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Dehydrogenation and Coupling Reactions in the Presence of Iodine and Molten Salt Hydrogen Iodide Acceptors

Charles T. Adams, Stanley G. Brandenberger,* J. B. DuBois, George S. Mill, M. Nager,
and Davis B. Richardson

Shell Development Company, Westhollow Research Center, P.O. Box 1380, Houston, Texas 77001

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Organic compounds are dehydrogenated cleanly and in high yield at 500–650 °C by iodine in the presence of molten salt hydrogen iodide acceptors; iodine is generated in situ by oxidation of the molten metal iodide-containing salt. This method provides a direct route to molecules not readily available by other synthetic methods. For example, *p*-diisopropenylbenzene is obtained in 72% yield by dehydrogenation of *p*-diisopropylbenzene. These reactions occur by a free-radical mechanism, and for structures which give rise to stable free-radical intermediates coupled, dehydrogenated products are obtained. Examples include *p*-xylene from isobutane or 2-methylpropene, *trans*-stilbene from toluene, and naphthalene from toluene and propene. This chemistry has been extended to nonhydrocarbons, and coupling to give nitrogen–nitrogen and carbon–nitrogen bonds has been observed. Benzonitrile is obtained from the reaction of aniline/toluene, and quinoline from aniline/propene.

The high-temperature reactions of iodine with hydrocarbons to form unsaturated hydrocarbons and hydrogen iodide have been investigated by Mullineaux and Raley.[1–3] They found that at temperatures above 400 °C a variety of paraffins react with stoichiometric amounts of iodine to yield the corresponding olefins and diolefins along with an equivalent amount of hydrogen iodide. In this way ethane and propane gave ethylene and propene, respectively; butenes, along with 1,3-butadiene, were obtained from butane; and isopentane gave a mixture of methylbutenes and isoprene.[2] With paraffins containing a chain of six or more carbon atoms, aromatization resulted. Thus benzene was obtained from hexane; toluene from heptane; and C_8 aromatics from octane or octene-1. As expected, cyclohexane was converted almost exclusively to benzene.[3] A free-radical mechanism was proposed for these reactions.[2,3]

Although the yields of olefins and diolefins far exceed those obtainable by catalytic dehydrogenation at any reasonable conditions, the extent of dehydrogenation is equilibrium limited.[2] As a consequence of this equilibrium limitation, the maximum extent of dehydrogenation, especially to diolefins, is far short of complete conversion of the paraffin to the desired product, e.g., 1,3-butadiene. This equilibrium effect can be offset partially by introduction of oxygen which oxidizes the product hydrogen iodide to iodine; however, some product degradation to carbon monoxide and smaller hydrocarbons is obtained along with increased conversion to dehydrogenated products.[2]

Iodine/hydrocarbon dehydrogenation processes whereby the equilibrium limitation is circumvented have been reported.[4–6] In these processes, three stepwise reactions are involved: (1) reaction of oxygen with a metal iodide to give elemental iodine, (2) reaction of the liberated iodine with the organic reactant to give a dehydrogenated product and hydrogen iodide, and (3) reaction of the hydrogen iodide with metal hydroxide to re-form metal iodide. With reaction 3, the equilibrium limitation is removed, and the overall chemistry is reaction 4, reaction of oxygen with the organic compound to give a dehydrogenated product and water. The hydrogen iodide acceptor may be either solid[6] or molten.[4,5] The present discussion will be limited to molten salt mixtures which serve both as the source of iodine and as the hydrogen iodide acceptor in a cyclic operating mode. The patent literature of both the acceptor and nonacceptor chemistry has been reviewed.[7]

$$MI_2 + H_2O + \tfrac{1}{2}O_2 \rightarrow M(OH)_2 + I_2 \quad (1)$$

$$I_2 + C_nH_{2n+2} \rightarrow C_nH_{2n} + 2HI \quad (2)$$

$$2HI + M(OH)_2 \rightarrow MI_2 + 2H_2O \quad (3)$$

$$\tfrac{1}{2}O_2 + C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2O \quad (4)$$

The results presented in the present paper serve to extend and define the scope of iodative dehydrogenation reactions of both hydrocarbons and nonhydrocarbons.

Results and Discussion

Dehydrogenation of Hydrocarbons. Ethane. Results obtained with ethane over two molten salts are presented in Table I. In both cases 75–80% conversion of ethane was obtained with a selectivity to ethylene of greater than 90%. There is, however, some hydrocarbon degradation, especially to carbon oxides, with a resultant inefficient utilization of oxygen; with an increased oxygen to hydrocarbon ratio, still higher ethane conversions could be achieved. It is not unexpected, of course, that with concurrent introduction of oxygen and

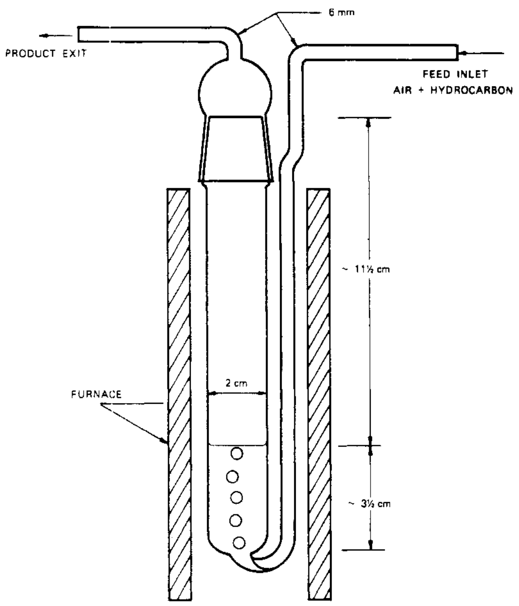


Figure 1. Single vessel for dehydrogenations in the presence of molten salts.

Table I. Dehydrogenation of Ethane and Butane

	Ethane		Butane	
Salt	LiI	PbI_2	LiI	LiI
Temp, °C	595	595	565	565
O_2/hydrocarbon (molar)	0.5	0.5	1.0	1.4
Residence time, s	1.0	1.0	3.0	3.0
Conversion, wt %	78	75	75	92
Product selectivity, % carbon				
Methane	0.8	1.4	3.5	2.4
Ethylene	97.2	93.4	6.0	6.0
Ethane			2.5	1.7
Propene	0.1	0.5	10.5	6.1
1,3-Butadiene	0.2	0.8	68.3	75.6
Butenes			4.8	2.3
Other products	0.9	1.2	2.8	2.3
Carbon oxides	0.7	2.6	1.6	3.6

hydrocarbon into a single vessel at 565 °C some carbon oxide formation would occur (Figure 1).

Butane. The effect of oxygen/hydrocarbon ratio on conversion is shown for butane dehydrogenation over molten lithium salts (Table I). At a ratio of 1.4, a butane conversion of 92% with a selectivity to 1,3-butadiene of 75.6 is obtained. The ratio of diolefin to olefin is relatively insensitive to conversion level or oxygen to hydrocarbon ratio. From this result, it is reasonable to conclude that the allylic hydrogens of the butenes formed as primary products are much more reactive than the secondary (or primary) hydrogens of butane.

Isopentane. Similar results are obtained with isopentane which yields isoprene as the major product (Table II). At an oxygen/isopentane ratio of 1.3, conversion of isopentane is 95.5% with an isoprene selectivity of 80.4%. Although isoprene is the major product, significant quantities of monoolefins are obtained, and the amount of monoolefin produced is dependent on the oxygen/isopentane ratio. This result suggests that the tertiary hydrogen of isopentane is considerably more reactive than secondary and primary hydrogens of *n*-butane.

In this case and in all subsequent examples, lithium iodide served as the source of iodine, and the reaction was carried out in a circulating lithium iodide/lithium hydroxide salt system containing separate iodide oxidation and hydrocarbon dehydrogenation zones (Figure 2).

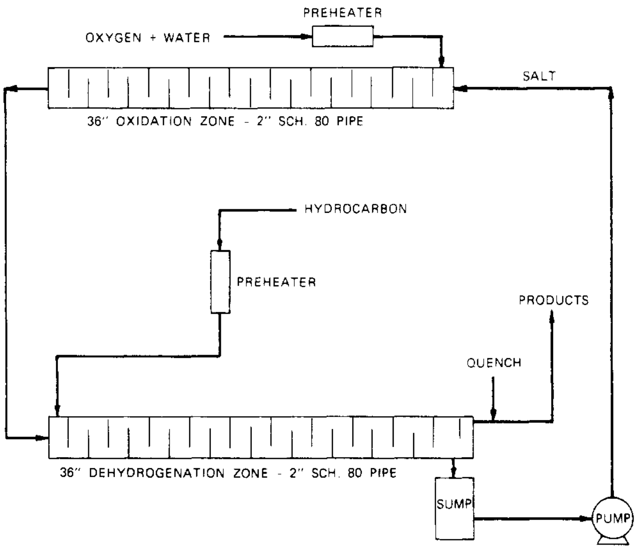


Figure 2. Reaction system with separate oxidation and dehydrogenation reactors.

Table II. Dehydrogenation of Isopentane at 565 °C and 2 s Residence Time

O_2/C_5H_{12} mole ratio	0.6	0.9	1.3
Isopentane conversion, %	62.4	77.3	95.5
Selectivity, wt % carbon			
Methane	2.4	1.5	0.7
Ethane + ethylene	1.2	0.9	0.8
Propene	1.9	1.8	2.4
1,3-Butadiene	1.2	1.2	1.0
2-Methylpropene	11.9	5.9	2.6
Isoprene	55.1	67.0	80.4
Methylbutenes	23.9	12.4	5.4
C_{6+}	1.7	8.2	1.3
Carbon oxides	0.8	1.1	5.3

Alkylbenzenes. Alkylbenzenes are readily converted to the corresponding alkenylbenzenes as illustrated by the data in Table III. The dehydrogenations of ethylbenzene and isopropylbenzene are extremely clean, yielding the alkenylbenzenes in 95% selectivity even at very high conversions. Propylbenzene is converted primarily to a mixture of *cis*- and *trans*-propenylbenzene and allylbenzene. It is noteworthy that with the longer alkyl side chain, fragmentation reactions become significant. For example, methane and styrene are formed in approximately equal molar amounts.

Dialkylbenzenes also are subject to iodative dehydrogenation. The relative amounts of olefin and diolefin obtained are dependent on the oxygen/hydrocarbon ratio. *p*-Diisopropenylbenzene has been prepared in 72.9% selectivity at a conversion level of 98.9% (Table III).

Relatively large amounts of higher boiling residue are obtained in this system as also was the case for the isopropylbenzene and propylbenzene dehydrogenations. The origin of this high-boiling material will be discussed in more detail below.

Butylbenzene. Hydrocarbons with a carbon chain of six or more undergo aromatization in the presence of iodine; e.g., hexane is aromatized to benzene and heptane to toluene.[2] These reactions also have been reported for molten salt acceptor systems.[4] An interesting extension of the aromatization reaction is illustrated by the data in Table III. Butylbenzene is dehydrogenated by iodine at 565 °C to yield naphthalene with 72% selectivity. The reaction sequence for this aromatization presumably is analogous to cyclization of hexatriene followed by dehydrogenation of the cyclohexadiene inter-

Table III. Dehydrogenation of Alkylaromatics

	Ethylbenzene	Isopropylbenzene	Propylbenzene	*p*-Diisopropylbenzene		Butylbenzene
Temp, °C	580	565	540	565	565	565
Residence time, s	3	3	1.6	2.0	2.0	1.5
O_2/hydrocarbon mole ratio	0.6	0.6	0.6	1.0	1.6	1.0
Hydrocarbon conversion, %	96.0	99.0	77.0	90.8	98.9	83.0
Selectivity, wt % carbon						
C_1–C_7	2.4	0.6	3.9	0.4	0.5	8.7
Ethylbenzene		0.1	0.3			1.6
Styrene	96.1	0.4	6.1			10.7
Isopropylbenzene			0.1			
Allylbenzene			7.7			
Isopropenylbenzene		94.7	0.6			
cis-Propenylbenzene			17.9			
trans-Propenylbenzene			54.9			
p-Isopropylisopropenylbenzene				37.0	13.0	
p-Diisopropenylbenzene				56.4	72.9	
Naphthalene						72.0
Other products		1.6	7.0	5.4	10.5	6.0
Carbon Oxides	1.5	2.6	1.5	0.9	3.0	1.0

Table IV. Relative Reactivities of Hydrocarbons at 540 °C

Compd	Relative rate	Hydrogen type (no.)	Relative hydrogen reactivity
Cyclohexane	1.0	Secondary (12)	1
Methycyclohexane	1.5	Tertiary (1)	8
Tetralin	15.8	Benzylic (4)	46
Cyclohexene	36.6	Allylic (4)	109

mediate as proposed for the aromatization of hexane to benzene.[2]

Hydrocarbon Reactivity. The relative reactivities of several hydrocarbons have been inferred from the preceding data. In additional competitive-rate experiments, the influence of structure on dehydrogenation rate was investigated. Equimolar mixtures of two hydrocarbons were reacted with a limited amount of iodine and the conversion of each compound determined. Assuming that hydrogen abstraction to form the initial hydrocarbon radical is the slow step in dehydrogenation, then for compounds A and B

$$\frac{dA}{dB} = \frac{k_A\,[A][I]}{k_B\,[B][I]}$$

and

$$\frac{k_A}{k_B} = \frac{\log([A]/[A_0])}{\log([B]/[B_0])}.$$

Results obtained for a series of six-membered ring compounds containing different hydrogen types are summarized in Table IV. In all experiments the reaction gave the expected aromatic product in high selectivity. Tertiary hydrogens are more reactive than secondary hydrogens; benzylic and allylic hydrogens are the most reactive. These results are consistent with the order or reactivity to be expected for a process in which a free radical is the intermediate. The high selectivity obtained with the iodine atom can be attributed to the relatively low hydrogen–iodine bond strength and the consequent low reactivity of the iodine atom.

Coupling Reactions of Hydrocarbons. For the reaction systems discussed above, radical coupling has not been significant. However, in the investigations of Mullineaux and Raley, coupled products (e.g., *p*-xylene from 2-methylpropene) were detected in minor amounts,[1] and in the presence of a hydrogen iodide acceptor, which permits higher radical concentrations, coupling is found to occur extensively with certain hydrocarbons. Benzene was obtained in 58.6% yield from propene;[4] isobutane or 2-methylpropene yielded *p*-xylene, and a mixture of 2-methylpropene and propane gave toluene in addition to benzene and *p*-xylene.[5]

Table V. Dehydro Coupling of Hydrocarbons

Temp, °C	595	620	565	595	540
O_2/hydrocarbon (molar)	0.6	0.6	0.65	0.3	0.3
Residence time, s	2	2.4	2.0	2.5	2.5
Conversion, wt %	61.2	41.0	37.5	11.3	12.7
Reactant composition, mol %					
Toluene	100	50	16.7		
Propene		50	83.3		64.3
Isopropenylbenzene				100	35.7
Product selectivity, % carbon					
Benzene		19.7	37.2		12.9
Styrene		1.7	1.3	4.8	1.8
Ethylbenzene		0.2	0.1		
Iodobenzene		3.7	7.4		
Iodotoluene		0.7	0.1		
1,2-Diphenylethane	10.7				
cis-Stilbene	3.9	1.7	0.1		
trans-Stilbene	72.2	13.5	0.7		
1,2-Diphenylacetylene	1.1		0.2		
Naphthalene		42.3	16.2		
Biphenyl		0.3	0.5		61.5
p-Terphenyl				87.5	9.1
Other products	11.1	10.8	14.8	5.9	7.3
Carbon oxides	1.0	5.4	21.4	1.8	7.5

Toluene. Aromatics also have been found to participate in coupling processes. Toluene is converted cleanly to *trans*-1,2-diphenylethylene (*trans*-stilbene); a minor product is the intermediate 1,2-diphenylethane. Reaction conditions and product composition are given in Table V. In a competitive experiment with a feed containing equimolar amounts of tetralin and toluene, no coupled products of toluene were observed in the presence of a limited amount of oxygen (0.25 oxygen/hydrocarbon). Since both compounds contain benzylic hydrogen, radical stabilities and rates of radical formation should be comparable. The absence of coupling indicates that (1) reaction of the radical derived from tetralin to give dehydrogenated products is fast compared to coupling and (2) hydrogen abstraction from tetralin by the benzyl radical is fast compared to radical coupling. The conclusion reached from these results is that coupling can occur only in the absence of a feasible dehydrogenation process. Consistent with this view is the observation that propene undergoes coupling whereas butene-1 dehydrogenates to 1,3-butadiene.

Toluene/Propene. Toluene does participate in coupling and cross-coupling reactions in the presence of propene.[5] Detailed results are given in Table V. The major products are benzene (propene coupling), stilbene (toluene coupling), and naphthalene (toluene/propene coupling). With an equimolar feed, allyl radical coupling is moderately favored relative to benzyl radical coupling. Naphthalene is the major product which is consistent with the expected statistical bias in favor of the cross-coupling reaction. Considerable control over product composition can be exercised by varying feed composition. At a feed ratio of five propene/toluene (molar), stilbene formation is effectively suppressed.

The dehydrocoupling results discussed above provide the outline of a general reaction sequence leading to the observed coupled products:

(1) Dehydrogenation occurs until a radical not capable of giving a stable product by loss of an additional hydrogen atom is produced. In general this radical will be either an allyl- or benzyl-type radical.

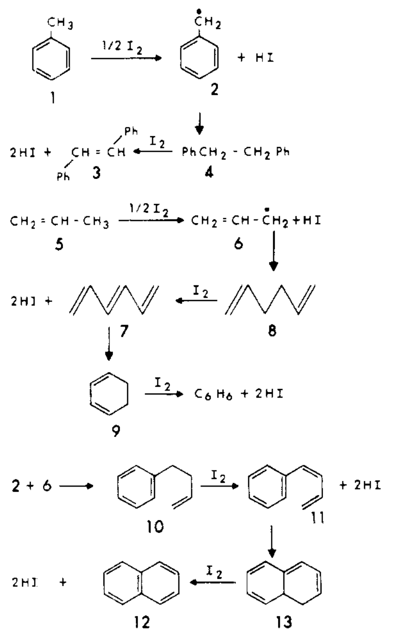
(2) The radicals thus produced will couple.

(3) Further dehydrogenation will occur, if possible.

(4) If a conjugated triene is formed, it will cyclize to the cyclohexadiene with subsequent dehydrogenation to an aromatic product.

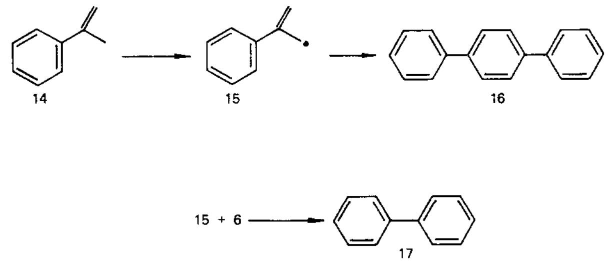
These reactions are illustrated for the allyl and benzyl systems in Scheme I.

Scheme I. Coupling Reactions of Toluene and Propene



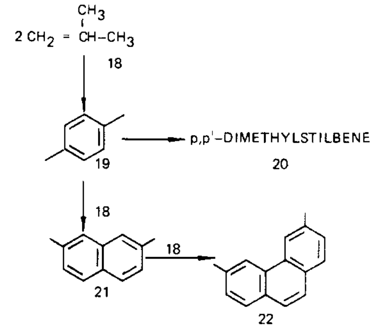
The chemistry outlined in Scheme I serves as a basis for consideration of other dehydro coupling reactions. Returning to the isopropenylbenzene system (Scheme II) it is seen that dehydro coupling can lead to *p*-terphenyl (**16**); cross-coupling of propene and isopropenylbenzene should yield biphenyl (**17**) in addition to terphenyl and benzene. As shown by the data in Table V, these expected products are indeed obtained in high selectivity.

Scheme II. Reactions of Isopropenylbenzene

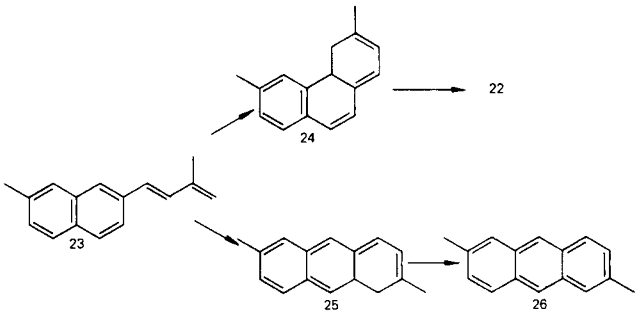


***p*-Xylene/2-Methylpropene.** Some additional dehydro coupling reactions are outlined in Scheme III. From a mixed *p*-xylene/2-methylpropene feed, *trans-p,p′*-dimethylstilbene (**20**), 2,7-dimethylnaphthalene (**21**), and 3,6-dimethylphenanthrene (**22**) are obtained; the amount of each is dependent on *p*-xylene/2-methylpropene ratio and the oxygen/hydrocarbon ratio. An interesting phenomenon is the absence of 2,6-dimethylanthracene (**26**) which could arise from the alternative cyclization mode for the coupled 2,7-dimethylnaphthalene/2-methylpropene (Scheme IV). Consideration of the cyclization reaction (Scheme IV) suggests that considerably more π-electron localization and loss of aromaticity would occur during cyclization to the anthracene thus favoring formation of 3,6-dimethylphenanthrene (**22**). To test the generality of this effect, the dehydro coupling of 2-methylnaphthalene and propene was investigated. Of the two possible products, phenanthrene was favored over anthracene by at least a factor of 50.

Scheme III. Some Coupling Reactions of 2-Methylpropene and *p*-Xylene



Scheme IV. Aromatization Routes Leading to Phenanthrenes and Anthracenes



Reactions of Nonhydrocarbons. Reaction with iodine at high temperature is not limited to hydrocarbons. For example, it has been shown that propionitrile is dehydrogenated to acrylonitrile at 535 °C in the iodine/molten salt system.[4] The reactions of nitrogen-containing compounds have been extended to include nitrogen–nitrogen and nitrogen–carbon coupling reactions.

Aniline. Formation of a nitrogen–nitrogen bond by iodative dehydro coupling is demonstrated by results obtained with aniline (Table VI). The expected primary dehydro coupled product, azobenzene (**30**), is indeed found, albeit in low selectivity. However, other products formed in higher selectivity indicate that extensive dehydro coupling to azobenzene occurred. Thus benzene and iodobenzene are major products

Table VI. Dehydro Coupling of Nonhydrocarbons

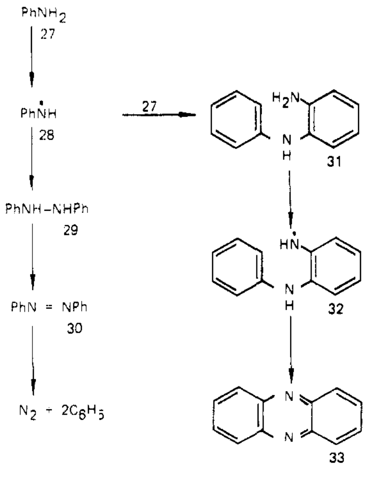
Temp, °C	620	620	620	620
O_2/reactant (molar)	0.5	0.8	0.8	0.75
Residence time, s	4.0	2.0	4.0	2.0
Conversion, wt%	23.0	40.5	75.2	24.5
Reactant composition, mol %				
Aniline	100	50		50
Toluene		50		
N-Benzylideneaniline			100	
Propene				50
Product selectivity, % carbon				
Benzene	19.1	9.3	15.4[b]	49.5
Iodobenzene	20.5	5.3	1.0	11.0
Toluene			7.2	
Aniline			10.9	
o-Iodoaniline	3.2	0.5		
Azobenzene	5.0			
Phenazene	28.0	9.3		
Carbazole	7.3	2.8		
Benzonitrile		20.2	29.8	
Quinoline				14.3
Biphenyl			11.2	
Stilbenes + diphenylacetylene		35.3		
Other products	9.6[a]	9.1	21.0	9.0
Carbon oxides	7.4	8.2	3.5	16.1

[a] In addition, 0.11 mol of N_2 per 100 g carbon feed also produced. [b] By difference.

and are assumed to arise via intermediate phenyl radicals formed by the thermal decompositon of azobenzene. In support of this hypothesis, molecular nitrogen is a reaction product.

To provide additional evidence for this reaction scheme, the thermal decomposition (no iodine present) of azobenzene in the presence of toluene was investigated. As expected the decomposition of azobenzene does lead to benzene and nitrogen. Formation of benzene requires a source of hydrogen atoms for abstraction by the intermediate phenyl radical. In this experiment the source was toluene as indicated by the products from benzyl radical coupling, 1,2-diphenylethane and *trans*-stilbene. The iodative dehydro coupling reactions of aniline are outlined in Scheme V.

Scheme V. Dehydro Coupling Reactions of Aniline

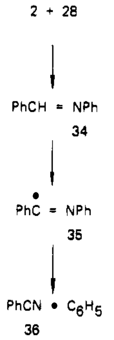


Two other major products of this reaction, phenazine and carbazole, involve nitrogen–carbon bond formation. Formation of these products can be rationalized either by homolytic substitution mechanisms or by a radical coupling mechanism. If the latter mechanism is operative the free-radical character of the anilino radical is shared to a considerable extent by the aromatic ring.

Aniline–Toluene. The above results with aniline demonstrate the formation and coupling of anilino radicals. Since toluene dehydro couples cleanly to give stilbene, it can be anticipated that with a mixture of toluene and aniline cross-coupling reactions will occur to give compounds containing carbon–nitrogen bonds. Results obtained in an aniline–toluene coupling experiment are given in Table VI. As expected the self-coupling products of toluene (diphenylacetylene, *cis*- and *trans*-stilbene) and of aniline (benzene and iodobenzene) are found. In addition phenazine and carbazole are again observed.

The major product containing a carbon–nitrogen bond is benzonitrile. Although unexpected, a straightforward pathway, outlined in Scheme VI, exists for benzonitrile formation via toluene–aniline dehydro coupling. Coupling of benzyl (**2**) and anilino radicals (**28**) leads to *N*-benzylideneaniline (**34**), the carbon–nitrogen analogue of stilbene. This product, however, contains only one more abstractable hydrogen. The radical thus formed fragments to give benzonitrile (**36**) and the phenyl radical.

Scheme VI. Formation of Benzonitrile from Toluene and Aniline



The proposed reaction scheme has been tested in an experiment starting with a benzene solution of *N*-benzylideneaniline (Table VI). Benzonitrile is indeed a major product. Further support for the reaction scheme is provided by the formation of significant quantities of toluene and aniline. This reversal of the dehydro coupling reaction presumably is brought about by the hydrogen iodide released by the iodative dehydrogenation and fragmentation of *N*-benzylideneaniline.

It is interesting to observe that the fate of the phenyl radical differs in this experiment. In the absence of large quantities of the hydrogen donors toluene and aniline, an appreciable quantity of the coupled product, biphenyl, is formed.

Aniline–Propene. To explore further the possibilities of carbon–nitrogen bond formation by dehydro coupling, the aniline–propene system was chosen. The results of the aniline–propene experiment are given in Table VI. As would be expected benzene from the self-coupling of propene is a major product. In addition the products from aniline alone also are found. The major product from cross-coupling of aniline and toluene is quinoline. Thus the reaction appears to proceed in a straightforward manner via coupling of anilino and allyl radicals followed by dehydrocyclization to quinoline.

Conclusions

The chemistry demonstrated and discussed above provides a facile route to many compounds not readily available by other synthetic methods. In general the products are easily predicted and are obtained in high yield. For cross-coupling reactions product mixtures are of course obtained, although even in these cases product composition can be controlled by feed composition and oxygen/feed ratio. There are many obvious variations of the chemistry outlined here. These include divinylbenzenes from diethylbenzene and coupling reactions to yield substituted stilbenes and numerous substituted aromatics.

Experimental Section

Two flow reactor systems were utilized. One of these was a single heated vessel containing the molten salt (Figure 1). Air (or oxygen) and hydrocarbon were introduced concurrently into the vessel, and after bubbling through the molten salt, the gaseous products left the vessel via a single exit line. A more elaborate system (Figure 2) consisted of separate salt oxidation and hydrocarbon dehydrogenation zones and was equipped with a pump to permit continuous recycle of the molten salt. The U configuration was mounted horizontally. The 2-in., schedule 80 pipe was baffled internally to promote gas–liquid contacting. The total system was heated by electrical resistance wire and insulated to maintain a uniform temperature. Care was taken to eliminate all cold spots which could lead to formation of salt plugs. Liberation of iodine occurred in the oxidation zone, and iodative dehydrogenation of the hydrocarbon, followed by reaction of hydrogen iodide, occurred in the dehydrogenation zone.

In general, gaseous products were analyzed by mass spectrometry. Liquid products were analyzed by either packed-column or capillary gas chromatography. As required, separated products were trapped and identified by mass spectrometry or by ultraviolet, infrared, or nuclear magnetic resonance spectroscopy. More complex product mixtures were handled by coupled capillary gas chromatography/mass spectrometric techniques.

To illustrate experimental procedures the dehydrogenation of *p*-diisopropylbenzene to *p*-diisopropenylbenzene is described fully.

Procedure. The reactor used in this case was the baffled pipe (Figure 2). After the salt mixture had melted, salt circulation was begun and heating continued until the desired reaction temperature was reached. Oxygen and water were introduced into the oxidation zone which was connected by a U tube to the dehydrogenation zone into which the hydrocarbon was injected by nitrogen pressurization of the feed tank. Flow rates, measured by rotometers, were adjusted to give the desired O_2/hydrocarbon mole ratio (1.0 or 1.6) and 2-s residence time. Nominal residence time was calculated from the unoccupied volume of the dehydrogenation zone divided by the total volume of gas (oxygen, water, and hydrocarbon) injected per second. The molten salt acceptor was LiI containing 2% LiOH.

The product was quenched with water as it emerged from the dehydrogenation zone; the molten salt passed into a sump and was recirculated by means of a centrifugal pump to the oxidation zone. The gaseous and liquid products were separated following the quench.

The run period was continued for a predetermined time period, and all products were collected to provide a material balance which for the two runs of Table V were 87 and 100%, respectively, basis carbon.

The total liquid product was removed from the quench system and the hydrocarbon and water phases separated. The hydrocarbon product was washed twice with 5% $NaHCO_3$ solution and twice with water.

Analyses. The liquid hydrocarbon was analyzed quantitatively by gas chromatography (GC). The *p*-diisopropylbenzene was identified by its known retention time, and the GC peaks corresponding to *p*-isopropylisopropenylbenzene (monoolefin) and *p*-diisopropenylbenzene (diolefin) were trapped and identified by mass spectrometry. When isolated, the diolefin (mp 63–64 °C) was identified by mass spectrometry (mass number 158), and by its ir and NMR spectra.

Nonvolatile residue was determined by GC using an instrument equipped with residue backflush and combustion of hydrocarbon to CO_2.

An integrated sample of the gaseous product collected during the material balance period was analyzed by mass spectrometry.

Product Isolation and Purification. After being washed, the crude product was distilled in a 30-plate Oldershaw column at a head pressure of 20 Torr and a reflux ratio of 4. A total C_{12} fraction was collected and the solid diolefin purified by two recrystallizations from 50% aqueous ethanol. The *p*-diisopropenylbenzene thus obtained contained 0.1–0.2% monoolefin and 10–100 ppm of organic iodide as the only detectable impurities.

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Registry No. —Iodine, 7553-56-2; ethane, 74-84-0; butane, 106-97-8; LiI, 10377-51-2; PbI_2, 10101-63-0; isopentane, 78-78-4; ethylbenzene, 100-41-4; isopropylbenzene, 98-82-8; propylbenzene, 103-65-1; *p*-diisopropylbenzene, 100-18-5; butylbenzene, 104-51-8; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; tetralin, 119-64-2; cyclohexene, 110-83-8; toluene, 108-88-3; propene, 115-07-1; isopropenylbenzene, 98-83-9; aniline, 62-53-3; *N*-benzylideneaniline, 538-51-2.

References and Notes

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