

HIGH TEMPERATURE REACTIONS OF IODINE WITH VARIOUS ORGANIC COMPOUNDS

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Abstract—Elemental iodine reacts with various organic compounds in the vapor phase at about 500° to produce dehydrogenated and dehydrocyclized products. 3-Hexanol was dehydrogenated to 3-hexanone. n-Heptanoic acid was dehydrocyclized to benzoic acid and n-heptanonitrile to benzonitrile. When ring closure could proceed by the formation of either a C—C bond or a C—N bond, the latter predominated; thus, n-hexylamine gave α -picoline. When ring closure could occur to form either a C—C or a C—O bond, the two paths were of about equal importance; thus, hexyl phenyl ketone gave benzophenone and 2-phenyl-5-propyl-furan.

THE reaction of elemental iodine at high temperatures (> 350°) with hydrocarbons results in dehydrogenation in the cases of C₂–C₅ paraffins, cyclopentane, and methylcyclopentane.^{1–5} Hydrogen iodide is formed in amounts equivalent to the reacted iodine. If the hydrocarbon contains a chain of six or more adjoining, nonquaternary C atoms, dehydrocyclization to aromatic hydrocarbons occurs.⁶ With certain hydrocarbon structures, rearrangement of intermediate aliphatic free radicals occurs.⁷ The application of the stoichiometric vapor phase reaction of iodine at 500° to the dehydrogenation and dehydrocyclization of various organic compounds other than hydrocarbons (alcohols, acids, nitriles, amines, and ketones) has now been demonstrated. Under the severe conditions employed with these compounds, the reactants, free radical intermediates, and products would be expected to have only limited stability. By operating at short contact times (~3 seconds) with the iodine vapor and organic substrate rapidly mixed and brought to 500° and the products rapidly quenched with steam and caustic, it was possible to obtain surprisingly selective reactions. Experimental details and tables of data are given in the experimental section.

3-Hexanol was dehydrogenated to 3-hexanone in 67%* yield at a conversion of almost 100%. A small amount of phenol was observed along with appreciable amounts of unsaturated oxygen-containing compounds. This result demonstrates that a weak free radical agent such as iodine can be very selective even at 500°. These results are in agreement with those reported in kinetic and mechanistic studies of the gas phase reaction of iodine and isopropyl alcohol at temperatures up to 300°.⁸ The present findings indicate that, at 500°, the C(OH)—H bond in 3-hexanol is not only weaker than primary C—H bonds, but is also weaker than secondary C—H bonds. This result confirms the estimation of Barnard⁹ that this bond energy should be about 4 kcal less than the iso-C₃H₇—H bond energy.

* All yield figures are basis converted organic substrate except in the case of the amines, where the yields are basis the organic substrate charged.

n-Heptanoic acid was readily converted into benzoic acid by the action of high temperature iodine. Yields of benzoic acid ranged from 40% at 90% conversion to 85% at 3% conversion. The depth of conversion was varied between these extremes by changing the reaction temperature from 550° to 400°. Although increasing the depth of conversion by raising the temperature resulted in a loss of yield, it was possible to increase the conversion without affecting the yield by increasing the iodine to acid mole ratio. The increased iodine could be supplied directly or by adding oxygen which reacts *in situ* with the HI being formed to generate more iodine. The major side reaction under all conditions examined was decarboxylation to give hydrocarbons, CO, and probably CO₂, which could not conveniently be determined due to its solubility in the alkaline quench solution. At temperatures up to and including 500°, the molar ratio of hydrocarbon to CO was approximately unity indicating that CO₂ loss was not appreciable. Above 500°, more hydrocarbon than CO was formed suggesting that CO₂ formation had become significant. Also, at the higher temperatures, more of the hydrocarbon produced had been dehydrocyclized to benzene.

n-Heptanonitrile also dehydrocyclized readily at 500° to give a 65% yield of cyclic products at a conversion of 61%. The products were 90% benzonitrile and 10% substituted pyridine, indicating a strong preference for new C—C bond formation rather than new C—N bond formation with nitriles.

Amines were also dehydrocyclized by iodine. *n*-Hexylamine gave α -picoline as the major product with only a trace of aniline formed. The yield* of α -picoline was 33%

TABLE I. REACTION OF 3-HEXANOL WITH IODINE

Temp	500°
Residence time	3.4 sec
I ₂ /Alcohol mole ratio	1.70
Conversion	
I ₂	85%
Alcohol	~98%
Products, moles/100 moles 3-hexanol	
Unreacted 3-hexanol	1.4
3-Hexanone	66
C ₆ H ₁₀ O	8.3
C ₆ H ₈ O	5.3
C ₆ H ₆ O*	3.5
Benzene	2.4
Toluene	0.4
CH ₄	0.34
C ₂ H ₆	3.94
C ₃ H ₈	0.64
C ₂ H ₄	0.64
C ₃ H ₆	2.74
CO	4.88

* 1.6 moles phenol/100 moles of feed actually identified in the aqueous quench. A peak at $m/q = 94$ in the mass spectra of the water-insoluble organic liquid was probably due at least in part to phenol.

* Yield basis amine charged.

TABLE 2. REACTION OF n-HEPTANOIC ACID WITH IODINE
Products, moles 100 moles heptanoic acid

Temp, °C	Residence time, sec	I ₂ /Acid mole ratio	Recovered heptanoic acid ^a	Benzoic acid ^a	Benzene	Hexane	Other ^b hydrocarbons	Total hydrocarbons	CO	Conversion, % I ₂	Yield, % benzoic acid
400	10.1	0.85	97.8	2.7	?	?	0.2	0.5	0.8	26	3
450	6.2	1.85	78.5	13.1	1.8	1.8	0.2	3.8	4.5	51	21
500	3.1	1.84	53.3	22.8	6.5	6.7	2.2	15.4	13.6	82	47
550	3.7	1.65	22.8	31.4	15.7	14.0	7.1	36.8	26.0	97	77
550	3.4	3.04	9.8	36.6	23.6	6.6	8.5	38.7	22.9	92	90
550	2.6	1.78	27.1	25.8	12.2	6.5	7.1	25.8	19.7	97	73
500 ^c	3.1	1.80	34	35	7.4	0.9	5.9	14.2	17.6	62	66

^a The values given for heptanoic and benzoic acids include qualitative corrections for the solubility losses of these acids during their isolation.

^b Calculated as C₆ compounds.

^c Oxygen added. I₂/O₂ mole ratio = 1.9.

with the major identified side reaction being the loss of the amino group to give *n*-hexane. Thus, with amines dehydrocyclization occurs preferentially to form a new C—N bond rather than a new C—C bond. Since the opposite preference prevailed with nitriles, it would appear that the dehydrocyclization of amines and nitriles does not involve a common intermediate. In particular, the mechanistic path by which amines are dehydrocyclized does not involve nitriles or intermediates readily obtained from them. The formation from amines of a new C—N bond in a 5-membered pyrrole ring was not as successful as the formation of the 6-membered pyridine ring, however, with *o*-aminobiphenyl, a 16% yield* of carbazole was obtained at low conversion.

Hexyl phenyl ketone was 76% converted by iodine at 500° with 70% of the reaction leading to dehydrocyclization products. The dehydrocyclization gave approximately equal amounts of benzophenone and 2-phenyl-5-propyl-furan, the first resulting from formation of a new C—C bond and the latter from formation of a new C—O bond. Another 15% of the reaction led to decomposition of the ketone into benzene, iodobenzene, and CO, probably by β -cleavage of the radical formed by the initial iodine attack. The $\phi\dot{C}O$ radical which would result from this cleavage could decompose to a phenyl radical and CO. Alternatively, in the presence of the large amount of iodine, the decomposition might involve $\phi C \begin{matrix} \text{=O} \\ \diagdown \\ \text{I} \end{matrix}$ as an intermediate much as formyl iodide is suggested as an intermediate in the gas phase reaction of iodine with formaldehyde.^{10, 11}

TABLE 3. REACTION OF HEPTANONITRILE WITH IODINE

Temp	500°
Residence time	4.7 sec
I ₂ /nitrile mole ratio	2.51
Conversion	
I ₂	75%
Nitrile	61%
Products, moles/100 moles heptanonitrile	
Unreacted heptanonitrile	39
Benzonitrile	~36
Substituted pyridine ^c	~4
Hydrocarbons	
C ₁	0.5
C ₂	1.0
C ₃	1.5
C ₄	0.5
C ₅	0.1
Soluble C ^b	7
Yield	
Benzonitrile	~59%
Substituted pyridine ^c	~6.5%

* Probably α -ethyl.

^b Organic carbon dissolved in quench liquid, calculated as C₆ compounds. Does not include the substituted pyridine.

* Yield basis amine charged.

EXPERIMENTAL

The apparatus used in this investigation was essentially the same as that used in the studies on the reactions of iodine with hydrocarbons.¹ In the present study, quenching was accomplished by atomizing a stream of 20% NaOH with superheated steam. An auxiliary steam injection prior to the hydroxide quench was also used in most cases. The products usually consisted of both a liquid and a gas. The gas was analyzed by GLC, mass spectrometry, or both. The liquids were usually analyzed by mass spectrometry; in some cases, preliminary separation techniques were necessary to isolate the organic products. The alkaline quench liquid was analyzed for iodine, iodide, and organic carbon. In those cases where the organic products were soluble in the quench, they were removed by extraction or distillation and then analyzed.

The results are presented in tabular form in Tables 1-5.

TABLE 4. REACTIONS OF AMINES WITH IODINE

Amine	Temp, °C	Contact time, sec	I ₂ /amine mole ratio	Conversion, %		Identified products	
				I ₂	amine	compound	moles/100 moles amine
n-Hexylamine	500	2.9	1.69	~100	?	α-Picoline	33
						n-Hexane	18
						C ₆ H ₁₂	2.7
						Benzene	0.6
						Aniline	0.5
o-Aminobiphenyl	500	3.0	0.96	62	~16	Carbazole	16

TABLE 5. REACTION OF HEXYL PHENYL KETONE WITH IODINE

Temp	500°
Residence time	3.3 sec
I ₂ /ketone ^a mole ratio	2.56
Conversion	
I ₂	86%
Ketone	76%
Products, moles/100 moles ketone	
Unreacted hexyl phenyl ketone	24
Benzophenone	27
2-Phenyl-5-propyl-furan ^b	25
Iodobenzene	11
Benzene	≤14
Hydrocarbons	
C ₁	0.5
C ₂	1.4
C ₃	0.8
C ₄	0.8
C ₅	0.8
CO	15
Yield	
Benzophenone	36%
2-Phenyl-5-propyl-furan	33%

^a Prepared from heptanoyl chloride.¹²

^b Isolated by vacuum distillation followed by chromatography on silica. The material is a liquid, $n_D^{20} = 1.5723$ (Found: C, 84.2; H, 7.6. C₁₃H₁₄O requires: C, 83.8; H, 7.6%). Identity determined by IR, UV, NMR, and mass spectrometry.

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