

COMPETING MODES OF DECOMPOSITION OF DIARYLIODONIUM ALKOXIDES

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We have recently presented evidence that triarylsulfonium salts undergo competing radical and ionic reactions with sodium alkoxides, aromatic hydrocarbons and aldehydes (which subsequently form aldol resins) or ketones arising by radical chain reactions, and alkyl aryl ethers arising by bimolecular aromatic nucleophilic displacement reactions; diaryl sulfides are formed in both types of reaction.^{1,2} We have also shown that, when all possible sources of radical chain inhibitors are excluded from the reaction mixtures, the aromatic hydrocarbons are usually the major products. On the other hand, the deliberate addition of an inhibitor, such as 1,1-diphenylethylene or diphenylpicrylhydrazyl, to the reaction mixtures causes the products of the aromatic S_N reactions to become the major ones. We now have evidence that diaryliodonium alkoxides behave in a similar manner.

The reaction of 5.0×10^{-4} mole of phenyl-p-tolyliodonium fluoroborate with 7.0×10^{-4} mole of sodium ethoxide in 2.0 ml. of ethanol solution at 71° for 90 min. was found to give phenetole (9.5% yield), p-methylphenetole (2.6%), benzene (3%), toluene (36%), iodobenzene (56%), p-iodotoluene (47%) and a mixture of biaryls (0.01%). When the same reaction was carried out in the presence of 5.0×10^{-4} mole of 1,1-diphenylethylene, however, there was obtained phenetole (55%), p-methylphenetole (22%), benzene (5.2%), toluene (4.8%), iodobenzene (31%), and p-iodotoluene (62%). These and additional data are shown in the accompanying Table of Results. Clearly, 1,1-diphenylethylene is functioning as an inhibitor of a radical reaction which produces benzene and toluene; however, the presence of 1,1-diphenylethylene does not affect the rate of production of phenetole and p-methylphenetole, which arise by conventional S_N reactions. It is evident from the data presented in the Table of Results that the effect of a relatively small amount of diphenylpicrylhydrazyl is also to inhibit the radical chain reactions and thus to permit the aromatic S_N reactions to become dominant.

We suggest that the radical chain reactions take place as shown for the diphenyliodonium cation and the isopropoxide anion, for example, in the accompanying Reaction Scheme. In addition to the inhibition data cited above, there are three additional facts which support the proposed mechanism. (1) The use of a phenyl-p-tolyliodonium salt leads to the formation of nearly equal amounts of benzene and toluene; this lack of discrimination in the formation of aryl radicals has been observed in other radical reactions of diaryliodonium salts.³ (2) The apparent rates of the radical processes vary with the alkoxide ion used in the order $i\text{-PrO}^- > \text{EtO}^- > \text{MeO}^-$. The order of carbonyl C-H bond dissociation energies for the corresponding alcohols is $\text{H-CH}_2\text{OH} > \text{H-CH}(\text{CH}_3)\text{OH} > \text{H-C}(\text{CH}_3)_2\text{OH}$,⁴ and therefore the apparent rate sequence cited above is that expected in consideration of the respective propagation steps. (3) Small amounts of biaryls, the products of chain termination reactions, are found in the reaction mixtures.

The fact that about 3 times as much phenetole as p-methylphenetole is produced in the reaction of phenyl-p-tolyliodonium fluoroborate with sodium ethoxide constitutes valid additional evidence for the aromatic nucleophilic substitution process.^{1,5} Whether the displacement takes place on the cation or on the adduct of the cation with ethoxide ion, $p\text{-CH}_3\text{C}_6\text{H}_4(\text{OC}_2\text{H}_5)\text{C}_6\text{H}_5\text{I}$, as suggested by Reutov and his co-workers⁶ for related systems, is unknown at present.⁷

It is of interest that oxygen of the air does not influence the reactions of the diaryliodonium salts with sodium alkoxides, whereas a marked influence was noted in the corresponding reactions of triarylsulfonium salts with sodium alkoxides.

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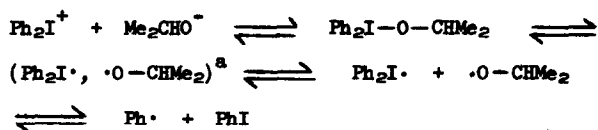
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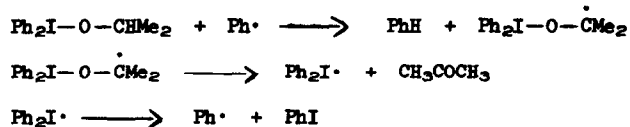
Reaction Scheme

Radical Chain Mechanism

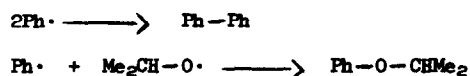
1. Initiation



2. Propagation



3. Termination



^a (Ph·, Ph-I-O-CHMe₂) may be formed at this point.

Table of Results

Reaction of $(C_6H_5IAr)^+ BF_4^-$ (0.0005 mole) with NaOR (0.0007 mole) in ROH (2 ml.)
for 90 min. in Argon Atmosphere in Sealed Tube

Ar	Additive	RO ⁻	% Yield Products					
			C ₆ H ₅	C ₇ H ₅	C ₆ H ₅ OR	p-C ₇ H ₇ OR	C ₆ H ₅ I	p-C ₇ H ₇ I
p-Tolyl	None ^a	EtO ⁻	34	36	9.5	2.6	56	47
"	DPE ^b	"	5.2	4.8	55	22	31	62
"	DPPH ^c	"	18	21	39	11	37	60
Phenyl	None ^a	"	68		14		92	
"	DPE ^b	"	6.0		80		100	
"	DPPH ^c	"	50		28		99	
"	None	i-PrO ⁻	81 ^{d,e}		47		68 ^k	
"	DPE ^b	"	32 ^f		69		100	
"	DPPH ^g	"	51 ^h		20		100	
"	None ⁱ	MeO ⁻	7		79		91	
"	DPE ^j	"	0.1		80		91	

^a Yields were essentially the same when reactions were carried out in air

^b 5.0×10^{-4} mole 1,1-diphenylethylene; 87-90% recovered unchanged

^c 2.5×10^{-5} mole diphenylpicrylhydrazyl

^d Acetone obtained in 74% yield

^e Yields were essentially the same when diphenyliodonium chloride was used

^f Acetone obtained in 33% yield

^g 2.0×10^{-4} mole

^h Acetone obtained in 37% yield

ⁱ 1.4×10^{-3} mole NaOMe

^j 1.4×10^{-3} mole NaOMe and 7.0×10^{-4} mole DPE (90% recovered)

^k An explanation for this result will be offered in a forthcoming paper.