listed below	83
Isopropylcyclopropane	28
1-Methyl-1-ethylcyclopropane	17
3-Methyl-1,2-pentadiene	16
2,2-Dimethylbutane	2
3,3-Dimethyl-1-butene	5
Eight materials whose gas chromatographic retention times indicate a C_6 composition but present in quantities insufficient for analysis	15
1,1,2-Trimethylcyclopropane	0
Acetylene	
Other products present, mg	
There was a trace of higher boiling material. Analytical gas chromatography showed it to be a mixture of many components. The mass spectrum of the mixture indicated them to be C_{10}'s	10

Noticeable by its absence is 1,1,2-trimethylcyclopropane which could possibly be formed from both 2-methyl-2-butylcarbene and 3-methyl-2-butylcarbene. However, as was the case with the *n*-butane reaction, the conformations for its formation are higher in energy by 2 to 3 kcal/mole than those leading to the other cyclopropanes (see Schemes VIII and IX). This is

Scheme VIII. For 2-Methyl-2-butylcarbene



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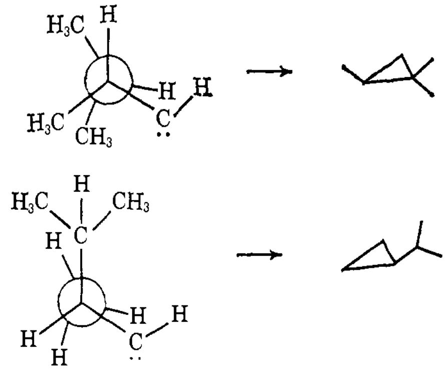
(28) J. G. Aston, M. L. Eidnoff, and W. S. Forster, *J. Am. Chem. Soc.*, **61**, 1539 (1939).

(29) K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

(30) The reactions of the *sec*-butyl- and *n*-butylcarbenes have been studied.

(31) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **81**, 4996 (1959).

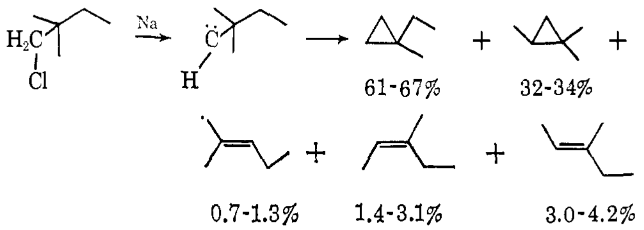
Scheme IX. For 3-Methyl-2-butylcarbene



enough to totally exclude significant formation of the 1,1,2-trimethylcyclopropane in this ring closure at liquid nitrogen temperature. At this time there is not enough evidence to define a single mechanism for the formation of the 3-methyl-1,2-pentadiene.

Voigt and Clark[32] have found in the reaction of recoil ^{11}C with isopentane the largest product to be acetylene (22.7%). In addition, other fragmentation products were found including methane, ethane, and ethylene. The products of addition of a carbon atom to isopentane were 3-methylpentane, 2-methylpentane, 3-methylpentene-1, and 4-methylpentene-1, totalling 36.3%. This is to be contrasted with the present result in which the major products were cyclopropanes and no fragmentation products were found.

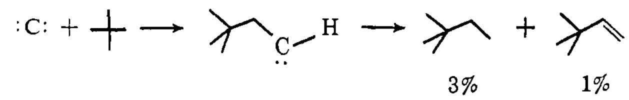
The 2-methyl-2-butylcarbene, produced in this system, also has been studied in solution.[33] There 1,1,2-trimethylcyclopropane was a major product in addition to 1-methyl-1-ethylcyclopropane. Small amounts of rearranged olefins were also found.



H. Reaction of Atomic Carbon with Neopentane. When an experiment was done with neopentane such that the temperature of the reaction flask was maintained at 77°K, by arcing for periods of short duration with relatively long times between periods, *no reaction* was observed. These were essentially the conditions in the time-delay experiments where neopentane was used as an inert matrix.

However, when the temperature of the reaction flask was 30 to 40° higher, as was the case with continuous arcing and with radiation from the arc increasing the temperature of the flask walls, a small amount of product was obtained (about 5% of that obtained from the reactions of the other paraffins). The experimental data for this reaction are shown in Table XI. The reaction is quite simple. Initial insertion on a carbon–hydrogen bond is followed by either hydrogen migration or hydrogen abstraction. A trace of what appears to be C_{10} radical coupling products was found but no acetylene (Scheme X).

Scheme X



In the reaction of energetic ^{11}C with neopentane, Wolf[8] found acetylene to be a major product, formed to the extent of 24.5%. The reaction of atomic carbon with neopentane seems to be rather anomalous. Insertion takes place rather readily on primary carbon–hydrogen bonds in the other paraffins studied, *i.e.*, isobutane, propane, and butane, but not so in the case of neopentane.

Table XI

Total carbon vaporized, mg	104
Amount $C^1(^1S)$ vaporized, mg	34
Mole % $C_1(^1S)$ accounted for by products listed below	(4)
2,2-Dimethylbutane	3
3,3-Dimethyl-1-butene	1
Acetylene	0
Other product present	
$C_{10}H_{22}$ (mass spectrum only)	Trace

I. Reaction of Atomic Carbon with Cyclohexane. In the reaction using cyclohexane as a substrate, a poor yield (based on carbon vaporized) was obtained (Table XII). With continuous arcing, approximately 10% of the ^1S atomic carbon formed could be accounted for in the products, the major ones being methylcyclohexane and norcarane. With short, intermittent, periods of arcing, carefully maintaining the substrate temperature close to −196°, only traces of product could be found; upon warm-up the walls became covered with carbon black. Cyclohexane thus seems to be slightly more reactive than neopentane but much *less* reactive than cyclopentane or the other paraffins.

Table XII

Total carbon vaporized, mg	93
Amount $C_1(^1S)$ vaporized, mg	30
Mole % $C_1(^1S)$ accounted for by products listed below	10
Methylcyclohexane	3
Norcarane	5
Other unidentified (C_7)	2

While neopentane has only primary carbon–hydrogen bonds, cyclohexane has only secondary. Yet, both are relatively inert toward atomic carbon. The common factor of these two substrates is a high melting point (+6° for cyclohexane and −16° for neopentane) compared to those for the "reactive" substrates (*e.g.*, −145° for isobutane, −187° for propane, and −159° for isobutane). This suggests that the source of "inertness" of cyclohexane (and neopentane) is the physical state of the matrix at liquid nitrogen temperature and not the nature of the carbon–hydrogen bonds.

J. Reaction of Atomic Carbon with a Mixture of Cyclopentane and Cyclohexane. A reaction was carried out using a mixture of cyclopentane and cyclohexane. Using a 1:1 mixture of these materials they should have equivalent matrix environments (assuming separate crystallization does not occur), and their relative reactiv-

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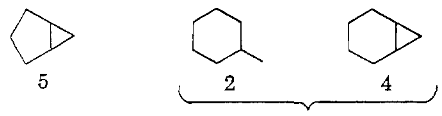
[32] A. F. Voigt and D. E. Clark, private communication.

[33] L. Friedman and Berger, *J. Am. Chem. Soc.*, **83**, 500 (1961).

ity should be independent of the natures of the matrices of the pure materials.

Although an exact analysis was made difficult by the overlap on the gas chromatograph trace of the cyclohexane substrate and some products of the cyclopentane reaction, a comparison could be made using the peak for the bicyclo[3.1.0]hexane (which accounts for 60% of the cyclopentane reaction products, *vide supra*) and the methylcyclohexane and norcarane peaks. The relative amounts of these products are shown below. This indicates that cyclopentane and cyclohexane are of comparable reactivity under these conditions. It also supports the assertion that the reactivity of a substrate toward carbon atom addition is greatly dependent on its physical state.



5/0.6 = 8.3 6/0.8 = 7.5 relative rates

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

π-Complex Multicenter Reactions Promoted by Binuclear Catalyst Systems. "Binor-S," a New Heptacyclotetradecane *via* Stereospecific Dimerization of Bicycloheptadiene

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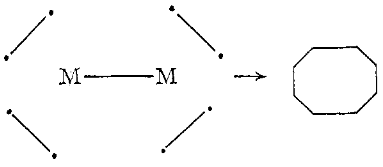
Contribution from the Shell Development Company, Emeryville, California.
Received June 17, 1966

Abstract: The principle of binuclear catalysis has been applied to the dimerization of bicyclo[2.2.1]heptadiene. In contrast to mononuclear catalysts, *e.g.*, those derived from nickel carbonyl, binuclear carbonyl catalysts such as $Zn[Co(CO)_4]_2$, and other heavy metal derivatives of $HCo(CO)_4$ dimerize bicycloheptadiene to a new dimer, *endo,-endo*-heptacyclo$[5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.0^{3,5}.0^{8,10}]$tetradecane ("Binor-S"). In this stereospecific dimerization of norbornadiene, intermediate π complexes giving rise to only one transition state are formed. These intermediates must contain one norbornadiene molecule coordinated to each of the two cobalt atoms in a fashion allowing the formation of the new dimer *via* a "π-complex multicenter process." Factors influencing the stereocontrol of the reaction, particularly the effects of Lewis acids and bases, are discussed.

Zero-valent transition metal complexes with ligands such as phosphines, olefins, and carbon monoxide constitute some of the most versatile catalyst systems for olefin and alkyne oligomerizations. Until now most catalysts used in these reactions were mononuclear or gave mononuclear reactive catalyst fragments. For instance, many of the reactions catalyzed by Ni^0 complexes are considered to proceed *via* "bare" nickel atoms. The scope of such reactions could be increased by using catalysts having at least two metallic centers connected close to each other and which would not dissociate during the reaction. Under these circumstances it is conceivable that the substrates could interact with the catalyst in a fashion substantially different from any previously known system and lead to transition state geometries from which new products could result. A series of compounds which are in essence metal salts of carbonyl hydrides (*e.g.*, $M[Co(CO)_4]_n$, $n = 2$ or 3, M = Zn, Cd, Hg, In, etc.) were considered to fulfill these requirements. Some of these compounds have been described in the literature[2] but they have not been used for any catalytic reaction. It was hoped that these compounds would form reactive intermediate π complexes which could catalyze the intermolecular formation of new products by way of "π complex multicenter reactions." The anticipated differences for monodentate substrates on mononuclear (I) and binuclear (II) centers are illustrated below.

I. mononuclear center



II. binuclear center

Stereospecific Dimerization of Bicycloheptadiene with Heterometal Carbonyl Catalysts

To test the validity of this concept a study was initiated to use the above-mentioned complexes with the highly reactive bicycloheptadiene as the substrate. In contrast to other metal–carbonyl catalyzed dimerizations of this diolefin[3-7] which yielded mixtures of

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(1) Department of Chemistry, University of California, San Diego, La Jolla, Calif.

(2) W. Hieber and U. Teller, *Z. Anorg. Allgem. Chem.*, **249**, 43 (1942).

(3) D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 368 (1961).

(4) (a) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *ibid.*, 373 (1961); (b) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind.* (London), 20 (1960).

(5) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 2764 (1962).

(6) P. W. Jolly, F. G. A. Stone, and K. Mackenzie, *J. Chem. Soc.*, 6416 (1965).