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o-Chlorobenzophenone readily undergoes Bayer-Williger oxidation to yield phenyl o-chlorobenzoate [1]; o-bromobenzophenone and, especially, o-iodobenzophenone undergo this reaction only with difficulty [2] and may react with peracids in another manner. Thus, in our earlier work [3], we showed that the oxidation of o-bromobenzophenone by sodium persulfate in acetic anhydride in the presence of H_2SO_4 and $Et_2O \cdot BF_3$ at $-30^{\circ}C$ gives a low yield of the 10-oxodibenz[b,e]brominium salt. This reaction apparently proceeds through a bromoso compound which is immediately cyclized to the bromonium salt



In the present work, we clarified the behavior of o-iodobenzophenone under the same conditions. In this case, in contrast to the findings of Odaira et al. [2], the Bayer-Williger oxidation of the ketone does not proceed at all (even traces of o-iodobenzoic acid or the corresponding phenyl benzoate were not detected) and the action of the oxidizing agent is directed exclusively toward the iodine atom to give the corresponding iodoso derivative (I), which, under the reaction conditions is partially cyclized to give 10-oxodibenz[b,e]iodinium bisulfate (II)



Iodosobisulfate (I) is readily soluble in water but has low solubility in ether, CHCl₃, and CH₂Cl₂ and is insoluble in hydrocarbons (Table 1). It is resistant to the action of peracids and does not undergo Bayer-Williger oxidation even at 40°C, probably since the very bulky ortho substituent completely blocks the CO group and hinders attack of the peracid molecule. On the other hand, the cyclization of (I) to an iodonium ion by the action of concentrated sulfuric acid at 20°C proceeds very slowly since the carbonyl group significantly hinders the electrophilic attack of the iodoso group, especially toward the ortho position relative to the CO group. The cyclization of (I) to the 10-oxodibenz[b,e]iodinium cation may be accomplished in 64% yield only by maintaining (I) for 4 h in concentrated sulfuric acid at 130°C. On the other hand, the condensation of (I) with benzene in the presence of concentrated sulfuric acid proceeds even at 20°C and leads to the formation of the o-benzoyldiphenyliodonium salt with a trace of (II)

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TABLE	TABLE 1									
- pu	Yield, %	mp, °C	Found Calculated, %			$\mathbb{R} \nu$, cm ⁻¹	PMR δ, ppm, rela-	Chemical		
Con			C	н	N		tive to TMS	formula		
(I)	65	148-150 (dec.)				1030 и 1205 (HSO ₄ -), 1590 (arom. ring) 1675 (CO), 2430-3550 (OH)		C13H11O9S2		
(I I I)	72	208-210 (from ethanol)	41,24 41,09	2,85 2,66			7,97m (8H) 4,43\$ (2H)	C13H10BF4I		
(IV)	77	224-227 (from ethanol)	39,93 39,61	2,18 2,03		1675 (CO), 1595 (arom. ring)	7,81–8,77 m	C ₁₃ H ₈ BF ₄ IO		
(V)	92 (from (IV))	237-239	45,61 45,54	2,56				C ₁₃ H ₈ ClIO		
(VI)	94 (from (IV)) 64 (from (I)) 73 (from (III))	172–173	36,05 35,94	1,83 1,86				C ₁₃ H ₈ I ₂ O		
(VIII)	89	256—256,5	39,75 39,74	2,12 2,09	9,15 9,76	1620 (C=N), 1590 (arom. ring) 1515, 1350 (NO ₂), 3410 (NH)		C ₁₉ H ₁₂ BF ₄ IN ₄ O ₄		
(IX)*	48	158-160	48,02 48,35	3,18 2,99				C ₁₉ H ₁₄ BF ₄ IO		

*o-Benzoyldiphenyliodonium tetrafluoroboride.



We have also obtained 10-oxodibenz[b,e]iodinium salts by the oxidation of the methylene group in 10H-dibenz[b,e]iodinium tetrafluoroboride (III) by CrO_3 in acetic acid in the presence of concentrated sulfuric acid



Exchange reactions of (II) also yielded other salts of this cation, namely, the tetrafluoroboride (IV), chloride (V), and iodide (VI).

The structure of the 10-oxodibenz[b,e]iodinium cation was demonstrated by the thermolysis of the iodide which gives, as in the case of other iodonium salts containing the onium atom in a six-membered ring [4], o,o'-diiodobenzophenone (VII) and <10% fluorenone and 1iodofluorenone (as indicated by gas-liquid chromatography) and iodine is liberated.

The structure of the cation was also confirmed by the formation of the corresponding 2,4-dinitrophenylhydrazone (VIII). We were unable to obtain other carbonyl group derivatives since the action of nucleophiles stronger than 2,4-dinitrophenylhydrazine such as hydroxylamine and semicarbazide is directed primarily not toward the carbonyl group but

rather to the onium site, leading to cleavage of the C-I bond and decomposition of the salt

cation. We also were unable to obtain the oxime of the 10-oxodibenz[b,e]iodinium cation by the nitrosation of (III) at the methylene group: both isoamyl nitrite and nitrosylsulfuric acid at about 20°C do not alter the salt. Only (VI) was obtained as the product of the reaction of (III) with nitrosylsulfuric acid at 130°C over 4 h



We also studied the behavior of 10-oxodibenz[b,e]iodinium salts under the conditions of the Bayer-Williger reaction. Doering and Speess [5] have reported that 4,4'-dinitrobenzo-phenone, containing strong electron-withdrawing substituents in both aromatic rings, which usually hinder this reaction, undergoes 50% oxidation by the action of Bayer-Williger reagents (40% AcO₂H and concentrated sulfuric acid) even at 20°C over 0.5 h. Thus, we were justified in our expectation that salt (IV) would also undergo this reaction. However, as seen in Table 2, the oxidation of (IV) by 50% AcO₂H in anhydrous acetic acid in the presence of a small amount of concentrated sulfuric acid virtually does not proceed even at 60°C. This salt is also not altered in the absence of sulfuric acid in anhydrous CH₂Cl₂ by the action of trifluoroperacetic acid, which is even a stronger reagent. On the other hand, peracetic acid in concentrated sulfuric acid gives 27% decomposition of (IV) at 20°C over two months, while persulfuric acid in concentrated sulfuric acid gives 70% decomposition in 48 h. In both cases, o-iodobenzoic acid was isolated as the reaction product. The phenol fragment could not be separated.

Under these conditions, the 10-oxodibenz[b,e]iodinium cation apparently initially adds to the carbonyl group of the peracid molecule, i.e., the first step of the Bayer-Williger reaction occurs*



However, the rearrangement itself is then preceded by the acidolysis of intermediate (X) which occurs with breakage of the C-I bond. The complex (XI) which is thus formed readily gives the normal Bayer-Williger oxidation products (o-iodobenzoic acid and pyrocatechol). Under the reaction conditions, pyrocatechol undergoes further transformations, namely, sulfuration, oxidation, and tar formation and thus it could not be isolated and identified.

It is not excluded that the rearrangement of (X) occurs intramolecularly. This may be facilitated by the nonplanar structure of the 10-oxodibenz[b,e]iodinium cation which is similar to that of the cation described by Gusev and Struchkov [6]

*Special experiments showed that 10-oxodibenz[b,e]iodinium salts are not decomposed by sulfuric acid in the absence of oxidizing agents.

TABLE	2
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(TV).	Oxidizing	Solvent,	Conc. H,SO,		Time,	Isolated, $g(\%)$	
g(mmoles)	agent, ml (mmoles)	m1	m l	т., ℃	h	(VI)	(XI) ^a
0,2(0,5)	50% AcO ₂ H 0,15 (1,0)	AcOH 3	0,75	20 60	48 4	0,19 (90)	-
0,74 (1,9)	CF3CO3H ^b 0,85(6,5)	${{\rm CH_2CI_2}^{\rm C}}^{\rm C}_{13}$	-	40	5,5	0,73 (94)	· _
0,62(1,6)	CF ₃ CO ₃ H ^d 0,95(5)	CH ₂ Cl ₂ C 11	-	40	15	0,66(100)	-
1,35(3,4)	40% AcO ₂ H 2(10,5)	-	4	20	2 months	1,0(70,5)	0,23(27)
0,55(1,4)	30% H ₂ O ₂ 1 (8,8)	_	62	20	48	0,14(24)	0,24(69)

^a(XI) is o-iodobenzoic acid.

^bObtained from 0.2 ml 84% $\rm H_2O_2$ and 0.65 ml (CF_3CO)_2O in 1 ml CH_2Cl_2.

CIn the presence of 1 g Na₂HPO₄.

 $^{\rm d}Obtained$ from 0.15 ml 84% $\rm H_2O_2$ and 0.8 ml (CF_3CO)_2 in 0.75 ml CH_2Cl_2.



The alternative reaction pathway entailing a Bayer-Williger rearrangement without prior cleavage of the C-I⁺ bond, which should give the intermediate formation of salt (XII), apparently does not occur since the formation of this salt in this reaction has never been established although salts of this type are known to be rather stable in acid media in the presence of an oxidizing agent [7, 8]



 $\mathbf{R} = \mathbf{Ac}, \ \mathbf{SO}_{3}\mathbf{H}$

The yields, physical constants, and analytical data for all compounds described for the first time are given in Table 1.

EXPERIMENTAL

<u>1. Oxidation of o-Iodobenzophenone by $Na_2S_2O_8$ in Conc. H_2SO_4 .</u> A sample of 20 ml Et₂O[•] BF₃ was added to a solution of 9.62 g o-iodobenzophenone^{*} in 104 ml acetic anhydride at from -25° to -30° C, followed by the dropwise addition of 260 ml conc. H_2SO_4 and, finally the addition of 28.5 g $Na_2S_2O_8$ in small portions. The mixture was stirred at this temperature for 3 h and then at 20°C for one week and then poured into 500 g ice. The aqueous solution obtained was repeatedly extracted with 3:1 MeNO₂-CHCl₃. The organic extracts were washed with a small amount of water and evaporated in vacuum to dryness to yield 10.7 g (65%) (I) as an oil which is difficult to crystallize. The addition of CH₂Cl₂ gave 4.15 g colorless, odorless crystals with mp 148-150°C (dec.) which has the same IR spectrum as oil (I). Iodometric titration indicated 93.7% purity for the product.

After extraction of (I), the aqueous solution was treated with Na_2SO_3 and then with NaI. The precipitate of (VI) was washed with water, ethanol, acetone, ether, and dried. The yield was 1.5 g (11%).

*Obtained by the pathway: anthranilic acid \rightarrow o-iodobenzoic acid [9] \rightarrow o-iodobenzoyl chloride [10] \rightarrow o-iodobenzophenone [9].

2. Attempt to Carry Out the Bayer-Williger Oxidation of o-Iodobenzophenone. A solution of 0.73 g (I) in a mixture of 14 ml Ac₂O 0.7 ml 29% peracetic acid, and 3.5 ml Et₂O•BF₃ was maintained for 48 h at 40°C and then 1 ml concentrated sulfuric acid was added at 20°C. The reaction mixture was maintained for an additional 10 days at 40°C and then poured onto 100 g ice. The aqueous solution obtained was treated with Na₂SO₃ and extracted with ether. The ethereal solution yielded 0.38 g (85%) o-iodobenzophenone (identified by thin-layer chromatography and IR spectroscopy). After extraction of o-iodobenzophenone, the aqueous layer was treated as in experiment 1 to yield 0.07 g (11%) (VI) which was identified by IR spectroscopy.

<u>3. Cyclization of o-Iodobenzophenone</u>. A solution of 1.02 g (I) in 12 ml conc. H_2SO_4 was maintained for 4 h at 130°C and then poured onto 100 g ice. The aqueous solution of (II) obtained was washed with ether to remove nonsalt reaction products and the addition of NaI gave a precipitate of 0.67 g (64%) (VI).

4. o-Benzoyldiphenyliodonium Tetrafluoroboride (IX). A sample of 10 ml benzene was added dropwise to a solution of 1.56 (I) in 10 ml conc. H_2SO_4 at -15°C. The mixture was stirred vigorously at 20°C for two days and poured onto 100 g ice. The benzene layer was separated. The aqueous layer was saturated with NaBF4 and repeatedly extracted with 3:1 MeNO₂-CHCl₃. The extracts were evaporated to minimal volume and a sample of (IX) containing a trace of (IV) was precipitated by ether. The product was recrystallized thrice from ethanol to give 0.8 g (48%) (IX).

<u>5. 10H-Dibenz[b,e]iodinium Tetrafluoroboride (III)</u>. An aqueous solution of 10H-dibenz[b,e]iodinium bisulfate (150 ml) obtained from 5.25 g o-iododiphenylmethane* according to Heyl [12] was saturated with NaBF4. The precipitate of (III) was filtered off and the filtrate was extracted with 3:1 MeNO₂-CHCl₃. The organic extracts were evaporated in vacuum to a small volume and an additional amount of (III) was precipitated by the addition of ether. The total yield of (III) was 5 g (72%). For purification, the salt was dissolved in water and the corresponding iodide was precipitated from solution. This iodide was thoroughly

washed with water, ethanol, acetone, and ether, and treated with excess $[Et_30]BF_4$ in MeNO₂ in order to reconvert it to (III).

<u>6.</u> 10-Oxodibenz[b,e]iodinium Salts. a) Tetrafluoroboride (IV). A solution of 2.4 g CrO₃ in 20 ml acetic anhydride was added slowly with stirring to a solution of 2.7 g (III) in a mixture of 54 ml acetic acid and 2.16 ml conc. H_2SO_4 at 70°C. After stirring for 6 h at 70°C, the excess acetic anhydride and acetic acid were distilled off in vacuum and the residue was diluted to 200 ml with water and heated until the precipitate of (II) dissolved. The hot aqueous solution was saturated with NaBF₄ and cooled. The precipitate of (IV) was separated and the filtrate was treated as in experiment 5. The total yield of (IV) was 2.16 g (77%).

b) Chloride (V) was precipitated from a solution of 0.2 g (IV) in 100 ml water by the addition of saturated aqueous NaCl with a yield of 0.16 g (92%).

c) Iodide (VI) was precipitated under analogous conditions from 0.67 g (IV) with a yield of 0.69 g (94%).

7. Thermolysis of 10-Oxodibenz[b,e]iodinium Iodide. A sample of 0.4 g (VI) in a sealed ampul was heated at 180°C for 10 min. Upon cooling, the contents of the ampul was heated solved in chloroform. A sample of 20 ml water was added and the iodide liberated (7.6%) was titrated with aqueous sodium thiosulfate. The chloroform layer yielded 0.37 g of a mixture of o,o-diiodobenzophenone (VII), fluorenone, and 1-iodofluorenone. Recrystallization of the mixture from ethanol gave 0.3 g (77%) (VII), mp 106-107°C [13].

<u>8.</u> 2,4-Dinitrophenylhydrazone of 10-Oxodibenz[b,e]iodinium Tetrafluoroboride (VIII). A sample of 10 ml ethanol was added to a hot solution of 0.4 g 2,4-dinitrophenylhydrazine in 10 ml freshly prepared 40% HBF₄ followed by the addition of 0.1 g (IV) in 1.5 ml ethanol. The mixture was heated at reflux for 36 h and then evaporated in vacuum almost to dryness. The residue was treated with 10 ml MeNO₂ and filtered. A sample of 0.13 g (89%) (VIII) was precipitated from the filtrate by ether.

<u>9. Reaction of 10H-Dibenz[b,e]iodinium Tetrafluoroboride with Nitrosylsulfuric Acid.</u> A sample of 1.025 g (III) was added gradually to a solution of 0.81 g NaNO₂ in 20 ml conc. H_2SO_4 at from -5° to 0°C. The mixture was heated for 4 h at 125-135°C, then poured onto 100 g ice, and treated as in experiment 1 to yield 0.86 g (73%) (VI).

*Obtained by the reduction of o-iodobenzophenone according to blackwell [11].

<u>10.</u> Reaction of 10-Oxodibenz[b,e]iodinium Tetrafluoroboride with Peracetic Acid. a) In acetic acid. A sample of 0.15 ml 50% peracetic acid was added dropwise to a solution of 0.2 g (IV) in a mixture of 3 ml acetic acid and 0.75 ml conc. H_2SO_4 at 0-5°C. The mixture was stirred for 48 h at 20°C and for 4 h at 60°C. The mixture was then diluted with a 10-fold volume of water and the solution obtained was treated initially with Na_2SO_3 and then with solid NaI. The precipitate was washed with water, ethanol, ether, and dried. The IR spectrum of the substance obtained was identical to that of (VI). The yield was 0.19 g (90%).

b) In conc. H_2SO_4 . A solution of 1.35 g (IV) in 4 ml conc. H_2SO_4 was combined with cooling with 2 ml 40% peracetic acid. This mixture was maintained for two months at 20°C and then poured into 100 ml ice water. The precipitate formed was extracted with benzene. Evaporation of the benzene in vacuum gave 0.23 g (27%) o-iodobenzoic acid with mp 157-159°C [9]. The aqueous solution was treated as in experiment 10a. The yield of (VI) (identified by its IR spectrum) was 1 g (70.5%).

<u>11. Reaction of 10-Oxodibenz[b,e]iodinium Tetrafluoroboride with Trifluoroperacetic</u> <u>Acid.</u> A sample of $(CF_3CO)_2O$ was added dropwise with external ice cooling to a vigorougly stirred emulsion of 0.15 ml 84% H₂O₂ in 0.75 ml CH₂Cl₂. After 15 min, the solution of CF₃-CO₃H thus prepared was gradually added at 20°C to a sample of 0.62 g (IV) and 1.0 g Na₂HPO₄ in 10 ml CH₂Cl₂. The reaction mixture was heated at reflux with stirring for 15 h. The inorganic precipitate was then filtered off and washed with CH₂Cl₂. The filtrate, which was shown by thin-layer chromatography not to contain nonsalt products, was evaporated in vacuum to dryness. The residue was dissolved in water. The further treatment and identification of the product were carried out as in experiment 10a. The yield of (VI) was 0.66 g (quantitative).

<u>12.</u> Oxidation of 10-Oxodibenz[b,e]iodinium Tetrafluoroboride by Hydrogen Peroxide.* A solution of 1 ml 30% H₂O₂ in 45 ml conc. H₂SO₄ was added slowly to a solution of 0.55 g (IV) in 17 ml conc H₂SO₄ at 5-10°C and maintained at 20°C. The reaction mixture gradually turned from yellow to cherry red. After 48 h, the mixture was poured onto 100 g ice and treated as in experiment 10b. The yield of o-iodobenzoic acid with mp 157.5-159°C was 0.24 g (69%) and the yield of (IV) was 0.14 g (24%).

A solution of 1.03 g (IV) in 30 ml conc. H_2SO_4 and 2 ml water was maintained for 48 h at 20°C and poured onto 200 g ice. The precipitate of (VI) was identified by its IR spectrum. The yield was 1.08 g (97%). o-Iodobenzoic acid was not detected.

CONCLUSIONS

1. The first reported 10-oxodibenz[b,e]iodinium salts were obtained by the oxidative cyclization of o-iodobenzophenone and the oxidation of the methylene unit in the 10H-dibenz-[b,e]iodinium cation. Some of the reactions of these compounds were studied.

2. o-Iodobenzophenone bisbisulfate was isolated and shown not to undergo the Bayer-Williger oxidation but undergoes ready condensation with benzene to form o-benzoyldiphenyliodonium salts and cyclizes upon heating to the 10-oxodibenz[b,e]iodinium cation.

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INFLUENCE OF THE RADICAL CENTER ON THE BASIC HYDROLYSIS REACTION OF 4-DIHALOMETHYL-3-IMIDAZOLINE-3-OXIDE

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We previously discovered the influence of the radical center (RC) on the reactivities of functional groups not directly connected to it in the instance of deoxygenation of the nitrone group in derivatives of 3-imidazoline-3-oxide [1]. Study of the chemical properties of the paramagnetic (Ia, b) and diamagnetic (IIa, b), (IIIa, b) derivatives of 3-imidazoline-3-oxide containing a dihalomethyl group showed that the nitroxyl RC has a substantial influence on its reactivity in the basic hydrolysis reaction. This influence is manifested either in a significant change in the reaction rate or in a change in its direction.



The choice of diamagnetic derivatives containing l-methyl-(IIa) [2], (IIb) and l-nitroso groups (IIIa, b) is dictated, first by the various electronic influences on the reaction center*, and second by their stabilities to oxidation to radicals (Ia) and (Ib) under the reaction conditions. On the strength of the second reason hydroxylamines (IVa) and (IVb) were excluded from consideration as diamagnetic analogs of radicals (Ia) and (Ib).

By the reaction of NaOH in aqueous methanolic solution the diamagnetic derivatives (IIa) (240 h) and (IIb) (120 h) (monitoring during the course of the reaction and at the end was carried out by TLC) were converted into acetal (V) (yield 60-90%) and to the carboxylic acid (VI) (1-2%), the 1-nitroso derivative (IIIb) (70 h) to the acetal (VII) (40%) and the acids (VIII) (20%) and (IX) (15%)



*Results of the study of the electronic influence of substitution in position 1 on the reaction center by the method of ¹³C NMR spectra, and also by measurement of the pK_{α} of 4-carboxylic acids will be published separately.

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