Reactions of Diaryliodonium Fluoroborates with Inorganic Anions

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Reactions of diphenyliodonium and phenyl-*p*-tolyliodonium fluoroborates with sodium nitrite, sodium azide, sodium thiocyanate, and potassium cyanide have been investigated. Nitrobenzene was obtained in 72–76% yield by treatment of diphenyliodonium fluoroborate with sodium nitrite in aqueous dioxane for 50 h at 100 °C. Phenyl azide was obtained in 97–99% yield by reaction of the iodonium salt with sodium azide at 80 °C for 2 h in the same solvent. Phenyl thiocyanate was obtained in 97–98% yield and phenyl isothiocyanate in 0.28–0.30% yield by treatment of the iodonium salt with sodium thiocyanate in the same solvent for 24 h at 100 °C. The reaction with potassium cyanide proved to be more troublesome, but a 42% yield of benzonitrile was ultimately obtained by reaction of the iodonium salt with potassium cyanide in aqueous dioxane for 50 h at 100 °C, 5 equiv of 1,1-diphenylethylene being added to the reaction mixture to suppress a competing free-radical chain reaction leading to benzene as a major product. Competition reactions have also been carried out, and interpretations of the results are presented.

In the reactions of sodium alkoxides with diaryliodonium salts, a radical chain reaction, which produces aromatic hydrocarbons, usually competes with the S_NAr reaction,[2] which gives alkyl aryl ethers.[3] In fact, the aromatic hydrocarbon products frequently are formed in greater yields than the alkyl ethers, unless radical traps are used as additives to inhibit the chain reactions. The most efficient inhibitor of the chain reactions leading to hydrocarbon products proved to be 1,1-diphenylethylene in the alkoxide reactions. By way of contrast, Beringer and his colleagues[4] have provided examples of reactions of diaryliodonium salts with simple, inorganic anions which appear to involve only an S_NAr reaction. For example, the reaction of diphenyliodonium bromide with sodium nitrite in aqueous solution gave nitrobenzene in 66% yield, while the reaction of phenyl-*o*-nitrophenyliodonium bromide with the same reagent afforded *o*-dinitrobenzene in 84% yield. No benzene was reported to have been formed. On the other hand, the reaction of diphenyliodonium bromide with potassium cyanide in ethanol solution gave but a 23% yield of benzonitrile (actually isolated as benzoic acid), thus suggesting the incursion of a major competing reaction.

In order to gain some insight into the factors determining whether the reaction of a diaryliodonium salt with a relatively simple inorganic anion will proceed mainly by an S_NAr reaction or by (presumably) a radical chain reaction, we decided to investigate in some depth the reactions of diphenyliodonium fluoroborate with sodium nitrite, sodium azide, sodium thiocyanate, and potassium cyanide, respectively.[5]

As shown in Table I, nitrobenzene was obtained in 72–76% yield by treatment of diphenyliodonium fluoroborate with sodium nitrite in aqueous dioxane at 100 °C for a prolonged period. In like manner, the corresponding reaction with sodium thiocyanate afforded phenyl thiocyanate in 97–98% yield, a trace amount (0.3%) of phenyl isothiocyanate also being detected. Phenyl azide was obtained in 97–99% yield by reaction of the iodonium salt with sodium azide at 80 °C for 2 h in the same solvent. The reaction with potassium cyanide proved to be more troublesome, but a 42% yield of benzonitrile was ultimately obtained by reaction of diphenyliodonium fluoroborate with the cyanide salt in aqueous dioxane at 100 °C for a prolonged period, 5 equiv of 1,1-diphenylethylene also being added to the reaction mixture to suppress a competing free-radical chain reaction.

It is clear from the data presented in Table I that aromatic hydrocarbon formation is a major competing reaction only when potassium cyanide is used as the inorganic salt. In the absence of 1,1-diphenylethylene as an additive, benzene is produced in 69% yield as against a 5% yield of benzonitrile. However, in the presence of a relatively large amount of 1,1-diphenylethylene, the yield of benzene drops to 5%, and the yield of benzonitrile increases to 42%. Very little benzene is formed in the reactions of diphenyliodonium fluoroborate with sodium nitrite, sodium thiocyanate, or sodium azide, even in the absence of 1,1-diphenylethylene. However, even these small amounts of benzene produced are decreased markedly when 1,1-diphenylethylene is present.

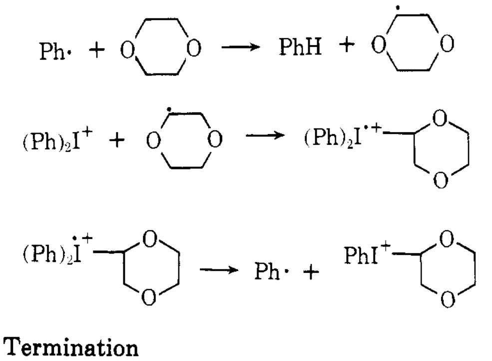
The initiation step of the radical chain reaction leading to the formation of benzene in the reaction of the diphenyliodonium ion with the cyanide ion probably consists of an electron-transfer reaction.[8] However, the formation and subsequent dissociation of a hypervalent iodine intermediate, $(C_6H_5)_2ICN$, may represent the detailed mechanism of the electron transfer process.[9] In any event, the concept of electron transfer permits one to suggest a fundamental reason why the reaction of diphenyliodonium fluoroborate with cyanide ion is more complex than those with nitrite, thiocyanate, and azide ions, respectively. It would be anticipated on the basis of the values of E_n (nucleophile constant characteristic of an electron donor) provided by Edwards[10] that the cyanide ion (E_n = 2.79) should be a more powerful electron transfer agent than the nitrite (E_n = 1.73), the thiocyanate (E_n = 1.83), or the azide (E_n = 1.58) ion; i.e., the order of E_n values parallels that of the abilities of the anions to quench fluorescence of a variety of fluorescent materials, which, in turn, parallels the abilities of the anions to function as electron-transfer agents.[11] Thus, the steps in the radical chain reaction may be postulated as:

(1) Initiation

$$PhI^+Ph + CN^- \rightarrow (Ph)_2I\cdot + \cdot CN$$

$$(Ph)_2I\cdot \rightarrow PhI + Ph\cdot$$

(2) Propagation



(3) Termination

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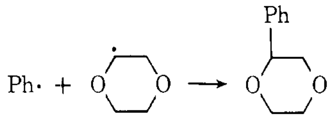
Table I. Reactions of Diphenyliodonium Fluoroborate with Inorganic Reagents in Dioxane–Water (70:30) in Sealed Tubes

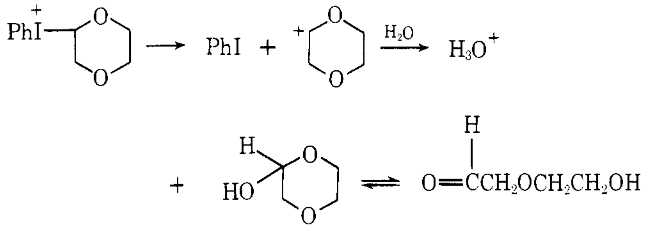
Inorganic reagent	Registry no.	Temp, °C	Time, h	Special conditions	% yield of products							
					$PhNO_2$[e]	PhN_3[f]	PhCN[g]	PhSCN[h]	PhI[i]	PhH[j]	PhOH	PhPh
$NaNO_2$	7632-00-0	100	50	Air	76				78	2.3	0.6	Trace
$NaNO_2$		100	50	Argon	72				77	2.3	0.7	Trace
$NaNO_2$		100	50	Argon, DPE[a]	75				79	1.3	0.6	Trace
NaN_3	26628-22-8	80	2	Air		99			100	0.8	Trace	Trace
NaN_3		80	2	Argon		98			96	0.9	Trace	Trace
NaN_3		80	2	Argon, DPE[b]		97			97	0.4	Trace	Trace
KCN	151-50-8	100	50	Air			5.3		99	69	5.0	2.7
KCN		100	50	Argon			8.8		98	76	0.4	6.0
KCN		100	50	Argon, DPE[b]			32		98	19	0.8	24
KCN		100	50	Argon, DPE[c]			42		97	5	0.9	26
NaSCN	540-72-7	100	24	Air				98[d]	98	0.6	Trace	Trace
NaSCN		100	24	Argon				97[d]	99	0.8	Trace	Trace
NaSCN		100	24	Argon, DPE[b]				98[d]	98	0.2	Trace	Trace

[a] 0.56 equiv of 1,1-diphenylethylene (DPE) present, of which 100% was recovered unchanged. [b] 1.0 equiv of DPE present, of which 100% was recovered unchanged. [c] 5.0 equiv of DPE present, of which 100% was recovered unchanged. [d] 0.28–0.30% yield of PhNCS also detected. [e] Registry no. 98-95-3. [f] Registry no. 622-37-7. [g] Registry no. 100-47-0. [h] Registry no. 5285-87-0. [i] Registry no. 591-50-4. [j] Registry no. 71-43-2.

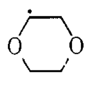
$$2Ph\cdot \longrightarrow PhPh$$



(4) Subsequent reactions



Evidence in support of this mechanism consists of the following. (1) Reports by Bachofner, Beringer, and Meites[12,13] indicate that the first of three polarographic waves in the electroreduction of the diphenyliodonium cation corresponds to the process $Ph_2I^+ + e^- \rightleftharpoons PhI\cdot$. Also, Beringer and Bodlaender[14] have shown that various metal ions, such as Cu(I), Ti(III), and Cr(II), are capable of transferring an electron to Ph_2I^+ to form essentially $Ph_2I\cdot$. Thus, the ability of the diphenyliodonium ion to accept an electron in an electron-transfer process is established. (2) Significant amounts of biphenyl have been detected.[15] This represents one of the possible chain termination products of a reaction involving phenyl radicals as chain carriers. Furthermore, independent evidence has been presented that $Ph_2I\cdot$ readily dissociates to give $Ph\cdot + PhI$.[12-14,16] (3) The formation of benzene is inhibited when 1,1-diphenylethylene is added to the reaction mixture.[15] (4) A significant yield of hydronium ion was detected by titration of the reaction mixture with standard base, and undoubtedly some HCN gas was lost when the ampule was opened. (5) The molar amount of iodobenzene produced when 1 equiv of 1,1-diphenylethylene is present in the reaction mixture[17] equals the sum of the molar amounts of benzonitrile and benzene and twice that of biphenyl. (6) It is well known that dioxane readily gives up a hydrogen atom to reactive radicals to produce



as an intermediate.[18]

Since azide, thiocyanate, and nitrite ions have but little tendency to enter into an electron-transfer reaction with the diphenyliodonium cation, then, by default, S_NAr reactions predominate, leading to high yields of phenyl azide, phenyl thiocyanate, and nitrobenzene, respectively.

Data for the reactions of nitrite, azide, thiocyanate, and cyanide ion, respectively, with phenyl-*p*-tolyliodonium fluoroborate are presented in Table II. As expected for an S_NAr reaction, the ratio of nitrobenzene to *p*-nitrotoluene produced in the reaction with nitrite ion was found to be about 5:2. In like manner, the ratio of phenyl azide to *p*-azidotoluene produced in the azide reaction was about 7:3, the ratio of phenyl thiocyanate to *p*-tolyl thiocyanate was also about 7:3 in the thiocyanate reaction, and the ratio of benzonitrile to *p*-cyanotoluene produced in the cyanide reaction was about 5:1. These ratios fall within the ranges reported for other typical S_NAr reactions in which there is a competition between attack of a nucleophile at a phenyl group vs. a *p*-tolyl group.[2,19-21] It is also significant that the ratios of benzene to toluene produced in these reactions are nearly 1:1. This is indicative of their origin by a radical process, i.e., a similar lack of discrimination in the formation of the hydrocarbons has been observed in other, related radical reactions.[2,19-23]

In the reaction of phenyl-*p*-tolyliodonium fluoroborate with potassium cyanide (Table II), it should be noted that the biaryls produced consist of a mixture of biphenyl (2.6%), *p*-methylbiphenyl (1%), and di-*p*-tolyl (0.8%). These results reinforce the concept that the biaryls do indeed result from chain termination reactions and not from an otherwise conceivable intramolecular decomposition of the hypervalent intermediate, $C_6H_5I(CN)C_6H_4CH_3$-*p*, which would have produced only *p*-methylbiphenyl.[24]

A recent report[25] indicates that the relative rates of reaction of N_3^-, NO_2^-, and SCN^- with 1-iodo-2,4-dinitrobenzene in methanol solution at 50 °C are about 100, 5, and 1, respectively. Our results with diaryliodonium cations as the aromatic substrates also suggest that the azide reactions are distinctly more rapid than the nitrite or thiocyanate reactions.[26] In order to provide a direct comparison of the reactivities of the anions, we carried out competition reactions in which 5 equiv of each of two salts were caused to react with 1 equiv of diphenyliodonium fluoroborate for a relatively brief period of time at a relatively low temperature, thereby limiting the reaction to about 35% of completion in most cases. The results are summarized in Table III. In direct comparison, it was found that azide ion is about 14.7 times more reactive than nitrite ion,

Table II. Reactions of Phenyl-*p*-tolyliodonium Fluoroborate with Inorganic Reagents in Dioxane–Water (70:30) in Sealed Tubes

Inorganic reagent	Temp, °C	Time, h	Special conditions	% yield of products							
				PhX	Tol-X	PhH	PhMe	PhI	Tol-I	Biaryls	Other products
$NaNO_2$	100	50	Air	41^{a}	18^{b}	0.4	0.4	23	44	Trace	Phenols^{c}
$NaNO_2$	100	50	Argon	48^{a}	21^{b}	0.5	0.4	24	48	Trace	Phenols^{d}
$NaNO_2$	100	50	Argon, DPE^{e}	52^{a}	21^{b}	0.3	0.4	24	57	Trace	Phenols^{f}
NaN_3	80	2	Air	69^{h}	29^{i}	0.3	Trace	29	67	Trace	Phenols^{g}
NaN_3	80	2	Argon	65^{h}	24^{i}	0.6	0.3	30	67	Trace	Phenols^{g}
NaN_3	80	2	Argon, DPE^{j}	70^{h}	29^{i}	0.2	Trace	26	71	Trace	Phenols^{g}
KCN^{k}	78	50	Argon	25^{l}	5.0^{m}	23	21	45	52	4.4^{n}	Ethers^{o}
KCN^{k}	100	50	Air	2.4^{l}	0.5^{m}	24	28	33	40	1.7^{p}	Phenols^{q}
KCN^{k}	100	50	Argon	3.4^{l}	0.7^{m}	28	28	32	40	1.7^{p}	Phenols^{q}
KCN^{k}	100	50	Argon, DPE^{r}	15^{l}	3.2^{m}	9.6	8.5	21	31	3.4^{p}	Phenols^{q}
NaSCN	100	24	Air	70^{s}	29^{t}	1.1	0.7	30	68	Trace	phenols^{u}
NaSCN	100	24	Argon	69^{s}	30^{t}	1.2	0.8	31	68	Trace	Phenols^{u}
NaSCN	100	24	Argon, DPE^{j}	71^{s}	32^{t}	0.3	0.2	32	69	Trace	phenols^{u}

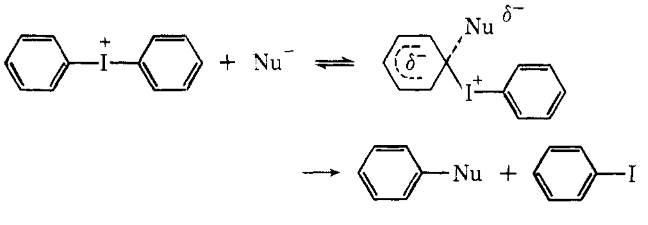
[a] Nitrobenzene. [b] *p*-Nitrotoluene. [c] Phenol (0.2%), *p*-cresol (1.5%). [d] Phenol (0.5%), *p*-cresol (1.8%). [e] 0.5 equiv of 1,1-diphenylethylene (DPE) present, of which 100% was recovered. [f] Phenol (0.6%), *p*-cresol (1.8%). [g] Phenol (trace). [h] Phenyl azide. [i] *p*-Azidotoluene. [j] 1.0 equiv of DPE present. [k] Reaction carried out in ETOH–H_2O (80:20). [l] Benzonitrile. [m] *p*-Cyanotoluene. [n] Biphenyl (2.6%), *p*-methylbiphenyl (1%), di-*p*-tolyl (0.8%). [o] Phenetole (14%), *p*-methylphenetole (5%). These products arise by aromatic S_N reaction of OEt^- with the diaryliodonium cation. Origin of OEt^- is $CN^- + EtOH \leftrightharpoons HCN + OEt^-$. [p] Biphenyl (0.9%), *p*-methylbiphenyl (0.4%), di-*p*-tolyl (0.4%). The same ratio of biaryls obtained in all three experiments. [q] Phenol (0.5%), *p*-cresol (1.9%). [r] 2.0 equiv of DPE present, of which 100% was recovered. [s] Phenyl thiocyanate (0.3% phenyl isothiocyanate was also detected). [t] Tolylthiocyanate (trace of *p*-tolyl isothiocyanate was also detected). [u] Traces of phenol and *p*-cresol were detected.

Table III. Competition Reactions of Diphenyliodonium Fluoroborate with Inorganic Reagents in Dioxane–Water (70:30) in Sealed Tubes

Inorganic reagents^{a}	Temp, °C	Time, h	Special conditions	% yield of products							
				PhN_3	$PhNO_2$	PhCN	PhSCN	PhI	PhH	PhOH	PhPh
$NaNO_2$ vs. NaN_3	25	2	Argon, DPE^{b}	21	2.4			26	2.4	0.03	Trace
	100	2	Argon, DPE^{b}	42	2.9			48	2.3	Trace	Trace
KCN vs. NaN_3	25	2	Argon, DPE^{b}	29		0.7		32	3.7	0.08	Trace
	100	2	Argon, DPE^{b}	40		2.0		48	5.0	1.4	Trace
$NaNO_2$ vs. KCN	25	2	Argon, DPE^{b}		29	2.9		34	3.3	Trace	Trace
	100	2	Argon, DPE^{b}		36	6.0		47	3.0	0.04	Trace
NaN_3 vs. NaSCN	100	2	Argon, DPE^{c}	68			5.0	74	0.9	1.5	Trace
$NaNO_2$ vs. NaSCN	100	2	Argon, DPE^{c}		66		9.0	76	0.9	1.2	Trace

[a] 5.0 equiv of each inorganic salt present. [b] 0.5 equiv of DPE present, of which 100% was recovered unchanged. [c] 1.0 equiv of DPE present, of which 100% was recovered unchanged.

about 13.5 times more reactive than thiocyanate ion, and about 20 times more reactive than cyanide ion toward the diphenyliodonium cation. In like manner, nitrite ion was found to be seven times more reactive than thiocyanate ion and six times more reactive than cyanide ion. Thus, toward the diphenyliodonium ion, the order of nucleophilic reactivities is $N_3^- > NO_2^- > SCN^-, CN^-$, in qualitative agreement with Parker's results.[25] The greater degree of reactivity of N_3^- over NO_2^- and SCN^- in the reaction with 1-iodo-2,4-dinitrobenzene as against that with the diphenyliodonium cation suggests that the transition state for the former reaction is somewhat tighter than that for the latter; i.e., Parker[27] has provided evidence that the tighter the transition state in an S_NAr reaction, the greater is the difference in reactivity between two nucleophiles of different nucleophilicities. Thus, we suggest that the transition state for the S_NAr reaction of the diphenyliodonium ion with a nucleophile is a relatively early one as depicted below; i.e., a significant degree of negative charge remains on the attacking nucleophile in the transition state, and this permits a favorable electrostatic interaction with the positively charged iodine atom to occur, thus lowering the energy of the transition state.



Since the negative charge of the attacking anion is more extensively delocalized in the S_NAr transition state of the reaction with 1-iodo-2,4-dinitrobenzene than in that of the reaction with the diphenyliodonium ion, the former transition state would be tighter than the latter. Thus, a greater spread in relative rates for the reactions with N_3^-, NO_2^-, and SCN^- would be expected in the 1-iodo-2,4-dinitrobenzene reaction than in the diphenyliodonium fluoroborate reaction.[28] Of course, the different solvents used for the two systems also affect the relative rates.[25,27]

Experimental Section

Diphenyliodonium Fluoroborate. Material of mp 134–136 °C was prepared by the method of Beringer et al.[29]

Phenyl-*p*-tolyliodonium Fluoroborate. This salt, mp 121–123 °C, was prepared by the method of Neilands.[30]

Typical Reaction Procedures. To 2 mL of dioxane-water (70:30) was added 5.0×10^{-4} mol of the diaryliodonium fluoroborate and 7.0×10^{-4} mol of sodium nitrite. The sealed tube was placed in an oil bath maintained at 100 °C and allowed to remain there for 50 h. After completion of the reaction, the tube was opened, neutralized with 85% phosphoric acid (usually requiring only 1 drop from a micropipet), and immediately analyzed on a Hewlett-Packard 5830A flame ionization gas chromatograph equipped with either a 6-ft 10%-SE 30, 80–100 Chromosorb W or a 6-ft 5%-FFAP, 80–100 Chromosorb W column. Product identities were determined by comparison of retention times with those of known compounds and by "mixture VPC tests."

To assure maximum reproducibility, the reactions were carried out in batches of four to eight at a time. The yields of the reaction products were determined from the areas of the peaks which constitute part of the data output of the gas chromatograph. Three standard solutions, having compositions near the approximate value obtained from the reaction mixture, were then prepared for each component and subjected to VPC analysis; the approximate areas were obtained and plotted graphically vs. composition. The actual product compositions were then obtained directly from the graphs.

Detection of Acid Following KCN Reactions. In a control experiment, a solution of diphenyliodonium fluoroborate in dioxene–water was subjected to the conditions specified in Table I for the KCN reactions. No acid could be detected by titration with standard NaOH solution. When the actual reaction with KCN was carried out, the yield of H_3O^+ was found to be 30%.

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Registry No.—Diphenyliodonium fluoroborate, 313-39-3; phenyl-*p*-tolyliodonium fluoroborate, 2665-59-0; *p*-nitrotoluene, 99-99-0; *p*-azidotoluene, 2101-86-2; *p*-cyanotoluene, 104-85-8; *p*-tolyl thiocyanate, 5285-74-5; toluene, 108-88-3; *p*-iodotoluene, 624-31-7.

References and Notes

(1) (a) Universidad Simon Bolivar; (b) Instituto Venezolano de Investigaciones Cientificas; (c) University of Massachusetts.

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(3) (a) J. J. Lubinkowski, J. W. Knapczyk, J. L. Calderon, L. R. Petit, and W. E. McEwen, *J. Org. Chem.*, **40,** 3010 (1975); (b) W. E. McEwen, J. J. Lubinkowski, and J. W. Knapczyk, *Tetrahedron Lett.*, 3301 (1972).

(4) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75,** 2708 (1953).

(5) Although Nesmeyanov, Tolstaya, and Isaeva have reported the preparation of nitrobenzene (54% yield), phenyl azide (55%), and benzonitrile (21%) by reactions of diphenylbromonium iodide with sodium nitrite, sodium azide and potassium cyanide, respectively, in aqueous solution,[6] these procedures presently have no synthetic value because the diphenylbrominium salt can be prepared in but 5–10% yield.[6,7]

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(15) The fact that the amount of biphenyl increases sharply when 1,1-diphenylene is present (Table I) suggests that the olefin combines with the phenyl radical to produce a relatively long lived molecule which serves as a reservoir for phenyl radicals. One possible sequence of reactions is the following:

$$(C_6H_5)_2C{=}CH_2 + C_6H_5\cdot \rightleftarrows (C_6H_5)_2\dot{C}CH_2C_6H_5$$

$$(C_6H_5)_2\dot{C}CH_2C_6H_5 + C_6H_5\cdot \rightarrow C_6H_5C_6H_5 + (C_6H_5)_2C{=}CH_2$$

(16) J. W. Knapczyk, J. J. Lubinkowski, and W. E. McEwen, *Tetrahedron Lett.*, 3739 (1972).

(17) We have pointed out in a previous paper[3] that ordinarily the material balance in reactions of diphenyliodonium salts with nucleophiles is excellent only when at least 1 equiv of 1,1-diphenylethylene is present in the reaction mixture. Among other effects, the olefin inhibits destruction of iodobenzene by a free-radical chain reaction.

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(24) Cf. B. M. Trost, R. W. LaRochelle, and C. R. Atkins, *J. Am. Chem. Soc.*, **91,** 2175 (1969).

(25) T. J. Broxton, D. M. Muir, and A. J. Parker, *J. Org. Chem.*, **40,** 3230 (1975).

(26) Bunnett[2] suggests that S_NAr reactions usually occur only when the aryl halide is activated by the presence of strongly electron withdrawing groups (such as nitro or diazonio) ortho or para to the site of nucleophilic attack. Inasmuch as 1-iodo-2,4-dinitrobenzene falls within the scope of this limitation, and since the reactivity profiles of this compound and of diaryliodonium salts toward the three nucleophiles are similar, it follows that the latter reactions are also of the S_NAr type. Furthermore, the only other conceivable mechanism which could give the same products, the $S_{RN}1$ mechanism,[2] can be ruled out because of the lack of inhibition by 1,1-diphenylethylene and other radical traps.[3] Data presented previously[3] also indicate that formation of arynes as intermediates is not a reasonable possibility.

(27) A. J. Parker, *Chem. Rev.*, **69,** 1 (1969).

(28) The direct estimate of the N_3^-/SCN^- reactivity ratio, for example, does not agree well with the indirect estimate with relay via the nitrite ion. This is probably attributable to the fact that the percent error in the determination of the minor component is much greater than that for the major component. For example, the yield of PhN_3 is probably 68 ± 2% and that of PhSCN 5 ± 2% in the appropriate competition reaction cited in Table III. Thus, the N_3^-/SCN^- reactivity ratio might range between 9 and 24 in the direct comparison, and the discrepancy would be magnified in the indirect estimate. However, there is no ambiguity in the given order of reactivities of N_3^-, NO_2^-, and SCN^- toward the diphenyliodonium ion. The reaction with cyanide ion is so complex that its position on the relative reactivity scale must be considered doubtful.

(29) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *J. Am. Chem. Soc.*, **81,** 342 (1959).

(30) O. Neilands, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 589 (1964).

Mixed Dehydrotrimerization of Biphenyl–Mesitylene by Aluminum Chloride–Cupric Chloride[1a]

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Coupling of biphenyl and mesitylene in the presence of aluminum chloride–cupric chloride provided an oligomer, 2,4,6,2‴,4‴,6‴-hexamethyl-*p*-quaterphenyl, as the main product. This apparently comprises the first example of dehydrotrimerization of two aromatic substrates to form a mixed product. Mechanistically, the process presumably entails initial formation of a radical cation from biphenyl, which then effects electrophilic attack on mesitylene, followed by fixation of the intermediate to a second mesitylene in a similar sequence of steps. Authentic material was obtained by reaction of mesitylene with *N,N′*-dinitroso-*N,N′*-diacetylbenzidine.

The Ullmann reaction comprises the classical method for joining aromatic nuclei.[2] Biaryls have also been synthesized by other routes involving aryl halides[3] or organometallic compounds.[4] Another approach consists of free-radical arylation.[5] Over the years, a substantial number of reagents have been found which effect dehydrodimerization of aromatic