1H-ISOBENZOFURYLIUM (PHTHALYLIUM) SALTS (A REVIEW)

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Data on the synthesis, reactions, structure, and stability of phthalylium salts are correlated.

One of the most important problems in the chemistry of carbenium ions is the dependence of their relative stability and reactivity on structure. In this respect, the five-membered cyclic heterocarbenium ions with heteroatom, viz., the 1H-isobenzofurylium (phthalylium) ions are extremely convenient materials for study; they can be synthesized with quite a large variety of substituents, their stability is susceptible to quantitative estimation, and their quantitative properties are extremely sensitive to structural change. Aside from the value of phthalylium ions in the development of theoretical organic chemistry, work in this direction is stimulated by the need to solve practical problems. Many phthalylium salts and covalently structured compounds based on phthalylium ions are used as dyes [1], medicinals [2-4], and phototropic compounds [5], and further research in this area could be extremely fruitful.

1. METHODS OF SYNTHESIS

The most important method of synthesizing phthalylium ions (R^1 = Alk, Ar, ArCH=CH–) is the ionization of 1-hydroxyphthalanes II (R^2 = H) in acid medium. Thus, by the action of $HClO_4$, picric acid, or Lewis acids stable crystalline salts containing phthalylium ions were separated: perchlorates [6-13], picrates [7], tetrachloroferrates (III) [6-9, 14], hexachloroantimonates (V) [9, 14], hexachlorostannates (IV) [6-8], and tetrafluoroborates [15]. It should be noted that in the case of the hydroxyphthalanes (II) that contain an acetylene group (R^1 = $R^3C{\equiv}C$–, R^2 = H) at position 2 of the heterocycle, reaction with $HFeCl_4$, $HClO_4$, or $HSbCl_6$ causes an acetylene–allene rearrangement, and the resulting salts have the structure of phthalylidene ketone salts [16-20].

In the synthesis of phthalylium salts ethers of the hydroxyphthalanes II (R^2 = Alk) can also be used [9, 21-23].

The action of acids causes heterolytic cleavage not only of the C–OR^2 bond in hydroxyphthalanes and their ethers (II), but also the C–NR^4R^5 bond in amino derivatives of phthalanes (III) that contain aromatic (R^4 = H, R^5 = Ar) [24], aliphatic (R^4, R^5 = Alk), or heterocyclic (NR^4R^5 = pyrrolidino, piperidino, morpholino) [25] radicals.

In the 1-substituted phthalanes the $C_{(1)}$–C bond does not as a rule undergo heterolysis. But in some derivatives, e.g., 1-phthalylphenylnitromethanes IV (R^6 = C_6H_5) and 1-phthalylnitroacetonitriles IV (R^6 = CN), that contain electron acceptor groups, acidic reagents cause the cleavage of the strongly polarized carbon–carbon bond to form phthalylium ions (I) [26]. The action of perchloric acid on 1-alkylidene phthalanes (V) gives 1-alkylphthalylium perchlorates I (R^1 = CH_2R^7) [1] (see scheme on following page).

Phthalylium salts form from hydrobases, viz., the 1H-phthalanes VI by oxidation with Lewis acids [27], and by exchange reactions with active hydride ion acceptors, e.g., tritylium hexachloroantimonate [14, 27]. As shown in [27], ortho substituents in the 1-Ar group do not sterically hinder the oxidation–reduction conversions that involve 1H-phthalanes.

Phthalylium salts of I containing an alkoxy group (R^1 = C_2H_5O) at position 1 can be synthesized by alkylation of phthalanes VII with triethyloxonium tetrafluoroborate [21, 28, 29]. The low basicity of phthalides prevents alkylating agents such as dimethyl sulfate and methyl iodide from being used for this purpose [28].

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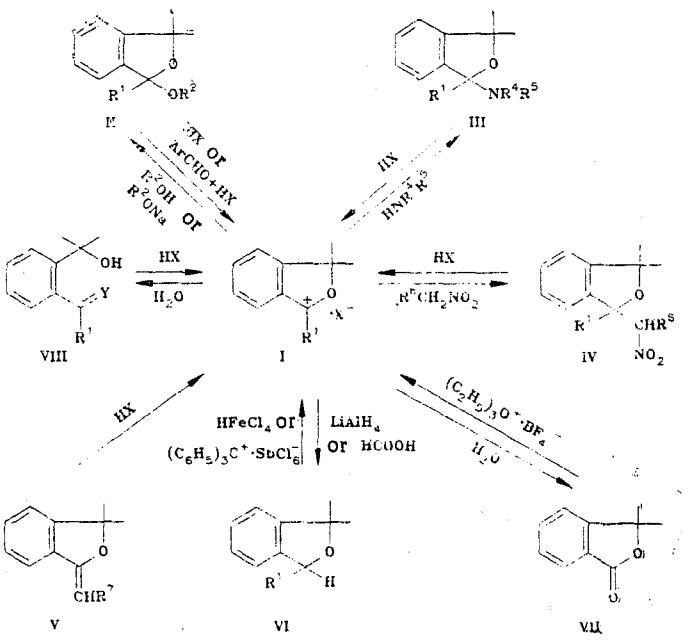
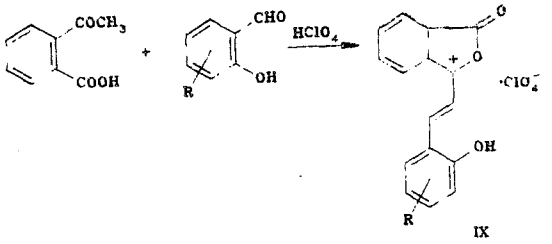


Phthalylium salts also form by the action of $HFeCl_4$, $HSbCl_6$, or $HClO_4$ on o-[dialkyl-(aryl)hydroxymethyl]phenyl aryl ketones VIII (Y = O, R^1 = Ar) [30, 31] and their oximes VIII (Y = NOH) [32].

1-Styryl substituted phthalylium ions (I, R^1 = ArCH=CH–) were synthesized by condensation of 1-methyl-1-hydroxyphthalane (II, R^1 = CH_3, R^2 = H) with aromatic aldehydes in acid medium [9, 33]. When o-acetylbenzoic acid was condensed with substituted salicylaldehydes in the presence of $HClO_4$, hydroxystyryl derivatives of 3-oxophthalylium (VX) were synthesized [33]:

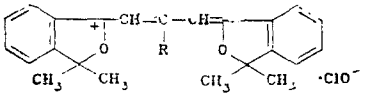


2. STRUCTURE OF PHTHALYLIUM IONS

The formation of phthalylium ions by the action of acids on pseudobases was demonstrated by analysis of the electron spectra of 1-hydroxyphthalanes in neutral and acidic solvents [10, 34, 35], and by the synthesis of salts [6-15]. Elemental analysis of the latter established unequivocally that the reaction of hydroxyphthalanes and acids proceeds with heterolytic cleavage of the C–OH bond by the equation: ROH + HX → RX + H_2O; consequently, the resulting cations are carbenium ions.

In contrast to the covalently structure hydroxyphthalanes, the phthalylium ions absorb in a longer wave region of the spectrum and are characterized by two absorption maxima of different intensities. The location of the less intense maximum around ~290 nm is practically independent of the nature of the substituents at $C_{(1)}$ and $C_{(3)}$ [36-38]. Analysis of the electron spectra of phthalylium ions and their sulfur analogs (thiophthalylium ions) or nitrogen analogs (isoindolinium ions) showed that this maximum is related to the presence of the heteronium grouping [37]. The location of the second absorption band is determined by the nature of the substituent at the positively charged carbon [11-13, 22, 35-43]. It was shown [13, 36-38] that the long wave absorption band undergoes a bathochromic shift with increase in the electron donor capability of the substituent at the para position of the 1-aryl group. Here a satisfactory correlation has been found of the wave numbers corresponding to this band with the Braun–Okamoto σ^+ constants of the substituents [13, 37, 38]. It should

be noted that the sensitivity of reaction series* to the effect of $C_{(1)}$ substituents on the long-wave band is independent of the nature of the $C_{(3)}$ substituents ($\rho \sim 4.9 \cdot 10^3$). Lengthening of the conjugation chain at position 1 (replacement in I of $R^1 = C_6H_5$ by $R^1 = C_6H_5CH{=}CH{-}$) causes a 78 nm bathochromic shift of the long-wave band [1, 9]. Any structural changes in the conjugated system are distinctly reflected in the location of this band, e.g., replacement of R = H by R = CH_3 in the X salts causes a 10 nm hypsochromic shift [1].



X

This set of data convincingly confirms the presence in phthalylium ions of a conjugated carbenium–oxonium grouping. The substituents at $C_{(3)}$, which are isolated from this grouping by the sp^3 hybridized carbon, do not significantly affect the location of the long-wave band [12, 13, 22, 36, 38].

The IR spectra of the phthalylium salts were compared with those of the respective pseudobases, the 1-hydroxyphthalanes [10, 44]. In going from the covalently structured compounds to the salts the band intensity decreases in the 920, 1020-1050, and 1150 cm^{-1} regions (C–O–C) and the intensity significantly increases in the 1400-1600 cm^{-1} region; this indicates an increase in the carbon–oxygen bond frequency and the appearance of a strong polar substituent.

The PMR spectra also confirm the conjugated carbenium–oxonium structure of the phthalylium ions. As has been shown [37], the spectrum of 3,3-dimethyl-1-para-tolylphthalylium perchlorate shows a weak-field shift of the proton signals of all alkyl groups as compared to the spectrum of the oxo compound. The shift of the signal of the methyl of the para-tolyl substituent is due to its conjugation with the cationic reaction center, while the shift of the gem-$C(CH_3)_2$ protons is due to the presence in the phthalylium ion of the electron acceptor grouping $-O^+=$ which decreases the electron density at $C_{(3)}$.

The molecular structure of 1-[2-(2-hydroxyphenyl)]vinyl-3,3-dimethylphthalylium perchlorate was studied by x-ray diffraction analysis [33]. The geometric parameters thus obtained and the calculations by the SSP MO method in the π-electron modification are evidence for strong delocalization of the positive charge on the cation.

3. CHEMICAL REACTIONS

The reactions of phthalylium salts with various nucleophilic reagents are the most typical and have been studied the most. Here, as a rule, the products of nucleophile addition to $C_{(1)}$ of the conjugated phthalylium ions are formed. Depending on the structure of the starting reagents and the reaction conditions, these reaction products can in a number of cases undergo further conversions to form acyclic compounds or to enlarge the ring; this is important in the synthesis of new heterocyclic systems.

3.1. Reactions with O-Nucleophiles

1-Aryl(styryl)phthalylium salts are easily hydrolyzed by aqueous salt solutions to form 1-hydroxy-1-aryl(styryl)phthalanes II (R^2 = H) [9, 12, 22, 36, 45, 46]. In the case of I salts with bulky substituents at position 1 (R^1 = mesityl, 9-anthryl) the final products are hydroxyphthalanes, the ketoalcohols VIII (Y = O) [30, 31].

Hydrolysis of 1-alkoxyphthalylium salts does not stop at the hydroxyphthalane stage, but gives the respective phthalides VII [47]. The labile 1-hydroxy-1-alkoxyphthalanes can be stabilized not only via cleavage of an alcohol molecule, but also by scission of the heterocycle. Thus, when an alcoholic solution of I salts ($R^1 = CH_3O$, C_2H_5O) is treated with 5% $NaHCO_3$ solution, along with phthalide VII the respective o-hydroxymethylbenzoate esters are also separated [23].

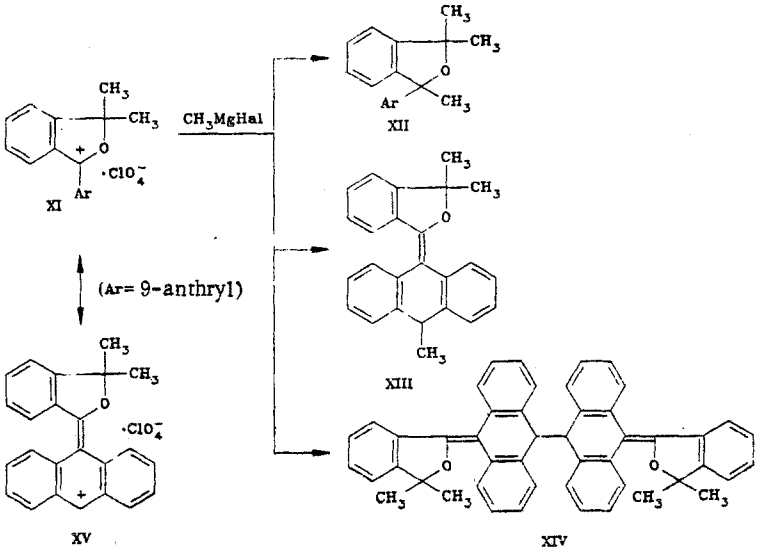
The reaction of phthalylium salts with alkali alcoholate forms ethers II ($R^2 = CH_3$, C_2H_5) [9, 21, 23, 29, 46-48]. It has been shown [23] that the reactions of 1-ethoxyphthalylium tetrafluoroborate with sodium methylate (in CH_3OH) and of 1-methoxyphthalylium tetra-

*For phthalylium ions, the concept "reaction series" here and subsequently means a series of compounds having a variable substituent at $C_{(1)}$ and constant substituents (within the limits of each series) at $C_{(3)}$.

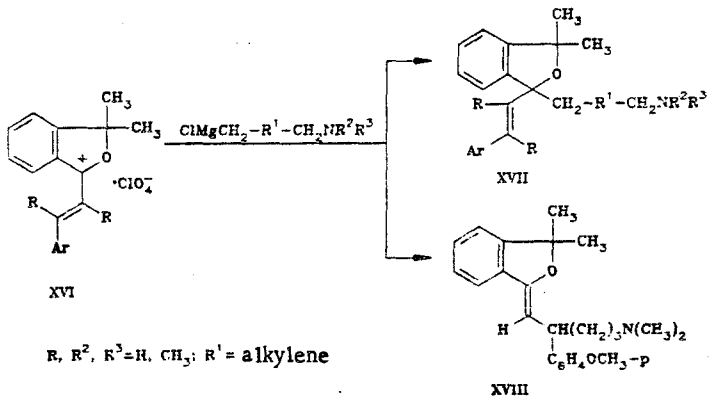
fluoroborate with sodium ethylate (in C_2H_5OH) give (beside the expected addition product, 1-methoxy-1-ethoxyphthalane), 1,1-dimethoxy- and 1,1-diethoxyphthalanes, respectively, in 80 and 70% yields. It should be noted that ethers II (R^2 = Alk) with R^1 = Ar are stable when stored, whereas ethers with R^1 = C_2H_5O are converted in time to phthalides VII.

3.2. Reactions with Nucleophiles

The reaction of methylmagnesium halide with 1-arylphthalylium perchlorate forms 1-methyl-1-arylphthalanes XII [1, 8, 15, 39-43, 45, 49, 50]. But in the case of salt XI (Ar = 9-anthryl), besides 1-methylphthalane XII (Ar = 9-anthryl) compounds XIII and XIV were also separated [31]. The yields of XII-XIV were 15, 53, and 15%, respectively. The similar course of the reactions was attributed to the low accessibility of position 1 of the heterocycle due to shielding by the bulky substituent, and the ready accessibility of the meso-position of the 1-anthryl group (resonance structure XV). These authors also conclude that phthalylium salts can react with a Grignard reagent both by ionic and free radical mechanisms, as indicated by the formation of compound XIV.

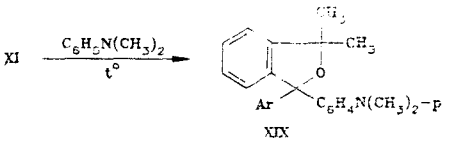


The main course of the reaction of 1-styrylphthalylium perchlorates XVI with aminoalkylmagnesium halide is nucleophilic addition of aminoalkyl to $C_{(1)}$ to form phthalanes XVII [51, 52]; however, in some cases the Grignard reagent can also add at the double bond. Thus, in the reaction of perchlorate XVI (R = H, Ar= p-$CH_3OC_6H_4$) with dimethylaminopropylmagnesium chloride, along with the main product XVII (R = H, R^1 = CH_2, R^2 = R^3 = CH_3, Ar = p-$CH_3OC_6H_4$) compound XVIII was separated in 19% yield [52].



The reaction of 1-arylphthalylium perchlorate with phenylnitromethane and nitroacetonitrile in the presence of organic bases forms (1-aryl-1-phthalyl)phenylnitromethanes IV (R^6 = C_6H_5) and (1-aryl-1-phthalyl)nitroacetonitriles IV (R^6 = CN) [26].

Heating 1-arylphthalylium perchlorate XI with excess dimethylaniline gives 1-aryl-1-p-dimethylaminophenylphthalanes XIX [31, 45, 50]:

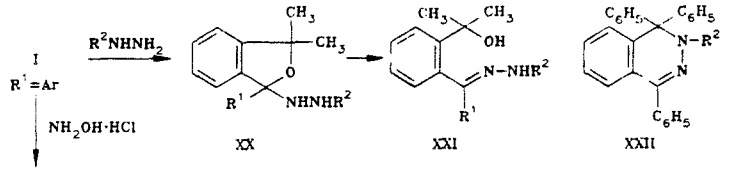


XIX

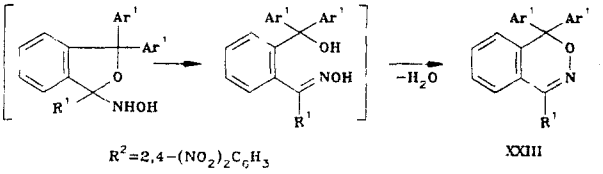
3.3. Reactions with N-Nucleophiles

The reaction of perchlorates XI with secondary aliphatic and cyclic amines forms the respective 1-aminophthalanes III [25, 53]. It was shown [25] that in ether–water medium the course of the reaction depends on the acidity of the cations and the basicity and steric structure of the amines. Thus, under these conditions 3,3-dimethyl-1-phenylphthalylium perchlorate did not react with most of the amines tested; only the hydrolysis product of the phthalylium salt, 1-hydroxy-3,3-dimethyl-1-phenylphthalane, was isolated. In those cases where aminophthalanes did form, the yields did not exceed 25%. When Ar = C_6H_5 was replaced by Ar = p-$CH_3OC_6H_4$, 1-aminophthalanes III were obtained with most of the amines and their yield was appreciably increased. But with amines such as dibutylamine, diisopropylamine, and 2,6-dimethylpiperidine in no case was the respective derivative obtained. The course of the reaction of phthalylium salts I (R^1 = C_6H_5, X = ClO_4) with primary aromatic amines (aniline, o- and p-toluidines) depends on the synthesis conditions. At room temperature in the presence of pyridine there is nucleophilic addition of amine to the conjugated carbenium-oxonium ion to form the amine N-derivative, 1-arylaminophthalanes III (R^1 = C_6H_5, R^4 = H, R^5 = Ar), whereas with heating the final products are the amine C-derivatives that are isomeric with the arylaminophthalanes, viz., 1-p-aminoarylphthalanes. With p-toluidine under these conditions compound III (R^1 = C_6H_5, R^4 = H, R^5 = p-$CH_3C_6H_4$) was obtained [24].

The reaction of phthalylium ions (using either the salts [50] or the hydroxyphthalanes in the presence of strong mineral acids that cause them to ionize [1, 7, 8, 11, 12, 31, 36, 39-43, 45, 49]) with 2,4-dinitrophenylhydrazine forms hydrazinophthalanes XX, which in the case of bulky radicals at $C_{(1)}$ can be converted to the acyclic isomers XXI [41, 45]. Boiling an alcoholic solution of 1-hydroxy-1,3,3-triphenylphthalane and 2,4-dinitrophenylhydrazine in the presence of concentrated hydrochloric acid gave phthalazine XXII, the product of intramolecular dehydration of a hydrazone like XXI [55].



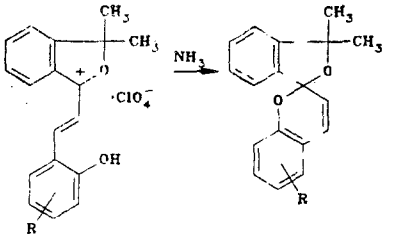
XX XXI XXII



R^2=2,4-$(NO_2)_2C_6H_3$ XXIII

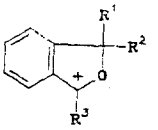
The formation of 1,1,4-triaryl-2,3-benzoxazines XXIII by the reaction of 1,3,3-triaryl-phthalylium ions with hydroxylamine also probably proceeds via the formation of oximinophthalane addition products followed by isomerization to the hydroxyoximes [56, 57].

When gaseous ammonia is passed through a suspension of perchlorate XXIV in benzene, spiropyranes of the 2-oxaindane series XXV form, that exhibit photochromic properties [5]:



XXIV XXV

TABLE 1. pK_{R+} Values of Phthalylium Ions

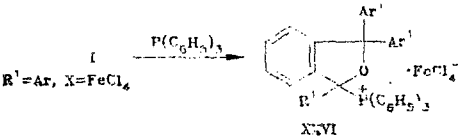


$R^1=R^2$	R^3	pK_{R+}	$R^1=R^2$	R^3	pK_{R+}
CH_3	CH_3	−2,46 [34]	CH_3	$2\text{-}BrC_6H_4$	−2,73 [10]
CH_3	C_6H_5	−1,71 [39], −1,77 [34]	CH_3	$3\text{-}BrC_6H_4$	−2,98 [43]
			CH_3	$4\text{-}BrC_6H_4$	−2,37 [43]
CH_3	$2\text{-}CH_3C_6H_4$	−0,31 [10], −0,29 [41]	CH_3	$3\text{-}FC_6H_4$	−2,86 [42]
			CH_3	$4\text{-}FC_6H_4$	−1,68 [42]
CH_3	$3\text{-}CH_3C_6H_4$	−1,48 [41]	CH_3	$4\text{-}(CH_3)_2NC_6H_4$	+4,94 [37]
CH_3	$4\text{-}CH_3C_6H_4$	−0,83 [34], −0,76 [41]	CH_3	$4\text{-}(C_2H_5)_2NC_6H_4$	+5,14 [37]
			CH_3	1-Naphthyl	−0,71 [35]
CH_3	$2\text{-}CH_3OC_6H_4$	−0,98 [10], −0,90 [40], −0,95 [67]	CH_3	2-Naphthyl	−1,46 [35]
			CH_3	$4\text{-}C_6H_5C_6H_4$	−1,44 [35]
			CH_3	Mesityl	+1,93 [30]
CH_3	$3\text{-}CH_3OC_6H_4$	−2,12 [40]	CH_3	9-Anthryl	+1,9 [31]
CH_3	$4\text{-}CH_3OC_6H_4$	+0,56 [34], +0,58 [40]	CH_3	$C_6H_5CH=CH-$	+1,08 [9]
			CH_3	9-Phenanthryl	−1,02 [45]
CH_3	$2\text{-}C_2H_5OC_6H_4$	−1,04 [10], −1,07 [67]	CH_3*	C_6H_5	−2,85 [13]
			CH_3*	$3\text{-}CH_3C_6H_4$	−2,58 [13]
CH_3	$4\text{-}C_2H_5OC_6H_4$	+0,58 [67]	CH_3*	$4\text{-}CH_3C_6H_4$	−1,91 [13]
CH_3	$2\text{-}ClC_6H_4$	−2,91 [10], −2,78 [39]	CH_3*	$4\text{-}CH_3OC_6H_4$	−0,60 [13]
			CH_3*	$4\text{-}ClC_6H_4$	−3,47 [13]
CH_3	$3\text{-}ClC_6H_4$	−2,96 [15, 39]	CH_3*	$4\text{-}(CH_2)_2NC_6H_4$	+3,58 [13]
CH_3	$4\text{-}ClC_6H_4$	−2,18 [39]	CH_3*	$4\text{-}(C_2H_5)_2NC_6H_4$	+3,99 [13]
C_2H_5	C_6H_5	−0,94 [11]	*iso*-C_3H_7	$3\text{-}CH_3C_6H_4$	+0,96 [12]
C_2H_5	$2\text{-}CH_3C_6H_4$	+0,72 [11]	*iso*-C_3H_7	$4\text{-}CH_3C_6H_4$	+1,64 [12]
C_2H_5	$3\text{-}CH_3C_6H_4$	−0,79 [11]	*iso*-C_3H_7	1-Naphthyl	+0,72 [12]
C_2H_5	$4\text{-}CH_3C_6H_4$	+0,05 [11]	*iso*-C_3H_7	2-Naphthyl	+0,58 [12]
C_2H_5	$2\text{-}CH_3OC_6H_4$	+0,03 [36]	*iso*-C_3H_7	$4\text{-}C_6H_5C_6H_4$	+0,84 [12]
C_2H_5	$3\text{-}CH_3OC_6H_4$	−1,45 [36]	C_6H_5	C_6H_5	−3,74 [68]
C_2H_5	$4\text{-}CH_3OC_6H_4$	+1,38 [36]	C_6H_5	$2\text{-}CH_3C_6H_4$	−2,27 [38]
C_2H_5	$3\text{-}ClC_6H_4$	−2,30 [36]	C_6H_5	$3\text{-}CH_3C_6H_4$	−3,21 [38]
C_2H_5	$4\text{-}ClC_6H_4$	−1,59 [36]	C_6H_5	$4\text{-}CH_3C_6H_4$	−2,74 [38]
C_2H_5	$3\text{-}BrC_6H_4$	−2,41 [36]	C_6H_5	$2\text{-}CH_3OC_6H_4$	−2,80 [38]
C_2H_5	$4\text{-}BrC_6H_4$	−1,76 [36]	C_6H_5	$4\text{-}CH_3OC_6H_4$	−1,06 [38]
C_2H_5	$3\text{-}FC_6H_4$	−2,20 [36]	C_6H_5	$4\text{-}ClC_6H_4$	−4,12 [38]
C_2H_5	$4\text{-}FC_6H_4$	−0,91 [36]	C_6H_5	$4\text{-}(CH_3)_2NC_6H_4$	+2,98 [66]
C_2H_5	$4\text{-}(CH_3)_2NC_6H_4$	+5,66 [66]	C_6H_5	$4\text{-}(C_2H_5)_2NC_6H_4$	+3,33 [66]
C_2H_5	$4\text{-}(C_6H_5)_2NC_6H_4$	+6,14 [66]	$4\text{-}CH_3C_6H_4$	C_6H_5	−3,22 [22]
C_2H_5	1-Naphthyl	−0,01 [11]	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	−2,49 [22]
C_2H_5	2-Naphthyl	−0,82 [11]	$4\text{-}CH_3C_6H_4$	$4\text{-}ClC_6H_4$	−3,83 [22]
C_2H_5	$4\text{-}C_6H_5C_6H_4$	−1,07 [11]	$4\text{-}ClC_6H_4$	C_6H_5	−4,51 [22]
iso-C_3H_7	C_6H_5	+0,71 [12]	$4\text{-}ClC_6H_4$	$4\text{-}CH_3C_6H_4$	−3,38 [22]
iso-C_3H_7	$2\text{-}CH_3C_6H_4$	+2,06 [12]	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	−5,27 [22]

*$R^2 = C_6H_5$.

3.4. Reactions with P-Nucleophiles

The reaction of triphenylphosphine and phthalylium tetrachloroferrates (III) forms stable phthalylphosphonium salts XXVI [58]:

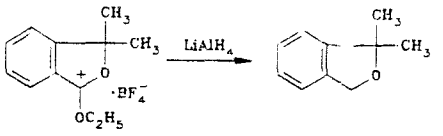


XXVI

3.5. Reduction Reactions

When phthalylium salts I (R^1 = Ar, X = $FeCl_4$) are treated with zinc dust in water–ether medium in the presence of HCl, diphthalides XXVII form by reductive dimerization [14, 59]. In contrast to their nonannelated analogs, the bisdihydrofuryls [60, 61], the latter are stable and do not tend to dissociate into radicals. The introduction of substituents at the ortho position of the 1-aryl group in order to sterically stabilize the intermediate radicals was unsuccessful [59].

1-Arylphthalylium tetrachloroferrates (III) are reduced by lithium aluminum hydride to 1H-phthalanes VI (R^1 = Ar) [27]. The reaction of 1-ethoxy-3,3-dimethylphthalylium tetrafluoroborate (XXVIII) with $LiAlH_4$ does not stop at the ethoxyphthalane stage, but forms 3,3-dimethylphthalane (XXIX) [47]:



XXVIII XXIX

Formic acid was also used as reducing agent [6, 8, 14, 27, 39-43, 49]. In that case, 1H-phthalanes VI were formed. It was shown [27] that the oxidizing activity of phthalylium ions changes in the same direction as their acidity. The action of HCOOH on 1,3,3-trimethylphthalylium perchlorate gives the salt X (R = H) [1].

Substances such as 1,3-dimethyl-2-phenylbenzimidazoline [14, 27], 1,2,4-triphenyl-1,2-dihydrophthalazine [62], and 3,3-dimethyl-2-phenyl-1-p-anisylisoindoline [63] that contain labile hydride hydrogens can also be used to reduce phthalylium salts. The reaction forms phthalanes VI and the respective benzimidazolium, dihydrophthalazinium, or isoindolinium salts. Attempts to use 2,3,3-triphenyl-1-arylisoindolines as hydride ion donors were unsuccessful [64].

3.6. Other Reactions

As exemplified by 1,3,3-trimethylphthalylium perchlorate, it was shown that the hydrogens of a methyl at position 1 are highly mobile. The perchlorate condenses easily with aromatic aldehydes to form 1-styrylphthalylium perchlorates I (R^1 = ArCH=CH–) [1, 9, 52, 65], and with acetic anhydride and ethyl orthoformate to form cyanine dyes X (R = CH_3 and R = H, respectively) [1, 65].

Tetrafluoroborate XXVIII takes part in exchange reactions with 1-ethoxy-1-ethylthio-3,3-dimethyl(phenyl)thiophthalanes to form ether II (R^1 = C_2H_5O, R^2 = C_2H_5) [47].

The action of sodium iodide in acetonitrile on 1-ethoxyphthalylium tetrafluoroborate gives phthalide, and as a byproduct ethyl o-iodomethylbenzoate [21].

When phthalylium tetrachloroferrate I is boiled with 57% $HClO_4$, the $FeCl_4$ anion (X) is easily replaced by ClO_4 [37].

4. STABILITY OF PHTHALYLIUM IONS

An important feature of phthalylium ions that distinguishes them from many other types of cyclic cations is the possibility of quantitative study of acid–base conversions in which they are involved; such reactions are not complicated by side reactions and are reversible (except for the 1-alkoxyphthalylium salts, see p.1051). Over a definite acidity range there is an equilibrium between the carbocations and the corresponding pseudobases [34, 35]: $R^+ + H_2O \underset{K_{R^+}}{\rightleftarrows} ROH + H^+$. In the case of phthalylium ions that have a dialkylamino group in the 1-aryl substituent, the solution contains ammonium ions in addition to the carbenium ions and the hydroxy compounds [37, 66]: $R^+ + H_2O \underset{K_{R^+}}{\rightleftarrows} ROH + H^+ \underset{K_a}{\rightleftarrows} HR^+OH$. A large number of publications have been devoted to the stability of phthalylium ions (pK_{R^+} values were determined by spectrophotometry) and the effect of various structural segments on stability and reactivity (Table 1).

Phthalylium ions are about 1/10 as stable as the analogously structured thiophthalylium ions [37, 44, 69], and 10^{-9} as stable as the isoindolinium ions [37, 70]; this convincingly demonstrates the participation of the heteroatom in ion stabilization and confirms the presence of the carbenium heteronium grouping. But the change of pK_{R^+} within the group of phthalylium ions over quite wide limits indicates that cation stability is not determined by the heterocyclic grouping only. The substituents in the heterocycle also take part in positive charge delocalization.

Substituents located alpha to the heteroatom and joined directly to a carbon carrying a positive charge have a significant effect on phthalylium ion stability: electron donor

substituents stabilize the ions, while electron acceptor substituents promote hydrolysis. The replacement of aryl by methyl, which shows only an inductive effect, reduces cation resistance in hydrolysis; lengthening the conjugation chain (replacement of $R^3 = C_6H_5$ by $R^3 = C_6H_5CH{=}CH{-}$) increases cation stability.

In a quantitative estimate of the effect of substituent in the 1-phenyl group on phthalylium ion stability, it was shown [71, 72] that the Hammett σ-constants are suitable for describing the effect of meta substituents as well as p-CH_3, p-F, p-Cl, and p-Br which do not have an appreciable tendency to undergo conjugation. The pK_{R^+} values of all the ortho and para substituents with distinct electron donor properties (CH_3O, C_2H_5O, and especially $(CH_3)_2N$ and $(C_2H_5)_2N$) deviate from the pK_{R^+}–σ straight line.

The electrophilic Braun–Okamoto σ^+ constants reflect quite fully the effect of direct polar conjugation of the above-mentioned para substituents with the reaction center [13, 37, 38]. In this case, it has been shown [13, 38] that the sensitivity of the reaction series to the effects of meta and para substituents in the 1-aryl group is practically independent of the nature of the substituents at position 3 (ρ ~ 3.7).

The effect of ortho substituents on the pK_{R^+} of phthalylium ions is ambiguous; in all the reaction series o-CH_3 increases cation resistance to hydrolysis as compared with the para isomer, whereas o-CH_3O, o-C_2H_5O, o-Cl, and o-Br decrease it. The effect of o-tolyl is due to the +I effect of methyl, which decreases the fractional positive charge on $C_{(1)}$ of the cation, and increases the hydroxy mobility in the pseudobases that are in equilibrium with the cations [10]. The low pK_{R^+} values of phthalylium ions that have CH_3O, C_2H_5O, Cl, or Br in the ortho position of the 1-aryl substituent are due mainly to two circumstances: the –I effect of these groups that destabilizes the cations, and to the strong BMBC intermolecular hydrogen bonds between the hydroxyls in the 1-hydroxyphthalanes and the ortho substituents that stabilize the pseudobases [10, 38].

It was shown [73] that in the phthalylium ions series the "ortho effect" is due not to steric, but to electronic factors. A satisfactory single correlation was found between pK_{R^+} for ortho, meta, and para substituted compound and the σ^+_d constants [73, 74].

Substituents in position 3 of the heterocycle that are structurally removed from the reaction center have somewhat less effect on cation stability than substituents at $C_{(1)}$. This effect is inductive in nature [12, 22, 36, 38]. As the inductive effect of the substituent increases, so does cation stability. Exceptions are phthalylium ions with bulky groupings, e.g., iso-C_3H_7, at $C_{(3)}$. The stability of cations with these groups is due, besides the inductive effect, to an additional steric effect [22]. The effect of substituents at $C_{(3)}$ on phthalylium ion stability can be described quantitatively in a one-parameter equation by the Taft inductive σ* constants (ρ ~ 1.8) [22].

With increasing temperature, phthalylium ion stability decreases. It was shown [75] that the entropy factor makes the principal contribution to the change in free energy of carbocation hydrolysis.

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MASS SPECTROMETRIC DECOMPOSITION OF β-PHENYLOXIRANECARBOXYLIC ESTERS

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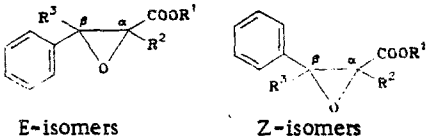
UDC 543.51:547.717

The electron-impact mass spectra of the E- and Z-isomers of the α,β-methyl substituted esters of β-phenyloxiranecarboxylic acids have been studied.

Ethylene oxide derivatives, particularly the β-phenyloxiranecarboxylic acids and their esters, are interesting materials for study in connection with their structural features, tendency to isomerize, and unequivocal course of their addition reactions; this has been responsible for the study of this class of compounds by various chemical and spectral methods [1-4]. However, the oxiranecarboxylic acids have been insufficiently studied by mass spectrometry. Hitherto, the electron-impact mass spectra have been considered for a series of ethyl and tert-butyl esters of β-phenyloxiranecarboxylic acids [5, 6]. The authors of [5] proposed an interpretation of those spectra on the basis of rearrangements of the molecular ion (M^+) before decomposition, opening of the oxirane ring at the C—C and C—O bonds, and migration of the substituents located at the α- and β-carbons. However, the methods used in [5] to establish the decomposition sequence were extremely limited in scope, due to the absence at that time of the DADI procedure and defocusing in the first field-free space.

The present work presents a chromato-mass spectrometric study of the E-isomer of α-methyl-β-phenyloxiranecarboxylic acid E-I, and the E- and Z-isomers of the oxiranecarboxylic esters II-V:



E-I $R^1=R^3=H$, $R^2=CH_3$; E-,Z-II $R^1=C_2H_5$, $R^2=CH_3$, $R^3=H$; E-,Z-III $R^1=R^2=CH_3$; $R^3=H$; E-,Z-IV $R^1=C_2H_5$, $R^2=H$, $R^3=CH_3$; E-,Z-V $R^1=C_2H_5$, $R^2=R^3=CH_3$

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