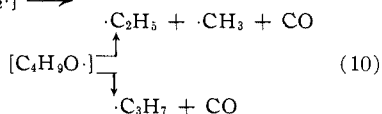


The proposed mechanism also is qualitatively consistent with the results given in Table V. At high initial I₂ concentration, the oxidation of hydrocarbon radicals *via* a sequence such as 10 should be minimized



by 5 or 4 and by 2' and the oxygen principally consumed by reaction with HI. With I₂ (and, hence, HI) in smaller amounts, or at higher oxygen concentrations, 10 becomes more important.

Acknowledgment.—The authors are indebted to L. H. Slaugh, E. F. Magoon, and J. J. Madison for performance of some of the experiments, and to Z. V. Jasaitis for aid with the g.l.c. analyses.

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

High Temperature Reactions of Iodine with Hydrocarbons. II. Aromatization

BY RICHARD D. MULLINEAUX AND JOHN H. RALEY

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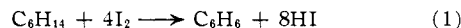
Aromatic hydrocarbons and hydrogen iodide are the predominant products from the reaction of elemental iodine with hydrocarbons containing a chain of six or more adjoining, nonquaternary carbon atoms. The structures of the aromatic products are defined by the structure of the reactant hydrocarbon and a specific mode of decomposition of a cyclic free radical intermediate. Ring closure is attributed to cyclization of a triene to a cyclohexadiene. If the hydrogen iodide decomposes *in situ*, further reaction of the resultant iodine ensues.

Introduction

In part I of this series,¹ the reversible, free radical reactions of elemental iodine with C₂–C₅ paraffins at high temperatures were discussed. This paper describes the reactions of iodine with straight and branched chain, higher members of the aliphatic series.

Results

The type of product obtained from the reaction of a higher alkane with elemental iodine at *ca.* 500° is markedly influenced by the mole fraction of reactant iodine. Typical results are illustrated in Fig. 1 for *n*-hexane. At the conditions used, *n*-hexane in the absence of iodine undergoes negligible reaction. The addition of ~1% iodine brings about an iodine-sensitized decomposition similar to that observed with many organic compounds,^{2,3} characterized by carbon-carbon scission reactions yielding methane and C₂–C₅ hydrocarbons, mainly olefins, and interpretable by a Rice-Herzfeld⁴ type of mechanism. With further additions of iodine, degradation reactions become less important and C₆ compounds account for more than 80% of the products at the highest I₂/C₆H₁₄ value shown. Benzene becomes the major product, accounting for 75% of the reacted hexane and corresponding to a 96% yield on iodine from reaction 1



Coincident with these increases is a rise in the saturate:olefin ratio of the C₂–C₅ products to a value of ~6.

The products from the reaction of several C₆–C₁₀ aliphatic hydrocarbons with one or more moles of iodine are given in Table I. Except in the case of 2,2,5-trimethylhexane, the products formed in highest yield are aromatic hydrocarbons containing the same number of carbon atoms as the reactant. With *n*-hydrocarbons containing seven or more carbon atoms, however, aromatic products of lower carbon number are also observed, their relative importance increasing with increasing chain length of the original compound. Significantly, each lower (C_{*n*-*x*}) aromatic is accompanied by a nearly equivalent yield of a C_{*x*} paraffin. These C_{*x*} paraffins constitute the other major group of de-

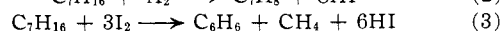
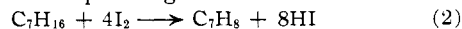
composition products. These data indicate a specific cleavage path rather than random or successive decomposition reactions. A single, specific cleavage process is also inferred from the structures of the aromatic products from *n*-decane. The infrared spectra showed that the C₁₀ fraction contained both monosubstituted and *o*-disubstituted benzenes, whereas the C₈ and C₉ aromatics consisted of only monosubstituted compounds. A very small yield of naphthalene, but no methylindanes nor methylindenes, was found.

The results for 2,5-dimethylhexane are in distinct contrast. Although the yield of total aromatics is comparable to that from *n*-octane and 1-octene, benzene and toluene account for less than 2% (instead of 40–50%) of the aromatic material.

Other pertinent observations are: (a) the high (≥95%) *o*-content of the xylenes from the straight-chain compounds and the high *p*-content of the xylenes from 2,5-dimethylhexane, (b) the formation of *n*-octane from 1-octene, and (c) the greater reactivity of an olefin compared to the corresponding paraffin. These observations demonstrate the absence of methyl migration and confirm other conclusions drawn in the preceding paper.¹

Cyclohexane is converted almost exclusively to benzene. With a 30-fold excess of cyclohexane at 350°, however, a product containing a cyclohexene/benzene ratio of 2 was obtained. Cyclohexadiene or five-membered ring structures were not detected under any reaction conditions investigated.

The small amount of H₂ formed in these reactions in Vycor tubes is consistent with the well known rate of the homogeneous, vapor-phase decomposition of HI.^{5,6} Since this decomposition is subject to surface catalysis, especially by noble metals,^{7,8} the reaction tube in some experiments was partially filled with platinum-containing solids. As illustrated in Table II, both H₂ formation and the combined yield of toluene and benzene increased markedly, the latter exceeding that corresponding to reactions 2 and 3



(5) J. H. Sullivan, *J. Chem. Phys.*, **30**, 1292 (1959), and references cited therein.

(6) L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," Reinhold Publishing Corp., New York, N. Y., 1932, pp. 148–156.

(7) C. N. Hinshelwood and C. R. Prichard, *J. Chem. Soc.*, **127**, 1552 (1925).

(8) C. N. Hinshelwood and R. E. Burk, *ibid.*, **127**, 2896 (1925).

(1) J. H. Raley, R. D. Mullineaux, and C. W. Bittner, *J. Am. Chem. Soc.*, **85**, 3174 (1963).

(2) S. Bairstow and C. N. Hinshelwood, *J. Chem. Soc.*, 1155 (1933).

(3) (a) See H. J. Schumacher, "Chemische Gasreaktionen," Theodor Steinkopff, Leipzig, 1938, pp. 388–395, for a review; (b) G. K. Rollefson and R. F. Faull, *J. Am. Chem. Soc.*, **59**, 625 (1937).

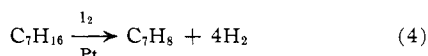
(4) F. O. Rice and K. F. Herzfeld, *ibid.*, **56**, 284 (1934).

TABLE I
REACTION OF IODINE WITH C₆-C₁₀ ALIPHATIC HYDROCARBONS
≤ 95% I₂ reacted; NaOAc-glycol quench¹

	n-Hexane	n-Heptane	n-Octane	1-Octene	2,5-Dimethyl-hexane	n-Decane	2,2,5-Tri-methylhexane
Temperature, °C.	498	498	490	490	480	460	475
I ₂ /hydrocarbon	1.9	2.4	2.3	0.93	2	1.5	1.0
Reaction time, sec.	37	20	11 ^a	0.8 ^a	6	8	8
Moles/100 moles hydrocarbon introduced							
C _n H _{2n+2}	40.9	38.0	36.2	9.8	45.9	70.4	31.2
C _n H _{2n} ^b	4.5	1.7	2.1	44.3	5.8	1.1	45.7
C _n H _{2n-2}	1.9		..	2.2 ^b
Benzene	44.6	8.3	4.6	5.7	0	1.6	0
Toluene	..	49.4	21.5	14.8	0.8	6.0	..
Xylenes	14.3 ^c	8.6 ^d	44.9 ^e	0	4.0 ^h
Ethylbenzene	21.2	10.5		4.2	0
Styrene	0.05	..
C ₉ aromatics	4.0	0
C ₁₀ aromatics	10.9 ^f	..
CH ₄	0.8	10.0	20.3	17.2	1.4	5.8	4.2
C ₂ H ₆	2.1	1.7	4.9	4.6	0.1	4.8	0.2
Other decompn. prod.	6.0	7.2	2.8	5.9	5.2	10.6 ^g	22.9 ⁱ
H ₂	4.7	3.4	1.2	2.6	1.3	0.4	0
Iodides	..	0	0	0.03	..	0	..

^a Selected so that a trace of unreacted I₂ remained. ^b No cyclic structures detected. ^c *o*-, 13.9; *m*-, 0.3; *p*-, 0.06. ^d *o*-, 8.2; *m*-, 0.3; *p*-, 0.1. ^e ≤ 98% *p*-xylene; companion expt. gave 99% *p*-, <0.2% *o*-, ≤ 0.8% *m*-xylenes, and <0.1% ethylbenzene. ^f C₁₀H₁₄, 7.6; C₁₀H₁₂, 3.0; naphthalene, 0.3. ^g C₃, 6.1; C₄, 2.0; C₅, 2.5. ^h See ref. 9. ⁱ C₃, 0.3; C₄, 12.2; C₅, 10.2; unidentified, 0.2.

A blank experiment with a packed tube under similar conditions but without iodine resulted in only a small amount of decomposition and very little hydrogen. From these observations it is clear that the elemental iodine produced by the surface-catalyzed decomposition of HI reacts again with the hydrocarbon and the effect is essentially a catalysis of the aromatization reaction



Discussion

The data given above show that aromatization is the general and predominant reaction of iodine with hydrocarbons containing a chain of six or more adjoining, nonquaternary carbon atoms. The absence of skeletal isomerization with these compounds, as well as with cyclohexane, and the small extent of random decomposition are consistent with the previous postulate of hydrocarbon free radical intermediates undergoing rapid hydrogen abstraction.

TABLE II
AROMATIZATION WITH HI DECOMPOSITION

	No catalyst	Pt on silica ^a	Pt gauze
Temperature, °C.	505	490	500
I ₂ /n-heptane	1.9	1.6	1.8
Moles/100 moles C ₇ H ₁₆ introduced			
C ₇ H ₁₆	44.4	33.8	26.3
C ₇ H ₁₄	0.8	3.2	2.4
C ₇ H ₈	43.4	48.7	51.8
C ₆ H ₆	5.8	7.6	8.8
CH ₄	5.8	8.1	9.1
Other decompn. products	2.3	4.1	4.3
H ₂	1.8	90.5	59.8
Yield on I ₂ , %			
C ₇ H ₈	92	125	113
C ₆ H ₆	9	15	14

^a 0.2% Pt on alumina-free silica (330 m.²/g.). ^b Equations 2 and 3.

With regard to the cyclization step, the intermediates which can be proposed are limited by the following observations: (a) Aromatization occurs much less readily if one of the six carbon atoms is quaternary. (b)

No compounds containing a five-membered ring have been detected in the products from an acyclic reactant.¹⁻⁹ (c) No compounds containing a nonaromatic six-membered ring were found—in particular, none with *gem*-methyl groups—from 2,2,5-trimethylhexane. (d) Under these conditions, alkylbenzenes do not dealkylate and specific cleavage of C₇-C₁₀-acyclic intermediates is highly unlikely. (e) Very little cleavage occurred with 2,5-dimethylhexane.

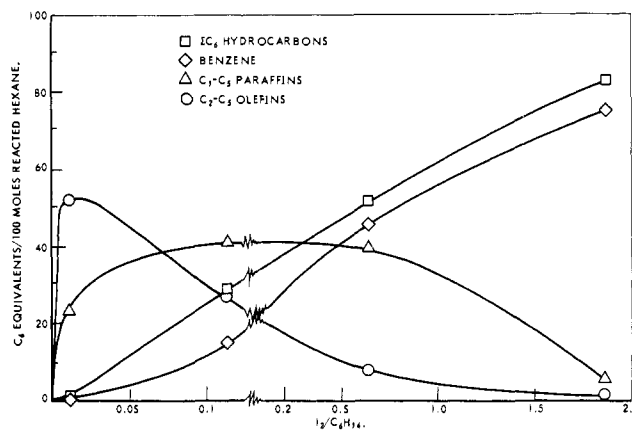


Fig. 1.—Dehydrocyclization of *n*-hexane.

These observations can be explained on the basis of a hexatriene intermediate. At 430° in contact with glass wool, 1,3,5-hexatriene cyclizes to 1,3-cyclohexadiene¹⁰ and at 550° over alumina, 2,5-dimethyl-1,3,5-hexatriene is converted to dimethylcyclohexadiene.¹¹ The cyclic dienes are also easily "disproportionated" to the corresponding aromatics.¹¹

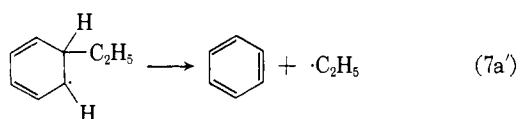
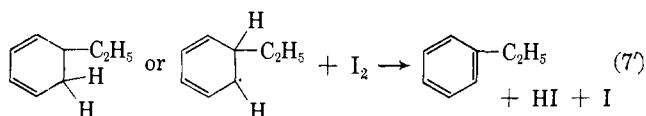
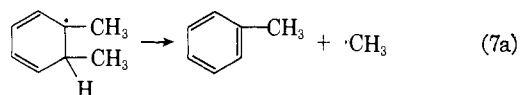
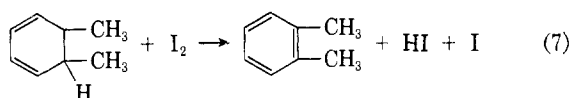
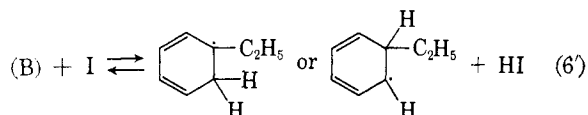
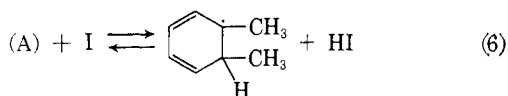
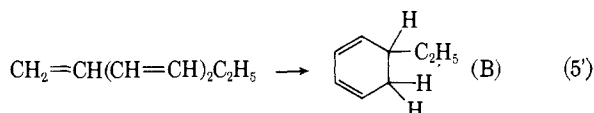
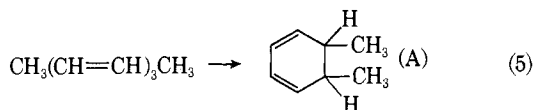
In reactions with iodine, further dehydrogenation of acyclic dienes by the steps suggested previously¹ would lead to trienes. With *n*-octane or an *n*-octene as the example, the two possible, conjugated triene intermediates (excluding stereoisomers) and the reactions

(9) L. H. Slaugh, R. D. Mullineaux, and J. H. Raley, *J. Am. Chem. Soc.*, **85**, 3180 (1963).

(10) K. Alder, H. von Brachel, and K. Kaiser, *Ann.*, **608**, 195 (1957).

(11) G. F. Woods and A. Viola, *J. Am. Chem. Soc.*, **78**, 4380 (1956).

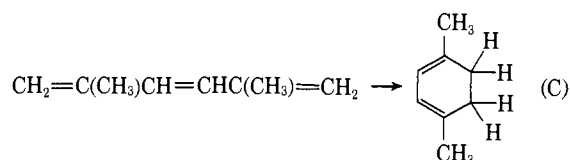
leading to the observed aromatic products are postulated as



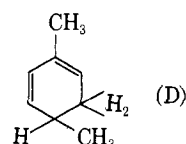
The persistence of the dealkylation steps 7a and 7a' at iodine concentrations which efficiently suppress cleavage of acyclic intermediates is attributed to the aromatization energy gained in 7a and 7a'. Since attack at either of two positions on A, but only one position on B, can lead to dealkylation, 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



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



Finally, the mechanism also accounts for the presence of both mono- and *o*-disubstituted C₁₀ aromatics, but only monosubstituted C₈ and C₉ 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 ($\geq 99\%$) 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 $\text{CH}_3\overset{\text{R}}{\text{C}}\overset{\text{R}'}{\text{C}}\text{H}=\text{CR}''$ (R, R', R'' = CH₃ or H) or those capable of attaining this structure by dehydrogenation or double bond migration rearrange to compounds having the structure $\text{CH}_3\overset{\text{R}}{\text{C}}\text{HCH}_2\overset{\text{R}'}{\text{C}}\text{H}=\text{CR}''$ 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 re-

sulting from an unusual rearrangement and subsequent dehydrogenation^{1a} or aromatization^{1b} of intermediate

(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.