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Alkylidenecarbenes from Acyclic Vinyl Bromides and Potassium *tert*-Butoxide

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The reaction of acyclic terminal vinyl bromides with potassium *tert*-butoxide afforded acetylenes, cyclopentenes, and lesser amounts of *tert*-butyl vinyl ethers. The reactive intermediate, an alkylidenecarbene, was seen as giving rise to the major products via two pathways: 1,5-carbon–hydrogen insertion leading to cyclopentenes and alkyl migration leading to acetylenes. In several instances 1,3-carbon–hydrogen insertion was also observed. The relative amount of 1,5-C–H insertion was found to depend on the C–H bond undergoing insertion, the ease of insertion decreasing in the order tertiary > secondary benzylic > secondary ≫ primary.

A previous report[2] from this laboratory elucidated the overall course of the reaction of terminal vinyl bromides with potassium *tert*-butoxide. The nature of the products and trapping experiments provided compelling evidence for the intermediacy of alkylidenecarbenes.

Other workers have independently reported the generation of alkylidenecarbenes.[3-9] The evidence for their claims includes trapping experiments,[3,4,6-8] dimerization,[5] and intra- and intermolecular insertions.[5,7,9] The present work was begun with the aim of providing additional information regarding the behavior of alkylidenecarbenes.

The terminal vinyl bromides employed in this study were prepared from the corresponding olefin via a bromination–dehydrobromination procedure.[10] In all cases the terminal vinyl bromide so prepared was a mixture of two geometric isomers.

The product mixtures obtained by heating vinyl bromides with potassium *tert*-butoxide at 240 °C were readily separated by GLC, and the individual components were identified on the basis of spectral data. Cyclopentene dervatives characteristically exhibit absorption near 6.1 μ in the infrared and 5.3 ppm in the NMR. Acetylenes were identified by an NMR triplet near 1.7 ppm, J = 2 Hz, which is diagnostic for a $-CH_2C{\equiv}C-CH_3$ type methyl group. *tert*-Butyl vinyl ethers can be recognized by their infrared absorption at 6.0 and 8.7 μ, NMR signals at 5.9 (–C=CHO–) and 1.2 ppm, and a substantial P − 56 ion in their mass spectra.

The major products isolated from the reaction of vinyl bromides **1**, **2**, **3**, and **4** with potassium *tert*-butoxide at 240 °C are illustrated in Chart I. The same proportion of products were obtained from fractions of **1** rich in the *E* or *Z* isomers, indicating that the products are not determined by the geometry of the starting material.

Although 1,4-dimethylcyclopentene could have been one of the three minor unidentified materials observed by GLC (8% total), it is not among the major products from vinyl bromide **4**. This demonstrates that 1,5 insertion into an unactivated primary C–H bond is not a major reaction of alkylidenecarbenes. Such behavior is in marked contrast to alkylcarbenes, which readily undergo intramolecular insertion into primary C–H bonds.[11]

Table I. Ratio of 1,5-Carbon–Hydrogen Insertion to 1,2-Alkyl Migration in the Reaction of Vinyl Bromides with Potassium *tert*-Butoxide

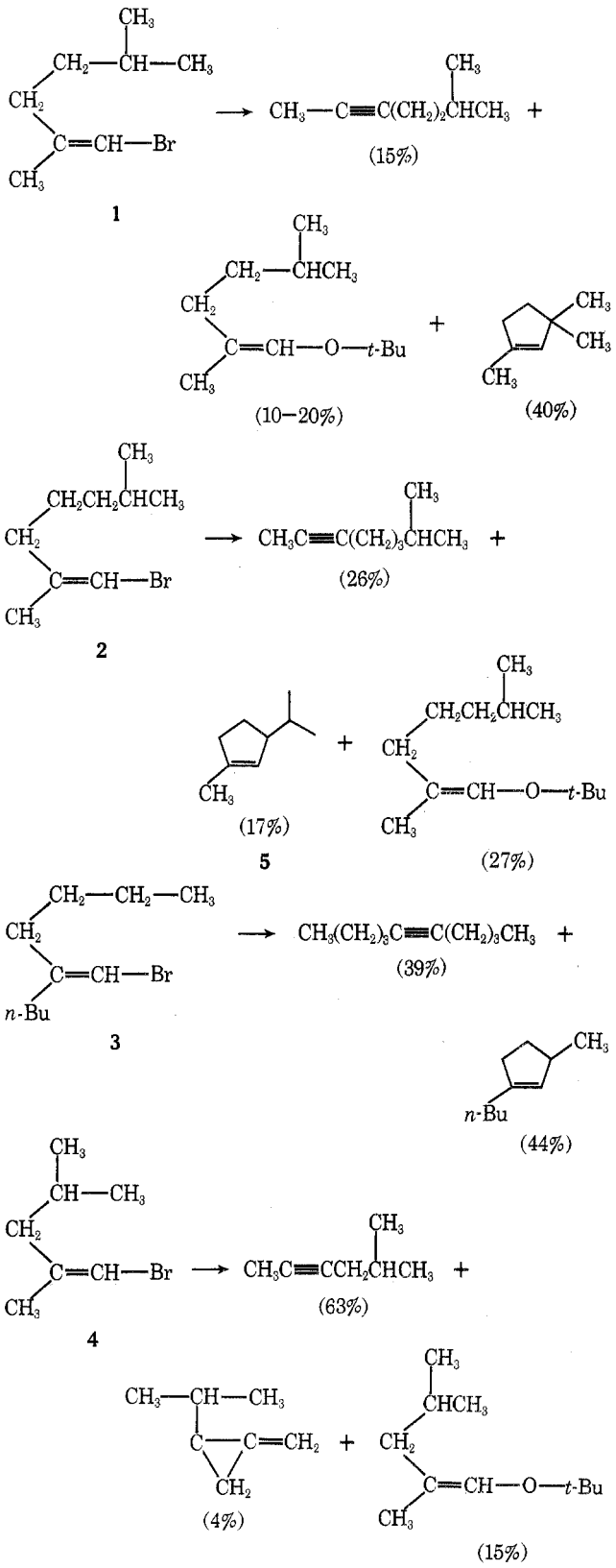
Vinyl bromide	H–C-5 bond type	1,5 insertion/ alkyl migration	Per H
4	Primary	0.05[a]	0.01
3	Secondary	1.13	0.28
2	Secondary	0.67	0.33
1	Tertiary	2.4	2.4

[a] Estimated assuming the formation of 3% of 1,5-insertion product, 1,4-dimethylcyclopentene.

Table I compares the relative amount of 1,5 C–H insertion as a function of the C-5 hydrogen bond type. It is clear that 1,5 insertion into a tertiary C–H bond is favored over insertion into a secondary C–H bond. The selectivity of alkylidenecarbenes is to be contrasted with alkylcarbenes whose insertion reactions are statistical,[11] or show only a slight degree of selectivity.[12]

Simple acyclic carbenes are reported to undergo intramolecular insertion via a 1,3 route to form cyclopropanes.[11] In the case of large ring carbenes, both 1,5- and 1,6-insertion reactions have been observed.[13] When a choice is possible, 1,5 insertion is favored over, but does not exclude, 1,6 insertion. The action of potassium *tert*-butoxide on 1-bromo-2,6-dimethyl-1-heptene (**2**) was examined since 1,6 insertion would occur at a tertiary center, whereas 1,5 insertion would necessitate attack at a secondary position. The reaction produced no detectable amount of 1,3,3-trimethylcyclohexene.[14] The isolation of 17% of 3-isopropyl-1-methylcyclopentene (**5**) suggests that whatever the reason for the preference for 1,5 insertion, it is more important in determining the overall course of carbon–hydrogen in-

Chart I

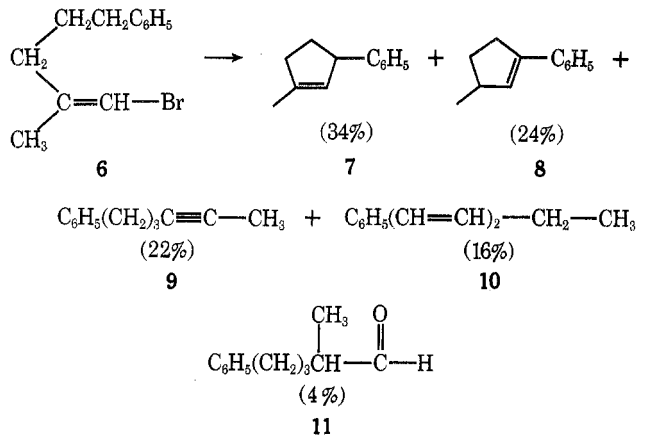


sertion than is the nature of the C–H bond undergoing insertion.

A series of reactions of 1-bromo-2,6-dimethyl-1-heptene (**2**) with potassium *tert*-butoxide carried out at temperatures ranging from 50 to 240 °C (see Experimental Section, Table IV) demonstrated that the product spread was insensitive to changes in temperature.

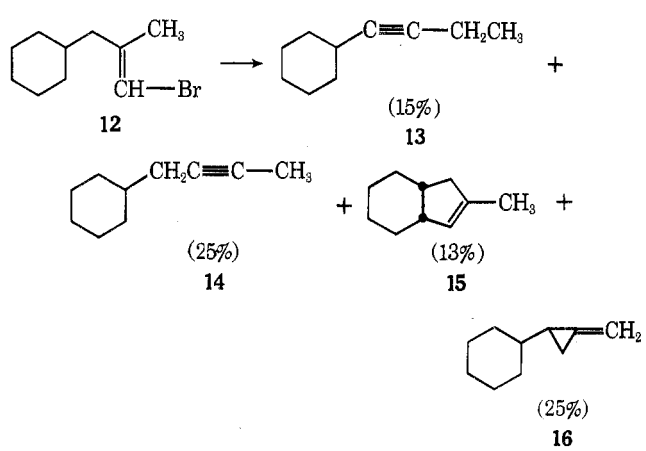
1-Bromo-2-methyl-5-phenyl-1-pentene (**6**) reacts with potassium *tert*-butoxide to give the product mixture illustrated in Chart II. 2-Methyl-5-phenylpentanal (**11**) most likely arises by hydrolysis of the vinyl ether normally produced in these reactions. 1-Phenyl-3-methylcyclopentene (**8**) and 1-phenyl-1,3-hexadiene (**10**) are most likely formed by base-catalyzed isomerization of the initially formed cyclopentene (**7**) and acetylene **9**, respectively.

Chart II



Comparison of the total amount of cyclopentene derivatives formed by 1,5 insertion (58%) to the total amount of products produced by alkyl migration (38%) suggests that a secondary benzylic C–H is intermediate in reactivity between a secondary and tertiary C–H bond. This enhanced reactivity is also contrary to the observation that alkyl carbenes form cyclopropanes with increased difficulty when insertion occurs at a benzylic C–H bond.[15]

The reaction of 1-bromo-2-methyl-3-cyclohexyl-1-propene (**12**) with potassium *tert*-butoxide afforded 1-cyclohexyl-1-butyne (**13**), 1-cyclohexyl-2-butyne (**14**), *cis*-8-methylbicyclo[4.3.0]non-7-ene (**15**), and 2-cyclohexyl-1-methylenecyclopropane (**16**). The identity of **15** was established by comparison with an authentic sample. The major hydrocarbon product, **16**, exhibited infrared absorption at 5.8[16] and 11.2 μ and a terminal methylene signal at 5.3 ppm[17] in the NMR. The structure of **16** was confirmed by an independent synthesis from cyclohexylallene.



Methylenecyclopropane **16**[18] most likely forms by way of a 1,3 insertion followed by isomerization of the resulting cyclopropene derivative.[21] Methylenecyclopropanes are also minor products in the reaction of **1**, **2**, and **4**. There is no apparent reason for the dominant formation of **16** in the reaction of **12**.

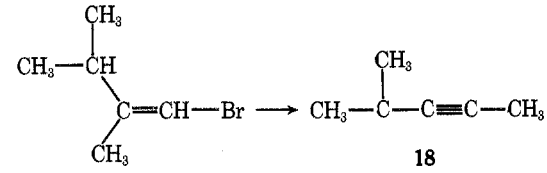
An attempt to maximize cyclopropane formation by making available a tertiary C–H bond for 1,3 insertion failed as the only hydrocarbon obtained in sufficient quan-

Table II. Properties of Vinyl Bromides[a,g]

Bromide	Bp, °C (mm)	n^{20}D	Mass spectrum,[h] m/e (rel intensity)
1	78–81 (23)		190* (11), 133* (7), 111 (30), 95 (15), 69 (100), 57 (51), 56 (93), 55 (64)
2[b]	44–45 (1)	1.4648	204* (7), 183 (20), 125 (7), 83 (20), 81 (13), 70 (16), 69 (100), 57 (10), 56 (11), 55 (34)
4	43–44 (7.5)	1.4631	176* (21), 134* (31), 97 (34), 56 (26), 55 (68), 53 (26), 43 (100)
3[c]	40–41.5 (0.3)		218* (18), 134* (26), 97 (23), 83 (26), 81 (17), 69 (20), 67 (23), 57 (15), 56 (66), 55 (92), 41 (100)
6[d]	116–118 (1.7)	1.5412	238* (6), 159 (9), 117 (16), 105 (28), 104 (100), 92 (23), 91 (69), 77 (17), 65 (25), 53 (24)
19[e]	102–103 (10)	1.5602	210* (22), 131 (32), 129 (40), 128 (33), 116 (56), 115 (100), 91 (95), 89 (26), 77 (26), 65 (31), 64 (21), 63 (46)
12[f]	96–98 (5.5)		216* (9), 83 (85), 82 (47), 81 (27), 67 (21), 55 (100), 54 (10), 53 (17)
17	47–48 (24)		162* (34), 147 (17), 85 (35), 83 (100), 67 (84), 65 (17), 55 (83), 53 (21)

[a] The vinyl bromides described above showed an ir band at 6.12–6.18 μ and NMR signals for the $CH_3C{=}C$ between 1.75 and 1.78 ppm and for C=CH at 5.84–5.90 ppm. [b] NMR and GLC analysis indicated a cis/trans ratio of 2:3. [c] 2-Butyl-1-hexene was prepared by the reaction of 5-nonanone with methylenetriphenylphosphorane in refluxing ether for 2 days followed by replacement of the ether with THF and heating for an additional 6 days. [d] The reaction of methyllithium with 4-phenylbutyric acid gave 5-phenylpentan-2-one, bp 92–93 °C (2 mm), n^{20}D 1.5094. A Wittig reaction converted this ketone to 2-methyl-5-phenyl-1-pentene. [e] An attempt to purify the intermediate dibromide by distillation led to dehydrobromination and the formation of allyl bromide (75%) and vinyl bromide (25%). [f] 2-Methyl-3-cyclohexyl-1-propene was prepared in 78% yield by a Wittig reaction using cyclohexylacetone. [g] Satisfactory analytical data (±0.3% for C, H) for all compounds listed were submitted for review. [h] An asterisk indicates presence of bromine.

tity for identification from the reaction of 1-bromo-2,3-dimethyl-1-butene (17) was 4-methyl-2-pentyne (18).



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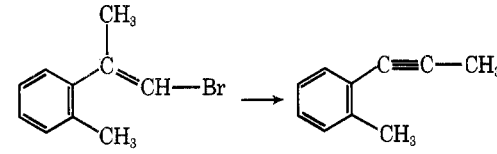
Finally, the reaction of 1-bromo-2-(*o*-tolyl)-1-propene (19) with potassium *tert*-butoxide gave 93% of 1-(*o*-tolyl)-1-propyne (20), demonstrating that C–H insertion does not compete with the extremely rapid[8b] 1,2 migration of an aryl group.



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Experimental Section[22]

General Procedure for the Preparation of Vinyl Bromides. 1-Bromo-2,5-dimethyl-1-hexene (1). To a solution of 10.0 g (0.079 mol) of 2,5-dimethyl-1-hexene in 100 ml of hexane and 4 ml of pyridine at 0 °C was slowly added 12.8 g (0.080 mol) of bromine. The mixture was then stirred at ambient temperature for 30 min. The solution was decanted from the yellow solid and washed with 150 ml of 5% aqueous sodium bicarbonate and 100 ml of saturated sodium chloride solution. The solution was dried ($MgSO_4$) and evaporated under diminished pressure to afford 20.9 g of 1,2-dibromo-2,5-dimethylhexane which was dissolved in 50 ml of ethanol containing 4.5 g (0.080 mol) of potassium hydroxide. After stirring for 16 h at ambient temperature the solution was diluted with water and extracted with ether. The ether solution was washed with saturated salt solution and dried ($MgSO_4$). Distillation gave 13.2 g of 1-bromo-2,5-dimethyl-1-hexene, bp 78–81° (23 mm). The presence of *Z* and *E* isomers (35:65 ratio) was revealed by GLC using a SE-30 column. An analytical sample containing both isomers was obtained by GLC using a 20% Carbowax column at 140°. For properties and NMR shifts of vinyl bromides, see Tables II and III.

General Procedure for Reaction of Vinyl Bromides with Potassium *tert*-Butoxide. A. 1-Bromo-2,5-dimethyl-1-hexene (1). A 2.0-g (0.018 mol) sample of potassium *tert*-butoxide (MSA Research Corp.) was added to a 50-ml side-armed flask, capped with a stoppule and equipped with a distillation head leading to a pair of dry ice–isopropyl alcohol cooled traps whose exit was protected by a calcium chloride drying tube. A slow stream of nitrogen was passed through the system throughout the course of the reaction. The flask was heated to 240° employing a silicone oil bath and then 3.0 g (0.016 mol) of 1-bromo-2,5-dimethyl-1-hexene (1) was injected, using a syringe via the side arm under the surface of the hot potassium *tert*-butoxide. The flask was heated for another 1 min and allowed to cool to room temperature. Water was added and the mixture extracted with ether. The ether was combined with the ether washings from the two traps and the resulting solution was washed with water and dried ($MgSO_4$). The ether was carefully distilled to leave 1.52 g of liquid whose analysis by GLC (20% Carbowax, 125°) showed the presence of at least six components.

Component 1 (retention time 1.6 min, 36%) was identified as 1,3,3-trimethylcyclopentene: ir (CCl_4) 3.40, 6.09, 6.91, 7.31, 7.40, and 8.99 μ; NMR (CCl_4) 0.99 [s, 6, $(CH_3)_2C$–]; 1.65 (d, 5, J = 1 Hz, $CH_3C{=}CH$– superimposed on $-CH_2-$), 2.24 (distorted t, 2, $-CH_2CH_2C{=}C-$), and 5.05 ppm (m, 1, C=CH–); mass spectrum (70 eV) m/e (rel intensity) 110 (13), 95 (100), 67 (17).

Component 2 (retention time 3.9 min, 15%) was identified as 6-methyl-2-heptyne: ir (CCl_4) 3.40, 6.92, 7.24, 7.33, 7.60, and 8.59 μ; NMR (CCl_4) 0.88 [d, 6, J = 5.5 Hz, $(CH_3)_2CH$–], 1.39 (m, 2, $-CH_2-$), 1.72 (t, 4, J = 2 Hz, $CH_3C{\equiv}C-CH_2-$ superimposed on CH), and 2.09 ppm (m, 2, $-CH_2C{\equiv}C-$); mass spectrum (70 eV) m/e (rel intensity) 110 (3), 95 (72), 81 (10), 67 (33), 65 (58), 55 (22), 53 (58), 52 (20), 51 (32), 43 (25), 41 (95), and 39 (100).

Table III. NMR Shifts for *gem*-Dimethyl Groups of Vinyl Bromides

$(CH_3)_2CH(CH_2)_n$—C(CH$_3$)=CHBr

n	δ_{trans}, ppm	δ_{cis}, ppm[a]	Δ, ppm
0	0.96	1.07	0.11
1	0.88	0.93	0.05
2	0.92	0.95	0.03
3	0.89	0.89	0.00

[a] The stereochemistry was assigned on the basis that the bromine should deshield the cis *gem*-dimethyl group. The *E* isomers were also shown to be the less volatile[7] by GLC.

Table IV. Temperature Dependence of the Reaction of 1-Bromo-2,6-dimethyl-1-heptene (*2*) with Potassium *tert*-Butoxide

Temp, °C	1-Methyl-3-isopropylcyclopentene	7-Methyl-2-octyne	1-*tert*-Butoxy-2,6-dimethyl-1-heptene
240	30	45	25
200	29	45	26
160	33	40	26
100	38	37	26
50	33	34	34

Component 3 (retention time 8.2 min, 7%) was identified as one of the isomeric 1-*tert*-butoxy-2,5-dimethyl-1-hexenes, ir 6.00 and 8.70 μ.

Component 4 (retention time 10 min, 5%) was the other geometric isomer of 1-*tert*-butoxy-2,5-dimethyl-1-hexene: ir 5.98 and 8.70 μ; NMR (CCl_4) 0.88 [d, 6, J = 5.5 Hz, $(CH_3)_2CH$–], 1.20 [s, 9, $(CH_3)_3CO$–], 1.50 (d, 3, CH_3C=CH–), 1.80 (m, 2, –CH_2C=C–), and 5.91 ppm (m, 1, C=CHO–); mass spectrum *m/e* (rel intensity) 184 (15), 128 (48), 110 (46), 99 (30), 95 (53), 85 (29), 72 (15), 71 (100), 69 (26), 68 (15), 59 (16), 58 (28), 57 (95), 56 (27), 55 (30), 43 (63), 41 (69), 39 (27).

Components 5 and 6 (retention time 13.1 and 14.9 min, 39%) were the starting vinyl bromides. The relative proportions of the two vinyl bromides were essentially identical with the proportions present in the original starting material.

When the experiment was repeated using 4.5 equiv of potassium *tert*-butoxide the proportion of vinyl ethers rose to 20% and the amount of recovered vinyl bromides dropped to 7%. The use of vinyl bromide fractions with differing isomeric composition resulted in identical product spreads.

B. 1-Bromo-2,6-dimethyl-1-heptene (2). Treatment of 3.22 g (0.016 mol) of 1-bromo-2,6-dimethyl-1-heptene (**2**) with 2.0 g (0.018 mol) of potassium *tert*-butoxide as previously described gave 1.85 g of crude product whose analysis by GLC (Carbowax, 110°) indicated the presence of seven components (Table IV).

Component 1 (retention time 2.6 min, 4%) was too volatile to collect.

Component 2 (retention time 4.6 min, 17%) proved to be a mixture of two components. This fraction was collected and then rechromatographed on a freshly prepared Carbowax column at 80 °C. Approximately 90% of this mixture was identified as 1-methyl-3-isopropylcyclopentene: ir (CCl_4) 6.08 μ; NMR (CCl_4) 0.87 [d, 6, J = 5.5 Hz, $(CH_3)_2CH$–], 1.72 (s, 3, CH_3C=C–), and 5.27 ppm (m, 1, CH=C–); mass spectrum *m/e* (rel intensity) 124 (11), 109 (6), 82 (7), 81 (100), 80 (8), 79 (10), 69 (7), 67 (5), 53 (5) and 41 (10). The remaining 10% of this fraction was collected and identified as 2-isoamylmethylenecyclopropane: ir (CCl_4) 3.40, 5.80 (w), 6.85, 7.26, 7.35, 8.89, and 11.24 μ (s). This infrared spectrum was identical with that of isoamylmethylenecyclopropane prepared by an independent route.[23]

Component 3 (retention time 10.3 min, 26%) was identified as 7-methyl-2-octyne: ir 4.90 μ (w); NMR (CCl_4) 0.89 [d, 6, J = 5.5 Hz, $(CH_3)_2CH$–], 1.1–1.6 (m, 5, $-CH_2CH_2CH$–), 1.72 (t, 3, J = 2.2 Hz, CH_3C≡C–CH_2–), and 2.04 ppm (m, 2, –CH_2C≡C–); mass spectrum *m/e* (rel intensity) 124 (0.1), 109 (100), 81 (30), 69 (70), 68 (37), 67 (43), 55 (28), 54 (16), 53 (12), 43 (43), and 39 (19).

Anal. Calcd for C_9H_{16}: C, 87.04; H, 12.98. Found: C, 87.29; H, 13.12.

Components 4 and 5 (retention times 25 and 28 min, 27%) were identified as geometric isomers of 1-*tert*-butoxy-2,6-dimethyl-1-heptene contaminated with a small amount of 2,6-dimethylheptanal: ir 5.80 (w) and 5.99 μ; NMR (CCl_4) 0.88 [d, 6, $(CH_3)_2CH$–], 1.20 [s, $-OC(CH_3)_3$], 5.90 (m, –C=CHO–), and 9.50 ppm (–CHO).

Components 6 and 7 (retention times 32 and 35 min, 27%) proved to be the original vinyl bromides.

The GLC retention time of an authentic sample of 1,3,3-trimethylcyclohexene[14] was found to be different from that of component 1 and did not correspond with any of the significant peaks found in the product mixture described above.

C. 1-Bromo-2,4-dimethyl-1-pentene (4). The reaction of 3.0 g (0.017 mol) of 1-bromo-2,4-dimethyl-1-pentene (**4**) with 2.0 g (0.018 mol) of potassium *tert*-butoxide gave 1.3 g of light brown liquid which was separated using a 20% Carbowax column at 104°. The first fraction (retention time 1.5–[2.5 min, 12%) was a mixture of at least four components. Infrared absorption at 5.82 and 11.30 μ and an NMR signal at 5.3 ppm suggested that one of these components was 2-isopropyl-1-methylenecyclopropane. The mass spectrum of a carefully collected sample of this 4% component showed a molecular ion at *m/e* 96 (33%) and a base peak at *m/e* 81.

The second fraction (retention time 3.3 min, 63%) was identified as 5-methyl-2-hexyne: NMR (CCl_4) 0.93 [d, 6, J = 5.5 Hz, $(CH_3)_2CH$–], 1.73 (t, 3, J = 2.2 Hz, CH_3C≡C–CH_2–), and 1.95 ppm (m, 2, –CH_2C≡C–); mass spectrum *m/e* (rel intensity) 96 (100), 81 (75), 79 (15), 68 (11), 67 (12), 55 (15), 54 (48), 53 (34), 51 (13), 43 (53), 41 (40), 39 (36), and 27 (24).

Fraction 3 (retention time 8.9 min, 3%) was identified as one of the isomeric 1-*tert*-butoxy-2,4-dimethyl-1-pentenes: ir 5.99, 8.09, and 8.70 μ.

Fraction 4 (retention time 9.2 min, 12%) was identified as the other geometric isomer of 1-*tert*-butoxy-2,4-dimethyl-1-pentene: ir 5.99, 8.09, and 8.70 μ; NMR (CCl_4) 0.85 [d, 6, J = 5.5 Hz, $(CH_3)_2CH$–], 1.20 [s, 9, $(CH_3)_3CO$], 1.50 (d, 3, J = 1 Hz, CH_3C=CH–), 1.72 (m, 3), and 5.90 ppm (m, 1, –C=CHO); mass spectrum *m/e* (rel intensity) 170 (8), 114 (35), 71 (100), 57 (37), 55 (14), 43 (40), 41 (33), and 39 (11).

Fraction 5 (retention time 12.2 min, 10%) proved to be unreacted vinyl bromide.

D. 1-Bromo-2-*n*-butyl-1-hexene (3). Treatment of 2.19 g (0.01 mol) of 1-bromo-2-*n*-butyl-1-hexene (**3**) with 3.40 g (0.03 mol) of potassium *tert*-butoxide gave 1.2 g of yellow liquid. Separation by GLC (20% Carbowax, 113 °C) revealed the presence of five major components. Component 1 (retention time 5 min, 44%) was identified as 1-*n*-butyl-3-methylcyclopentene: ir 6.10 μ; NMR (CCl_4) 0.98 (d, 3, J = 6.5 Hz, $-CHCH_3$), 1.0–1.7 (m, 7, $-CH_2CH_2CH_3$), 1.9–2.4 [m, 4, $(-CH_2)_2C$=C–], 2.67 (m, 1, CHC=C–), and 5.19 ppm (m, 1, –CH=C–); mass spectrum *m/e* (rel intensity) 138 (39), 93 (28), 82 (25), 81 (100), 79 (27), 67 (35), 55 (39), and 41 (43).

Component 2 (retention time 7 min, 6%) was an allene,[26] ir 5.11 μ.

Component 3 (retention time 9 min, 39%) was identified as 5-decyne:[27] ir 3.40, 6.85, 7.29, and 10.21 μ; NMR (CCl_4) 0.91 (dist t, 6, $-CH_2CH_3$), 1.44 (m, 8, $-CH_2$–), 2.10 ppm (dist t, 4, $-CH_2C$≡C–CH_2–). This compound and an authentic sample of 5-decyne[28] showed identical retention times on Carbowax and tricresyl phosphate columns. Catalytic hydrogenation of component 3 gave a product whose mass spectrum was identical with that of *n*-decane.

Component 4 (retention time 14 min, 10%) was not identified, ir 6.05 μ, molecular ion at *m/e* 184.

Component 5 (retention time 24 min, 9%) was not identified, ir strong 9.10 μ, molecular ion at *m/e* 184.

E. 1-Bromo-2-methyl-5-phenyl-1-pentene (6). The reaction of 1.60 g (6.7 mmol) of 1-bromo-2-methyl-5-phenyl-1-pentene (**6**) with 1.03 g (9.2 mmol) of potassium *tert*-butoxide gave 0.95 g of crude product which was separated using a 20% Carbowax column at 200°. Component 1 (retention time 13.6 min, 34%) was identified as 1-methyl-3-phenylcyclopentene (**7**): ir 6.02, 6.24, and 6.70 μ; NMR (CCl_4) 1.81 (broad s, 3, CH_3C=C–), 1.5–2.7 (m, 4, $-CH_2CH_2$–), 3.85 (m, 1, C=C–CHC_6H_5), 5.35 (m, 1, C=CH–), and 7.10 ppm (s, 5, ArH); mass spectrum *m/e* (rel intensity) 158 (24), 143 (70), 128 (75), 115 (87), 105 (26), 102 (32), 91 (100), 78 (55), 77

(94), 65 (54), 63 (61), 52 (34), 51 (69), 50 (66), 43 (36), 41 (61), and 39 (43).

Component 2 (retention time 19.3 min, 22%) was identified as 6-phenyl-2-hexyne (**9**):[29] ir 3.30, 3.41, 6.26, 6.71, 6.91, 9.23, and 9.66 μ; NMR (CCl_4) 1.75 (t, 3, J = 2.2 Hz, $CH_3C{\equiv}C-CH_2-$), 2.1 (m, 4, $-CH_2CH_2-$), 2.68 (t, 2, J = 7.5 Hz, $C_6H_5CH_2CH_2-$), and 7.13 ppm (m, 5, C_6H_5-); mass spectrum m/e (rel intensity) 158 (43), 143 (55), 130 (28), 129 (55), 128 (25), 105 (31), 104 (100), 92 (29), 91 (99), 77 (24), and 65 (27).

Component 3 (retention time 20.8 min, 24%) was identified as 1-phenyl-3-methylcyclopentene (**8**): ir 6.15, 6.26, and 6.71 μ; NMR (CCl_4) 1.10 (d, 3, J = 6.5 Hz, CH_3CH-), 6.01 (m, 1, $C_6H_5C{=}CH$), and 7.23 ppm (m, 5, C_6H_5-); mass spectrum m/e (rel intensity) 158 (14), 143 (47), 129 (38), 128 (70), 115 (100), 102 (34), 91 (42), 78 (38), 77 (63), 65 (33), 63 (55), 51 (98), 50 (59), 41 (34), 39 (38), and 27 (31).

Component 4 (retention time 28 min, 16%) was identified as 1-phenyl-1,3-hexadiene (**10**): ir 3.30, 3.40, 5.96, 6.11, 6.30, 6.71, 7.71, 9.32, 9.71, 10.15, and 10.99 μ; uv (EtOH) λ_{max} 285 nm (ϵ 2 × 10^4); NMR 1.04 (t, 3, J = 6.5 Hz, CH_3CH_2-), 2.17 (m, 2, $C{=}C-CH_2-$), 5.9, 6.4, and 7.2 ppm (m's, 9, $C_6H_5CH{=}CHCH{=}CH-$); mass spectrum m/e (rel intensity) 158 (46), 143 (36), 131 (24), 129 (100), 128 (51), 115 (22), 91 (17), and 77 (19).

Component 5 (retention time 40.5 min, 4%) was identified as 2-methyl-5-phenylpentenal (**11**): ir (CCl_4) 3.33, 3.45, 3.75, 5.75, 6.25, and 6.70 μ.

F. 1-Bromo-2-methyl-3-cyclohexylpropene (12). The reaction of 1.37 g of 1-bromo-2-methyl-3-cyclohexylpropene with 0.71 g of potassium *tert*-butoxide gave 0.95 g of crude product which was separated using a 20% Carbowax column at 130°. The first component (retention time 4.5 min, 39%) proved to be a mixture of two olefins which was separated by rechromatography employing a freshly prepared 20% carbowax column. The major olefin (65%) was identified as 2-cyclohexylmethylenecyclopropane (**16**): ir (CCl_4) 3.40, 5.82 (w), and 11.23 μ; NMR (CCl_4) 1.1–1.7 (m, 14) and 5.30 ppm (m, 2, $-C{=}CH_2$); mass spectrum m/e (rel intensity) 136 (5), 121 (46), 107 (21), 94 (30), 93 (43), 81 (100), 80 (31), 79 (54), 67 (32), 55 (21), 41 (33), and 39 (24). This compound was identical in all respects with a sample of 2-cyclohexylmethylenecyclopropane prepared by an independent method. The minor olefin (35%) in the first fraction was identified as *cis*-8-methylbicyclo[4.3.0]non-7-ene (**15**) on the basis of the following spectral data and by comparison with an authentic sample prepared by an independent route: ir (CCl_4) 3.29, 3.40, and 6.10 μ; NMR (CCl_4) 1.39 (m, 8), 1.70 (d, 3, J = 1 Hz, $CH_3C{=}C-$), 1.9–2.7 (m, 4), and 5.22 ppm (m, 1, $C{=}CH-$); mass spectrum m/e (rel intensity) 136 (45), 121 (100), 107 (18), 94 (56), 93 (83), 91 (23), 81 (21), 80 (22), 79 (51), 77 (25), 67 (15), 41 (17), and 39 (16).

Fraction 2 (retention time 6.4 min, 15%) was identified as 1-cyclohexyl-1-butyne (**13**): ir (CCl_4) 3.39 and 5.09 μ; NMR (CCl_4) 1.10 (t, 3, J = 7 Hz, $-CH_3$), 2.10 (q, 2, J = 7 Hz, $-CH_2-$), and 0.8–2.0 ppm (broad m); mass spectrum m/e (rel intensity) 136 (59), 121 (31), 107 (67), 94 (32), 93 (48), 91 (30), 82 (20), 81 (45), 80 (20), 79 (100), 77 (29), 68 (26), 67 (46), 55 (27), and 41 (28).

Fraction 3 (retention time 9.8 min, 25%) was identified as 1-cyclohexyl-2-butyne (**14**): ir 3.41 and 6.90 μ; NMR (CCl_4) 0.8–1.6 (m, 10), 1.71 (t, 3, J = 2 Hz, $-CH_3$), and 1.90 ppm (m, 3, $-CH-$ and $-CH_2-$); mass spectrum m/e (rel intensity) 136 (39), 121 (34), 107 (42), 94 (36), 93 (20), 83 (76), 82 (49), 81 (31), 79 (21), 67 (40), 55 (100), and 41 (31).

Fraction 4 (retention time 17.2 min, 21%) was identified as a mixture of 1-t-butoxy-2-methyl-3-cyclohexylpropene (ir absorption at 6.0 and 8.7 μ) and an unidentified impurity which was present in the original vinyl bromide.

***cis*-8-Methylenebicyclo[4.3.0]nonane.** A 6.2-g sample of 2-indanone was hydrogenated in ethanol using platinum oxide as catalyst (3 days). The catalyst was removed and the filtrate added to water and extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated. The residue was taken up in acetone and treated with chromic acid in sulfuric acid–water. The usual work-up gave 5 g of a mixture which was largely *cis*-bicyclo[4.3.0]nonan-8-one. A GLC sample of the ketone showed ir 5.73 μ; NMR 1.3–1.6 (m, 8), 1.9–2.4 ppm (broad with sharp spike at 2.09, 6); mass spectrum m/e 138 (32).

To a solution of methylenetriphenylphosphorane (prepared from 10.8 g of methyltriphenylphosphonium bromide and 11.4 ml of 2.25 M butyllithium in hexane) was added 4.62 g of the crude ketone. The mixture was refluxed for 15 h, 75 ml of dry THF was added, and heating was continued for 24 h, after which 25 ml of dimethyl sulfoxide was added and the mixture was heated at reflux for an additional 36 h. Work-up in the usual manner gave 1.87 g of a liquid which was found to be a four-component mixture by GLC using a 20% Carbowax column at 210°. The four components were separated by preparative GLC. Component 1 (retention time 4 min, 23%) was identified as *cis*-bicyclo[4.3.0]nonane, NMR (CCl_4) two envelopes at 1.57 and 1.40 ppm. Component 2 (retention time 5.5 min, 18%) was identified as *cis*-8-methylenebicyclo[4.3.0]nonane: ir (CCl_4) 3.23, 3.42, 6.03, and 11.33 μ; NMR (CCl_4) 1.41 (m, 8), 2.15 (m, 6), and 4.81 ppm (quintet, 2, $C{=}CH_2$). Component 3 (retention time 8 min, 14%) was identified as indan: NMR (CCl_4) 2.04 (quintet, 2), 2.83 (t, 4), and 7.05 ppm (m, 4, ArH). Component 4 (retention time 23.5 min, 44%) was identified as *cis*-bicyclo-[4.3.0]nonan-8-one.

***cis*-8-Methylbicyclo[4.3.0]non-7-ene (15).** To a solution of methylmagnesium iodide (prepared from 0.725 g of methyl iodide and 0.124 g of magnesium) in dry ether was added an ether solution of 0.7 g of *cis*-bicyclo[4.3.0]nonan-3-one. The resulting solution was heated at reflux for 2 h, and then a 2% solution of hydrochloric acid was added and the ether layer was separated, washed with 5% sodium bicarbonate solution, and dried ($MgSO_4$). The ether was removed, affording an oil which showed strong infrared absorption at 2.90 μ, in addition to weak absorption at 5.74 μ (carbonyl). The reaction mixture was dehydrated by passage through a Carbowax GLC column at 210 °C affording a broad band collected between retention times of 5 and 10 min. Analysis of this material indicated it to be mixture of *cis*-8-methylbicyclo[4.3.0]non-7-ene (80%) and *cis*-8-methylenebicyclo[4.3.0]nonane (20%). A pure sample of the major product obtained by careful GLC showed ir (CCl_4) 6.05 μ; NMR ($CDCl_3$) 1.70 (s, 3, $CH_3C{=}C-$), 2.0–2.7, and 5.27 ppm (m, 1, $CH{=}C-$).

***trans*-8-Methylenebicyclo[4.3.0]nonane.** To a suspension of 5.66 g of triphenylphosphonium bromide in ether was added 6.2 ml of a 2.25 M solution of *n*-butyllithium in hexane. An ether solution of *trans*-bicyclo[4.3.0]nonan-8-one[30] was added and the mixture was refluxed for 1 h, at which time 13 ml of Me_2SO was added. Heating was continued for 15 h and the mixture was worked up in the usual manner to afford 0.74 g (39%) of *trans*-8-methylenebicyclo[4.3.0]nonane. A pure sample isolated by GLC showed $n^{20}D$ 1.4721 (lit.[31] $n^{20}D$ 1.4720); ir 3.23, 3.40, and 6.00 μ; NMR (CCl_4) 1.0–2.6 (14) and 4.78 ppm (m, 2, $C{=}CH_2$).

Cyclohexylallene. Attempts to prepare cyclohexylallene by the reaction of cyclohexylmagnesium bromide or chloride with propargyl bromide gave only a small amount of allene and cyclohexyl bromide as the major product.[32] The allene was prepared in good yield from propargyl chloride as follows.

To a 0.4 M solution of cyclohexylmagnesium bromide in ether (prepared from 6.52 g of cyclohexyl bromide and 1.22 g of magnesium) was added 2.4 g of propargyl chloride in ether. Saturated ammonium chloride solution was added, the layers were separated, and the ether layer was washed with 5% sodium bicarbonate solution and water and dried ($MgSO_4$). The ether was removed to leave 2.0 g (50%) of crude cyclohexylallene, contaminated with a small amount of the isomeric terminal acetylene. An analytical sample of the allene was obtained by GLC: mass spectrum m/e (rel intensity) 122 (42), 107 (60), 93 (62), 81 (73), 80 (83), 79 (100), 77 (41), 67 (67), 55 (78), 41 (63), and 39 (65).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.66; H, 11.38.

2-Cyclohexylmethylenecyclopropane (16). A slurry of 0.6 g of active zinc–copper couple[33] in 15 ml of ether containing 2.43 of diiodomethane and a crystal of iodine was refluxed for 30 min and then 1.0 g of cyclohexylallene was added. After heating for 40 h, the reaction mixture was worked up as described in the preparation of 2-isoamylmethylenecyclopropane to afford 1.1 g of liquid which proved to be a six-component mixture by GLC analysis (SF-96 at 130 °C). The first component was the terminal acetylene contaminant in the starting allene; the second component was dioodomethane. Component 3 (retention time 16 min, 36%) was identified as unreacted allene and component 4 (retention time 22 min, 6%) was the desired 2-cyclohexylmethylenecyclopropane: ir (CCl_4) 3.25, 3.41, 5.76 (w), 11.01, and 11.24 μ; NMR (CCl_4) 5.29 ppm (m, 2, $C{=}CH_2$); mass spectrum m/e (rel intensity) 136 (1.6), 121 (50), 107 (22), 94 (29), 93 (41), 81 (100), 80 (30), 79 (52), 67 (32), 55 (23), 41 (36), and 39 (30).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.90; H, 12.00.

Component 5 (retention time 29 min, 25%) was tentatively identified as cyclohexylspiropentane: ir 3.40, 6.89, and 9.70 μ. Component 6 (retention time 35 min, 13%) was not identified.

G. 1-Bromo-2,3-dimethyl-1-butene (17). Reaction of 4.89 g of

1-bromo-2,3-dimethyl-1-butene (**17**) with 3.50 g of potassium *tert*-butoxide was carried out in the usual manner and the ether was distilled off through a 16-in. Vigreux column to afford a liquid which proved to be a seven-component mixture by GLC (20% Carbowax at 110 °C). Component 1 (retention time 3.3 min, 22%) was identified as 4-methyl-2-pentyne: ir 3.35, 6.80, 7.22, 7.33, and 7.58 μ; NMR (CCl_4) 1.10 (d, J = 6 Hz), 1.71 (d, 3, J = 2.2 Hz, $CH_3C{\equiv}C-$), and 2.50 ppm (m, 1, $-CHC{\equiv}C-$); mass spectrum *m/e* (rel intensity) 82 (69), 67 (100), 65 (22), 41 (66), and 39 (48).

Components 2 and 3 together amounted to about 4% of the product and were not further examined. Component 4 (retention time 9.5 min, 3%) was an impurity present in the starting vinyl bromide. Component 5 (retention time 12.5 min, 13%) was identified as 1-*tert*-butoxy-2,3-dimethyl-1-butene, ir (CCl_4) 6.00 and 8.70 μ. Components 6 and 7 (retention times 16.2 and 18.1 min, 56%) were unreacted vinyl bromides.

H. Reaction of 1-Bromo-2-(*o*-tolyl)propene (19). A 2.1-g sample of 1-bromo-2-(*o*-toly)propene (**19**) was treated with 1.3 g of potassium *tert*-butoxide to yield 1.25 g of crude product. GLC analysis using a Carbowax column at 180 °C showed the material to be an eight-component mixture; however, one component comprised 93% of the mixture and the largest of the remaining seven amounted to 2%. The major component, 1-(*o*-tolyl)-1-propyne (**20**), was isolated by GLC and showed ir 4.42, 6.26, and 6.73 μ; NMR (CCl_4) 2.05 (s, 3, $CH_3C{\equiv}CAr$), 2.38 (s, 3, CH_3Ar), and 6.9–7.3 ppm (m, 4, ArH); mass spectrum *m/e* (rel intensity) 130 (100), 129 (57), 128 (48), 127 (23), and 115 (56). None of the minor products were examined.

Registry No.—(*E*)-**1**, 57496-96-5; (*Z*)-**1**, 57496-97-6; (*E*)-**2**, 57496-98-7; (*Z*)-**2**, 57496-99-8; **3**, 54265-12-2; (*E*)-**4**, 57497-00-4; (*Z*)-**4**, 57497-01-5; **5**, 13828-12-1; **6**, 57497-02-6; **7**, 57497-03-7; **8**, 57497-04-8; **9**, 34298-75-4; **10**, 41635-77-2; **11**, 36613-11-3; **12**, 57497-05-9; **13**, 57497-06-0; **14**, 57497-07-1; **15**, 57497-08-2; **16**, 57497-09-3; (*E*)-**17**, 57497-10-6; (*Z*)-**17**, 57497-11-7; **18**, 21020-27-9; **19**, 57497-12-8; **20**, 57497-13-9; 4-phenylbutyric acid, 1821-12-1; 5-phenyl-2-pentanone, 2235-83-8; 2-methyl-5-phenyl-1-pentene, 6683-49-4; 2-methyl-3-cyclohexyl-1-propene, 3990-93-0; cyclohexylacetone, 103-78-6; 2,5-dimethyl-1-hexene, 6975-92-4; bromine, 7726-95-6; 2,6-dimethyl-1-heptene, 3074-78-0; 2,4-dimethyl-1-pentene, 2213-32-3; 2-*o*-tolylpropene, 7399-49-7; 2,3-dimethyl-1-butene, 563-78-0; potassium *tert*-butoxide, 865-47-4; 1,3,3-trimethylcyclopentene, 57497-14-0; 6-methyl-2-heptyne, 51065-64-6; (*E*)-1-*tert*-butoxy-2,5-dimethyl-1-hexene, 57497-15-1; (*Z*)-1-*tert*-butoxy-2,5-dimethyl-1-hexene, 57497-16-2; 2-butyl-1-hexene, 6795-79-5; 2-isoamylmethylenecyclopropane, 57497-17-3; 7-methyl-2-octyne, 57497-18-4; (*E*)-1-*tert*-butoxy-2,6-dimethyl-1-heptene, 57497-19-5; (*Z*)-1-*tert*-butoxy-2,6-dimethyl-1-heptene, 57497-20-8; 2-isopropyl-1-methylenecyclopropane, 57497-21-9; 5-methyl-2-hexyne, 53566-37-3; (*Z*)-1-*tert*-butoxy-2,4-dimethyl-1-pentene, 57497-22-0; (*E*)-1-*tert*-butoxy-2,4-dimethyl-1-pentene, 57497-23-1; 1-*n*-butyl-3-methylcyclopentene, 57497-24-2; 5-decyne, 1942-46-7; *cis*-8-methylenebicyclo[4.3.0]nonane, 57497-25-3; 2-indanone, 615-13-4; *cis*-bicyclo[4.3.0]nonan-8-one, 5689-04-3; *cis*-bicyclo[4.3.0]nonane, 4551-51-3; indan, 496-11-7; *trans*-8-methylenebicyclo[4.3.0]nonane, 57497-26-4; *trans*-bicyclo[4.3.0]nonan-8-one, 16484-17-6; cyclohexyl bromide, 108-85-0; cyclohexyl chloride, 542-18-7; propargyl bromide, 106-96-7; propargyl chloride, 624-65-7; cyclohexylallene, 5664-17-5; cyclohexylspiropentane, 57497-27-5; 5-nonanone, 502-56-7.

References and Notes

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