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Abstract

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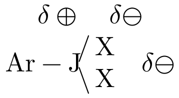
A NEW PRINCIPLE FOR THE PREPARATION OF IODONIUM COMPOUNDS

At the present time several methods are known for the preparation of diaryliodonium salts. In the classical Hartmann and Meyer method (^{1}), aryliodoso and aryliodo compounds are used, which are not always readily accessible. In the Willgerodt method (^{2}), aryliodoso chlorides and arylmercury compounds are used. Freidlina and Nesmeyanov showed (^{3}) that organotin compounds can be used instead of mercury compounds. Widely used is the method of aryliodination of aromatic hydrocarbons with aryliodoso compounds or inorganic compounds of polyvalent iodine in the presence of conc. sulfuric acid (^{4,5}) or trifluoroacetic acid (^{6}). Recently it was shown that aryliodination by aryliodoso compounds proceeds very readily with substances containing a mobile hydrogen atom: nitrophenols (^{7}) and β-dicarbonyl compounds (^{8,9}).

The available experimental material permits one, with sufficient justification, to assign the aryliodination reaction to electrophilic substitution at an aromatic or other nucleophilic carbon atom (^{10}). The electrophilic particle is the molecule of the aryliodoso compound (I), with strongly polarized bonds



$$\mathrm{Ar}-\overset{\delta\oplus}{\mathrm{J}}\begin{matrix}\overset{\delta\ominus}{\mathrm{X}}\\ \mathrm{X}\end{matrix}\quad\delta\ominus$$

(I)

It may be assumed that the lower the basicity characterizing the anion $X^{\ominus}$ (and the higher the acidity of HX), the more strongly the electrophilicity of iodoso particle I increases. This explains the necessity of the presence of strong acids in the aryliodination of aromatic hydrocarbons. The electrophilicity of iodoso compounds, although diminished, should also be retained in alkaline media, where in I $X = \mathrm{OH}$, which is in fact confirmed already by the very first reaction for obtaining iodonium salts from iodoso and iodoaryls in the presence of silver oxide (^{1}). It may be assumed that, in the presence of a sufficiently nucleophilic component, aryliodination will also take place in an alkaline medium. Recently this was experimentally confirmed in the reaction of iodosobenzene with 5,5-dimethylcyclohexanedione-1,3 in an alkaline medium (^{8}).

It turns out that the reaction of iodoso compounds with nucleophilic components in an alkaline medium is of a general character, and that the reaction products are aryliodonium betaines. We investigated the interaction of phenyliodosoacetate (I, $\mathrm{Ar} = \mathrm{C_6H_5};\ X = \mathrm{OOCCH_3}$) in the presence of alkali or an alkoxide at temperatures from -5 to $+5^\circ$ in methanol solution with a series of substances capable of forming nucleophilic anions: indandione-1,3 (^{10}), malonic ester, acetoacetic ester, acetylacetone, benzoylacetone, dibenzoylmethane, phenol, resorcinol, cyclopentadiene, pyrrole, indole, phenylnitromethane, cyclohexanone. All the substances reacted. In the case of phenol, resorcinol, and cyclopentadiene, dark decomposition products were formed—oxi-

···All of the β-dicarbonyl compounds studied, with the exception of acetylacetone, formed crystalline, rather unstable phenyl iodonium enolate betaines (II). In the case of acetylacetone, a noncrystallizing, unstable oil with the properties of enolate betaines was formed, which could not be obtained in pure form.

(II) phenyl iodonium enolate betaine structure (III) (IV)

a) $RR' =$ ortho-phenylene residue bearing two methyl substituents
b) $R = R' = OC_2H_5$
c) $R = CH_3; \quad R' = OC_2H_5$
d) $R = CH_3; \quad R' = C_6H_5$
e) $R = R' = C_6H_5$

(V)

Pyrrole and indole also formed yellow phenyl iodonium betaines with the proposed structures III and IV. In the case of cyclohexanone and phenyl nitromethane, such betaines could not be isolated. Only decomposition products were found (iodobenzene and unidentified oils).

The reaction may be represented as an ordinary electrophilic substitution through an intermediate complex.

$$\left[\begin{matrix} \delta\ominus \\ \Rightarrow C - H \end{matrix}\right]^{\ominus} + C_6H_5J^{\delta\oplus OR}_{\delta\ominus OR} \longrightarrow \left[\begin{matrix} H \\ \backslash C \cdots OR \\ / \quad J \cdots OR \\ C_6H_5 \end{matrix}\right]^{\ominus} \longrightarrow \delta\ominus C \oplus J C_6H_5 + HOR + OR^{\ominus}$$

$$R = H,\ Alk$$

The isolated phenyl iodonium betaines are very unstable substances, rapidly decomposing on recrystallization or during storage. The decomposition point depends strongly on the rate of heating. The presence of acids accelerates decomposition. Indole betaine IV forms unstable iodonium salts of type V. On treatment of V with alkali, IV is again obtained. Analogous iodonium salts of pyrrole cannot be obtained in pure dry form. On drying the presumed bromide, explosive-like decomposition was observed.

The structure of the phenyl iodonium enolate betaines (II) is partly confirmed by IR absorption spectra, in which no stretching vibrations of normal carbonyl groups are observed. Strongly lowered frequencies are observed, which indicates the formation of systems with nonintegral bonds—conjugated enolate anions (9,11,12). The structure is also confirmed by low stability toward acids, by the formation of iodobenzene on decomposition, and by the intensely yellow color of chloroform solutions (8,9,12). The structure of the pyrrole and indole iodonium derivatives is partly confirmed by their chemical behavior and low stability. The site of substitution (α or β) has not yet been established.

Thus it turns out that aryliodosocompounds with nucleophilic particles in an alkaline medium readily form iodonium betaines—unstable, but very reactive compounds which presumably can be used for various subsequent transformations. It is evident that this reaction also extends to many other compounds capable of providing a strongly nucleophilic center and, after substitution, of being converted into a betaine.

Table 1

Phenyliodonium betaines

Substance	Color, decomp. (on rapid heating)	Found, % J	Found, % N	Calculated, % formula	Calculated, % J	Calculated, % N	IR absorption spectra. Suspension in paraffin oil	Intensity. Solution in chloroform
IIa	Yellow needles 107–109° (non-crystalline)	36.84	–	$C_{15}H_9O_2J$	36.45	–	1560(74); 1605(50); 1662(45)	1595(ϵ = 630)1630(ϵ = 600)
II	White crystals 89–90°	34.8034.82	–	$C_{13}H_{15}O_4J$	35.04	–	1560(shoulder); 1600; 1620(shoulder)	1631(ϵ = 350)1654(ϵ = 350)
II	Yellowish crystals 84–85°	37.9538.11	–	$C_{12}H_{13}O_3J$	38.21	–	1538(60); 1630(53)	1568(88)1650(87)
II	Yellow needles 88–89° (explosively)	34.6934.56	–	$C_{16}H_{13}O_2J$	34.85	–	1482(85); 1580(64)	1536(ϵ = 800)

Substance	Color, decomp. (on rapid heating)	Found, % J	Found, % N	Calculated, % formula	Calculated, % J	Calculated, % N	IR absorption spectra. Suspension in paraffin oil	Intensity. Solution in chloroform
II	Yellow needles 92–93° (explosively)	28.86 30.16	–	$C_{21}H_{15}O_2J$	29.77	–	1465-1477(98); 1569(39)	1524-1530(ϵ = 800)1568(shoulder);1602(shoulder)
III	Yellow crystals 75° (with explosion)		5.33	$C_{10}H_8NJ$	47.21	5.20		
IV	Yellow crystals 95° (explosively)		3.88 4.13 4.68	$C_{14}H_{10}NJ$	39.76	4.39		
VX = Br	White needles 84° (explosively)	31.02 30.71 32.47		$C_{14}H_{11}NBrJ$	31.72	3.50		

Some experimental data are presented in Table 1. Iodine was determined by the method of Schöniger (13). For substances III and IV it was not even possible to obtain satisfactory results, since on heating an explosive decomposition occurs and part of the decomposition products volatilizes without burning. The IR spectra were recorded on IKS-12 and IKS-14 instruments in the form of suspensions in paraffin oil and in chloroform solution.

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REFERENCES

1. C. Hartmann, V. Meyer, Ber., **27**, 502 (1894).
2. C. Willgerodt, Ber., **30**, 56 (1897).
3. R. H. Freidlina, A. N. Nesmeyanov, DAN, **29**, 567 (1940).
4. J. Masson, E. Race, J. Chem. Soc., **1937**, 1718.
5. F. Beringer, M. Drexler, E. Gindler, Ch. Lumpkin, J. Am. Chem. Soc., **75**, 2705 (1953).
6. F. Beringer, H. Bachofner, R. Falk, M. Leff, J. Am. Chem. Soc., **80**, 4279 (1958).
7. A. Fox, K. Pausacker, J. Chem. Soc., **1937**, 295.
8. E. Gudriniece, O. Neiland, G. Vanag, ZhOKh, **27**, 2737 (1957).
9. O. Ya. Neiland, G. Ya. Vanag, DAN, **131**, 1351 (1960).
10. O. Neiland, Collection "Cyclic β-Diketones," Riga, 1961, p. 291.
11. O. Ya. Neiland, G. Ya. Vanag, DAN, **129**, 337 (1959).
12. O. Ya. Neiland, G. Ya. Vanag, ZhOKh, **31**, 146 (1961).
13. W. Schöniger, Microchim. acta, **1955**, No. 1, 123.

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