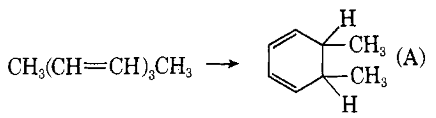
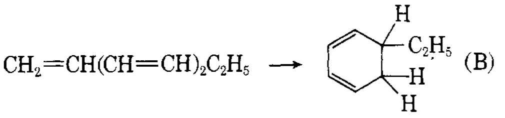
leading to the observed aromatic products are postulated as



(5)



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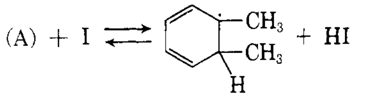
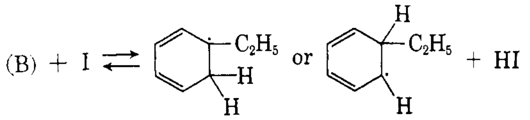


(6)



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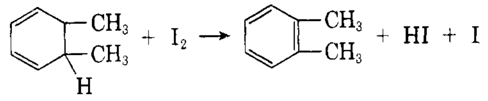

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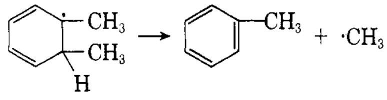
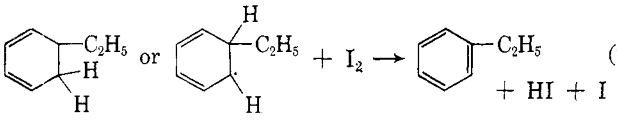


(7a)



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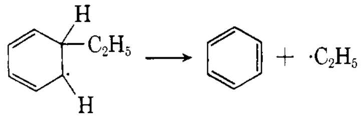
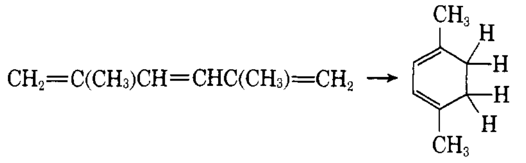


(7a')

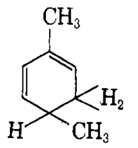
The persistence of the dealkylation steps 7a and 7a′ at iodine concentrations which efficiently suppress cleavage of acyclic intermediates is attributed to the aromatization energy gained in 7a and 7a′. Since attack at either of two positions on A, but only one position on B, can lead to dealkylation, the former should show the greater tendency to cleave. This is in agreement with the toluene/*o*-xylene and benzene/ethylbenzene ratios for *n*-octane and 1-octene in Table I. These data also yield a ratio of 1.40 ± 0.03 for the frequency of formation of A *vs.* B.

Dealkylation should not occur, according to this mechanism, during dehydrocyclization of internally substituted six-carbon chains, *e.g.*, 2,5-dimethylhexane, since attack at the methylene groups in (C) produces a radical incapable of β-elimination of an alkyl substituent



(C)

Furthermore, conversion of C to D, a species which could lead to dealkylation, is apparently not an important reaction.



(D)

Finally, the mechanism also accounts for the presence of both mono- and *o*-disubstituted C_{10} aromatics, but only monosubstituted C_8 and C_9 aromatics, in the product from *n*-decane.

Experimental

The apparatus and experimental and analytical procedures have been described previously.[1] Most of the hydrocarbons were commercially available "pure" grade (≧99%) materials. The *n*-decane and 2,5-dimethylhexane were distilled fractions from, respectively, a commercial product and a laboratory synthesis. Reagent grade, resublimed iodine was used without further purification.

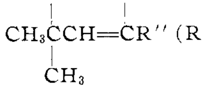
Acknowledgment.—It is with pleasure that we acknowledge the assistance of J. M. Gordon and P. A. Wadsworth, Jr., for carrying out the infrared and mass spectral analyses, of R. C. Olberg for supplying data for Table II, and of S. A. Ballard for many invaluable discussions.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

High Temperature Reactions of Iodine with Hydrocarbons. III. Rearrangement of Aliphatic Free Radicals

BY LYNN H. SLAUGH, RICHARD D. MULLINEAUX, AND JOHN H. RALEY

RECEIVED FEBRUARY 18, 1963

Compounds of the general structure  $CH_3\overset{R}{\underset{CH_3}{C}}CH{=}\overset{R'}{C}R''$ (R, R′, R″ = CH_3 or H) or those capable of attaining this structure by dehydrogenation or double bond migration rearrange to compounds having the structure  $CH_3\overset{R}{C}HCH_2CH{=}\overset{R'}{C}R''$ upon reaction with iodine in the vapor phase at elevated temperatures and atmospheric pressure. The rearranged product may undergo further reaction to form alkadienes or aromatic compounds. The rearrangements are believed to involve intramolecular 1,2-vinyl group migrations in aliphatic free radicals.

Discussion

Certain hydrocarbons containing a chain of less than six adjoining, nonquaternary carbon atoms react with iodine at elevated temperatures to form products resulting from an unusual rearrangement and subsequent dehydrogenation[1a] or aromatization[1b] of intermediate

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(1) (a) Part I: J. H. Raley, R. D. Mullineaux, and C. W. Bittner, *J. Am. Chem. Soc.*, **85**, 3174 (1963); (b) part II: R. D. Mullineaux and J.

Table I

Products of Rearrangement[a]

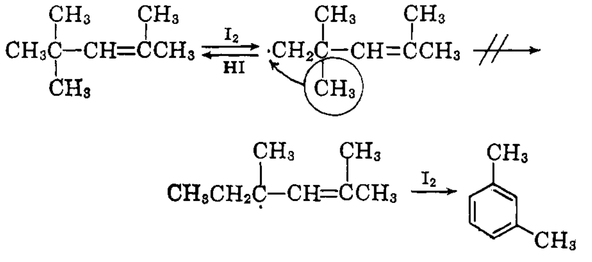
500°, 1.0 ± 0.5 I_2/RH, 3.0 ± 0.4 sec. reaction time

RH introduced[b]	Rearranged product	Moles/ 100 moles RH introduced[c]
Diisobutylene[d]	*p*-Xylene	37.0
4,4-Dimethyl-1-pentene	Toluene	26.0
3,3-Dimethyl-1-pentene	Toluene	18.0
3,3-Dimethyl-1-butene[e]	2-Methylpentenes and 2-methylpentadienes	6.1
	Benzene	7.1
2,2,5-Trimethylhexane[f]	*o*-Xylene	≦0.1
	m-Xylene	2.9
	p-Xylene	1.1
2,2-Dimethylbutane	2-Methylpentenes and 2-methylpentadienes	2.6
2,4-Dimethylpentane	Toluene	1.6
4-Methyl-2-pentene	Benzene	2.1
2,2-Dimethylpropane	Isopentane, isopentenes, and isoprene	0
2-Methylbutane	*n*-Pentenes and *r*-pentadienes	2

[a] Only those products resulting from rearrangement are listed. [b] Rapid dehydrogenation and double bond isomerization occur under these conditions. [c] When the material balance was <100%, the unaccounted for material was assumed to have the same composition as that of the gross hydrocarbon product. [d] A mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. [e] 3,3-Dimethyl-1-butene (91.4%), 2,2-dimethylbutane (7.1%), and 2-methyl-2-butene (1.5%). [f] 475°; 8-sec. reaction time.

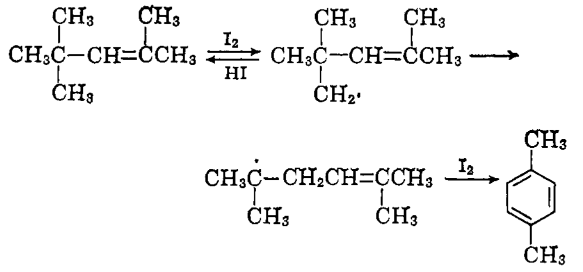
free radicals.[1] Several examples are listed in Table I. Since dehydrogenation of paraffins and double bond isomerization readily occur under these conditions, it should be noted that the reactant hydrocarbons listed are not necessarily those that rearrange.

From the data, two particularly pertinent conclusions are: 1. Methyl migrations *do not* occur. Thus, 2,2-dimethylpropane does not rearrange to 2-methylbutane or 2-methylbutenes under the reaction conditions that induce rearrangement of the other hydrocarbons. Also, 3-methylpentane or 3-methylpentenes are not formed during the reaction of iodine with either 3,3-dimethyl-1-butene or 2,2-dimethylbutane. Furthermore, methyl migration (eq. 1) was not involved in the reaction of iodine with diisobutylene since *p*-xylene was essentially the only C_8-aromatic product formed (eq. 2).



(1)

m-xylene



(2)

p-xylene

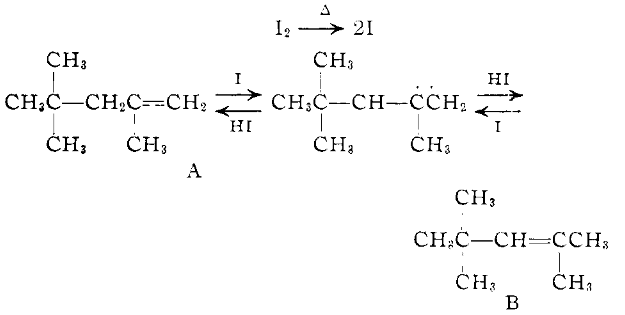
2. It appears that unsaturation is a prerequisite for rearrangement. As noted above, 2,2-dimethylpropane does not rearrange. Furthermore, saturated compounds rearrange to a lesser extent than do the corresponding unsaturated compounds, for example, 3,3-dimethyl-1-butene (13%) and 2,2-dimethylbutane (2.6%).[2]

Mechanism of Rearrangement.—From the evidence presented in parts I[1a] and II[1b] and in view of the lack of methyl group migration, a gas-phase, free radical mechanism probably is in operation. The specific structures of the products, such as *p*-xylene from diisobutylene, further limit the number of mechanisms which can be postulated. Using this conversion as an example, possible mechanisms are presented and discussed below.

Whether or not the rearrangement is a true intramolecular reaction or an intermolecular recombination of fragments resulting from prior cleavage of the reactant hydrocarbon is the most critical question. Since some decomposition of diisobutylene occurs under the experimental conditions, the rearranged product, *p*-xylene, might be attributed to coupling of two methallyl radicals or the addition of a methallyl radical to isobutylene to provide the 2,5-dimethylhexenyl structure which then aromatizes[1b] (mechanism I).

The evidence against this mechanism is substantial: (1) Reaction of iodine with C_2–C_4 hydrocarbons or pyrolysis of a mixture of isobutyl iodide and isobutylene produced only small amounts of dimeric products.[1a] (2) The degradation of 4,4-dimethyl-1-pentene (Table I) to C_4- and C_3 fragments also occurs. If mechanism I were operative, benzene and *p*-xylene should result from C_3–C_3 and C_4–C_4 recombinations, respectively. However, toluene was the only product of rearrangement. (3) Conclusive evidence against the above condensation mechanism was obtained by incorporating C^{14}-labeled isobutylene (formed *in situ* from isobutane-C^{14}) into the reaction zone along with the reactant diisobutylene. According to mechanism I, the isobutylene-C^{14} would mix with the unlabeled isobutylene and terminate in the *p*-xylene product. However, the product *p*-xylene was completely devoid of C^{14}.

With the intramolecular character of the reaction established, other mechanisms may be considered. One of these would involve the formation of a cyclopentyl intermediate (mechanism II).



The evidence strongly indicates that mechanism II is also incorrect: (1) Methylcyclopentane which should be an intermediate from 4-methyl-2-pentene (Table I) (more precisely, 4-methyl-1-pentene derived by rapid double bond migration) was not converted by iodine to benzene,[1a] the rearranged product from 4-methyl-2-pentene. (2) A hydrocarbon containing a chain of

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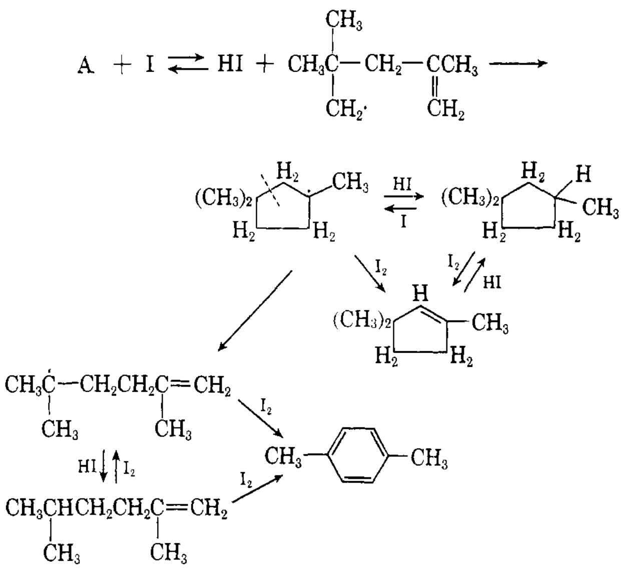
H. Raley, *J. Am. Chem. Soc.*, **85**, 3178 (1863). The free radical nature of high temperature, iodine–hydrocarbon reactions was discussed in part I.

(2) The 2.6% rearrangement probably occurred *via* 3,3-dimethyl-1-butene which was formed in 26% yield from 2,2-dimethylbutane.

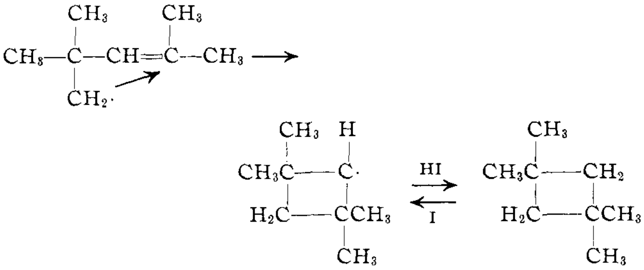
Mechanism II



only four carbon atoms, 3,3-dimethyl-1-butene, underwent 13.2% rearrangement.

Cyclization of the diisobutyl free radical to form a cyclobutyl intermediate also has been considered as a rearrangement path for diisobutylene (mechanism III).

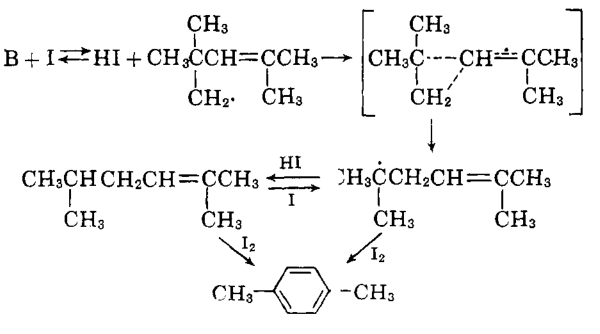
Mechanism III



However, any ring cleavage of this intermediate always leads back to the unrearranged diisobutylene structure.

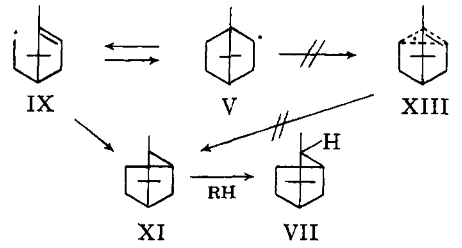
Finally, we propose *1,2-vinyl group migrations* to explain the free radical rearrangements observed (mechanism IV). This mechanism meets all of the requirements outlined above and is not subject to the criticisms against mechanisms I and II. The proposed 1,2-vinyl migrations are analogous to the 1,2-phenyl migrations which have been well established for certain free radicals in solution,[3,4] and recently for free radicals generated in the gas phase by the reaction of iodine or other radical sources with alkylbenzenes at 450–500°.[5]

Mechanism IV



According to mechanism IV, 2,5-dimethylhexene should be an intermediate in the reaction. A compound (1–2%) in the liquid product having the same g.l.c. emergence time as an authentic sample of a mixture of 2,5-dimethylhexenes was identified by mass spectrometric analysis as having the empirical formula C_8H_{16}. A second compound, C_8H_{14}, is thought to be a 2,5-dimethylhexadiene.

In conclusion, other reported rearrangements merit comment in light of the present disclosures. Berson, Olsen, and Walia[6] reported that the bornyl radical (V),[7] generated by thermal (255–290°) decomposition of 2,2′-bis-azocamphane gives, among other products, some isocamphane (VII). They presented evidence indicating that the rearranged product was the result of a cleavage–recyclization mechanism (V → IX → XI → VII), rather than a single-step, alkyl group migration involving a mesomeric bridged radical (XIII). This mechanism is different from the present 1,2-vinyl group migrations. The direct analogy of their mechanism to the present rearrangement is mechanism I. In their example, however, the olefin and radical resulting from β-elimination are tied by a linking carbon chain and thus are probably more prone to recombine.



Dominguez and Trotman-Dickenson[8] recently studied the addition of isopropyl and *tert*-butyl radicals, generated by photolysis (100–200°) of the appropriate aldehydes, to acetylene. In addition to the expected products 3-methyl-1-butene and 3,3-dimethyl-1-butene, respectively, isomerized products, 1-pentene and 4-methyl-1-pentene, were obtained. They postulated that the rearranged products resulted from methyl group migrations of the intermediate alkenyl radicals. It is difficult to visualize how these particular products would be formed by such processes. It seems more likely that these isomerizations are the result of 1,2-vinyl group migrations within radical D (eq. 4). Among other possibilities, D might be formed *via* an intramolecular 1,4-hydrogen transfer[9] reaction occurring either simultaneously with the radical addition to acetylene or subsequently within intermediate C, provided the latter has a *cis* configuration (eq. 3).[11]

There is a striking parallel between the vapor-phase reactions discussed herein and the heterogeneously catalyzed dehydrogenations of similar hydrocarbons over chromia–alumina.[12] With the latter, the aromatization of 2,2,4-trimethylpentane to *p*-xylene also is

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(3) M. S. Kharasch and W. H. Urry, *J. Am. Chem. Soc.*, **66**, 1438 (1944).

(4) S. Winstein and F. H. Seubold, Jr., *ibid.*, **69**, 2916 (1947).

(5) L. H. Slaugh and J. H. Raley, *ibid.*, **82**, 1259 (1960); **84**, 2640 (1962).

(6) (a) J. A. Berson, C. J. Olsen, and J. S. Walia, *ibid*, **82**, 5000 (1960); (b) **84**, 3337 (1962).

(7) The compound numbering used here for convenience is that of Berson, Olsen, and Walia, ref. 6a.

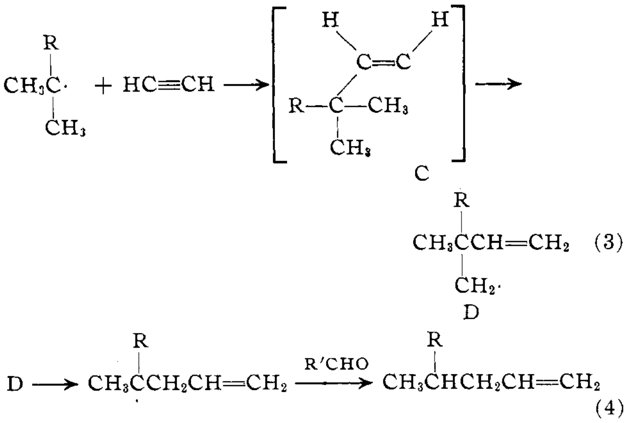
(8) J. A. G. Dominguez and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 940 (1962).

(9) Intramolecular hydrogen transfer reactions previously have been well established.[10]

(10) C. A. Grab and H. Kammüller, *Helv. Chim. Acta*, **40**, 2139 (1957); O. A. Reutov and T. N. Shatkina, *Proc. Acad. Sci. USSR, Chem. Sect.*, **133**, 381 (1960); *Tetrahedron*, **18**, 305 (1962); A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **31**, 853 (1959).

(11) A molecular model (Stuart and Briegleb) of *cis*-C shows that the methyl hydrogens are in very close proximity to the radical site, thus probably meeting the steric requirements for the hydrogen transfer (eq. 3). If C were initially *trans*, an isomerization about the double bond would be necessary. Although E_a for this process is not known, Dominguez and Trotman-Dickenson[8] have pointed out that radical C has about 30 kcal. mole^{-1} excess energy before collisional deactivation.

(12) (a) F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes, and R. S. Smith, *Chem. Ind.* (London), 228 (1960); (b) H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, 313 (1962), and references cited therein.



(3)

(4)

intramolecular, apparently proceeding *via* an intermediate with a 2,5-dimethylhexyl structure.[12a] Likewise, 2,2-dimethylbutane is converted to 2-methylpentenes while 2,2-dimethylpropane does not isomerize.[12b]

Experimental[13]

The apparatus and procedures are essentially the same as those described in part I.[1a] The effluent product was cooled rapidly and the HI and unreacted I_2 removed with an aqueous, sodium hydroxide spray. The compositions of the products were determined by a combination of mass spectrometric, infrared, and gas-liquid chromatographic analyses.

Reaction of Iodine with Diisobutylene and Isobutane-C^{14}.—The 110-cc., tubular, quartz (Vycor) reactor was constructed to permit the introduction of reactants at two different sections. Isobutane-C^{14} and iodine were introduced into the first section (45 cc.) at 450° and 1 atm. pressure and diisobutylene into the second section (65 cc.). The isobutane-C^{14} was dehydrogenated to isobutylene to the extent of 36.5% during the entire reaction period (5.3 sec.). However, most of this dehydrogenation undoubtedly occurred during the 3.2 sec. before it mixed with the diisobutylene.

A total of 0.767 mole of diisobutylene, 0.779 mole of isobutane-C^{14}, and 0.575 mole of iodine was used. The moles of products per 100 moles of diisobutylene introduced were: isobutylene, 5.5 (estimated); recovered diisobutylene, 81.5; *p*-xylene, 5.5; isooctane, 4.7; dimethylhexenes, 0.1; and miscellaneous hydrocarbons, 2.7. Total reactant hydrocarbon accounted for was 95%.

The following distillative fractions of the liquid product were collected for radioactivity measurements: no. 1, 91–99° (1.4 g.); no. 2, 99–105° (73.6 g.); no. 3, 105–135° (15.1 g.); no. 4, 135° (4.5 g.), xylene (≧ 97.2% *para* isomer). A total of 93.3% of the original C^{14} introduced was accounted for, 92.9% in the gaseous product and 0.4% in distillation fraction no. 2. Some mechanical losses occurred. No C^{14}-activity could be detected in the purified *p*-xylene.

Radioactivity Measurements.—The liquid scintillation method[14] was employed for the determination of the C^{14}-activity of the liquid samples. The activity of the gaseous product (38% v. He and ~62% v. *i*-C_4's) was measured in an ionization chamber as a gas and cross-calibrated with the liquid scintillation counter *via* the isobutane-C^{14}. The counting efficiency for all of the liquid samples was ~70%. Counting error was ~1%. The specific activity of the original isobutane-C^{14} was ~390,000 d.p.m./g.

3,3-Dimethyl-1-pentene.—3,3-Dimethyl-2-pentanol (284 g., b.p. 142–144°, 19% yield) was prepared by the reaction of the *tert*-amylchloromagnesium Grignard reagent with acetaldehyde according to the procedure of Edgar, Calingaert, and Marker.[15] The *tert*-amyl chloride and acetaldehyde were freshly distilled.

The methyl xanthate of 3,3-dimethyl-2-pentanol (170.2 g., b.p. 104–105° (5.4 mm.), 82.5% yield) was prepared from 116 g. of 3,3-dimethyl-2-pentanol by following the procedure of Schurman and Boord.[16] The xanthate was slowly decomposed with quiet ebullition by gently heating a flask containing the ester. The distillate was washed three times with strong potassium hydroxide solution, twice with water and dried over calcium chloride. Distillation of the product from sodium metal gave 3,3-dimethyl-1-pentene (54.5 g., b.p. 76.6–77°, $n^{20}\text{D}$ 1.3984, 67.3% yield; literature values[17] b.p. 77.5°, $n^{20}\text{D}$ 1.3984). Mass spectrometric and g.l.c. analyses failed to reveal the presence of any impurities.

4,4-Dimethyl-1-pentene was prepared in 20.5% yield *via* the coupling reaction of allyl bromide and *tert*-butylchloromagnesium Grignard reagent following the procedure of Whitmore and Homeyer.[18] However, additional purification was found necessary. The product was refluxed with 20% sodium hydroxide solution, shaken with excess silver nitrate solution, and washed with water before drying over calcium chloride. The 4,4-dimethyl-1-pentene thus obtained was free of bromides (72.2 g., b.p. 69.2–70.3°, $n^{20}\text{D}$ 1.3914; literature values[17] b.p. 72.5°, $n^{20}\text{D}$ 1.3918). Infrared, mass spectrometric, and g.l.c. analyses indicated the olefin to be free of impurities.

3,3-Dimethyl-1-butene.—The passage of 2,2-dimethylbutane and iodine through a Vycor tube at 500° (3-sec. reaction time) produced approximately 25% 3,3-dimethyl-1-butene. The liquid product was washed with 20% sodium hydroxide followed by water and dried over calcium chloride. Careful distillation through an 85-plate Helipak column gave a product (b.p. 48.7–48.9°) containing 91.3% 3,3-dimethyl-1-butene, 7.0% 2,2-dimethylbutane, 1.5% 2-methyl-2-butene, and 0.2% butenes and propylene. Purity was determined by g.l.c. analyses (30% dimethylsulfolane on firebrick).

Hydrocarbons.—The other hydrocarbons used in this study were commercial products of 99+% purity except for the diisobutylene which was ≧ 97.4% pure. The impurity in the diisobutylene had an emergence time on a g.l.c. column slightly longer than diisobutylene but different from 2,5-dimethylhexenes and 2,5-dimethylhexadienes.

Acknowledgment.—We wish to express our gratitude to V. P. Guinn for the radioactivity measurements. Appreciation is also extended to J. M. Gordon and P. A. Wadsworth, Jr., for carrying out the infrared and mass spectrometric analyses. E. F. Magoon kindly prepared the 3,3-dimethyl-1-butene.

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(13) Melting points and boiling points are uncorrected.

(14) C. D. Wagner and V. P. Guinn, *Nucleonics*, **13**, 56 (1955); V. P. Guinn, "Liquid Scintillation Counting," Pergamon Press, New York., N. Y., 1958, p. 126.

(15) G. Edgar, G. Calingaert, and R. E. Marker, *J. Am. Chem. Soc.*, **51**, 1483 (1929).

(16) I. Schurman and C. E. Boord, *ibid.*, **55**, 4930 (1933).

(17) "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Institute of Technology, Pittsburgh, Penna., April, 1957.

(18) F. C. Whitmore and A. H. Homeyer, *J. Am. Chem. Soc.*, **55**, 4555 (1933).