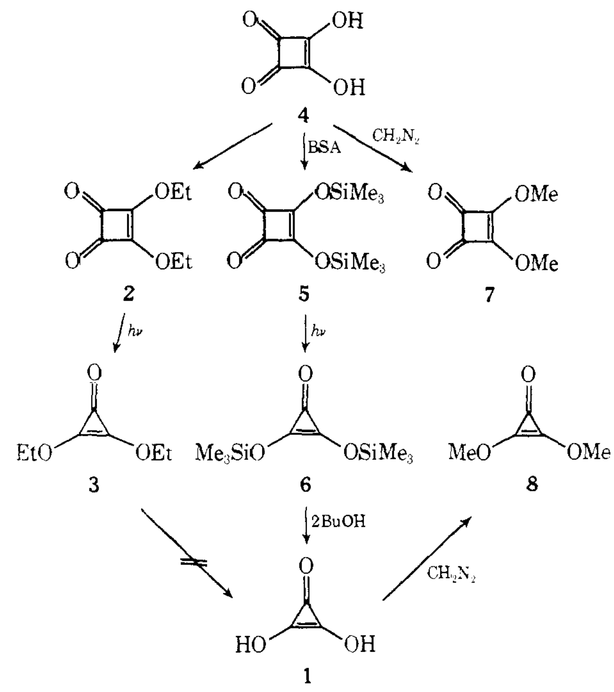
Scheme I



We report here the synthesis of deltic acid (dihydroxycyclopropenone, **1**) the conjugate acid of this anion.

Several unsuccessful attempts to synthesize the deltate dianion or deltic acid have been reported.[3-5] Recently, the photochemical extrusion of carbon monoxide from diethyl squarate (diethoxycyclobutendione, **2**) gave diethoxycyclopropenone (**3**), but **3** could not be hydrolyzed to **1**. Our route to **1** is similar but with the ethyl groups replaced by trimethylsilyl. The resulting bis(trimethylsiloxy)cyclopropenone (**6**) can be smoothly and quantitatively cleaved to deltic acid.

Squaric acid (**4**) was converted to bis(trimethylsilyl) squarate (**5**) by treatment with 2 equiv of bis(trimethylsilyl)acetamide in refluxing acetonitrile (Scheme I). Work-up by vacuum distillation gave **5** as a low-melting colorless solid: pmr δ 0.44; ir in CCl_4 ν 1820, 1745, 1610 cm^{-1}.[6] (*Cf.* diethyl squarate, 1810, 1735, 1605 cm^{-1}.)

Prolonged photolysis of **5** in hexane using a Vycor-filtered 450-W Hanovia lamp results in the disappearance of **5** and the formation of several products. After removal of solvent, Kugelrohr distillation at 60–70° (0.1 Torr) followed by crystallization from hexane at −78° and redistillation gave nearly pure bis(trimethylsiloxy)cyclopropenone (**6**), a low-melting solid, in ~15% yield. The identity of **6** is established by its infrared spectrum which shows characteristic cyclopropenone bands at ν 1870 and 1655 cm^{-1} (*cf.* diethoxycyclopropenone, 1890 and 1680 cm^{-1} [5]).

When an ethereal solution of **6** at −78° was treated with 2 equiv of 1-butanol, **1** was formed quantitatively as a white precipitate. *Anal.* Calcd for $C_3O_3H_2$: C, 41.87; H, 2.35. Found: C, 41.79; H, 2.43. The infrared spectrum of **1** in the 2000–4000-cm^{-1} region is quite similar to that of squaric acid,[7] showing a very strong broad band with a maximum near 2300 cm^{-1}. The structure of **1** was further established by its reaction with diazomethane to give dimethoxycyclopropenone (**8**) in 75% yield, identified by comparison of its ir spectrum (1890, 1680, 1305, 1030 cm^{-1}) with that of cyclopropenone **3** (1890, 1680, 1310, 1045 cm^{-1}).[5] High resolution mass spectroscopy showed the expected molecular ion at *m/e* 114.03168 (calcd for $C_5H_6O_3$, 114.03168). Squaric acid is converted analogously to dimethyl squarate by diazomethane.[8]

Deltic acid decomposes at *ca.* 180° but is unchanged by brief heating to 150°. The compound is stable to atmospheric moisture and oxygen but appears to decompose when dissolved in water–ethanol. The pH of the solution is initially *ca.* 1 but increases with time. Further studies of **1** and attempts to prepare the deltate dianion are currently in progress.

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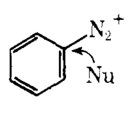
Onium Ions. XII.[1] Heterolytic Dediazoniation of Benzenediazonium Ions by Halide Ions in Pyridinium Polyhydrogen Fluoride Solution Giving Isomeric Halobenzenes Reflecting Ambident Reactivity of Benzenediazonium Ions and Intermediate Phenyl Cation as Well as Subsequent Aryne Formation

Sir:

The structure and reactivity of arenediazonium ions have been well reviewed.[2] In a recent article,[3] Zollinger reviewed the reactivity of arenediazonium ions and classified their reactions with nucleophiles (Nu) as (a) heterolytic dediazoniations at carbon-1 (*i.e.*, the ipso carbon) (I), (b) reactions with nucleophiles at the β-nitrogen (II), (c) substitution of nucleofugal leaving groups (such as nitro and halogens) in the ortho and para positions of the diazonium ions (III), and (d) aryne formation *via* the loss of N_2 and deprotonation (IV).



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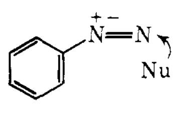
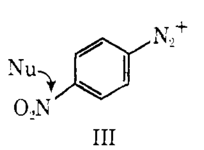
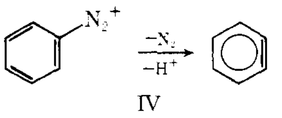


II



III

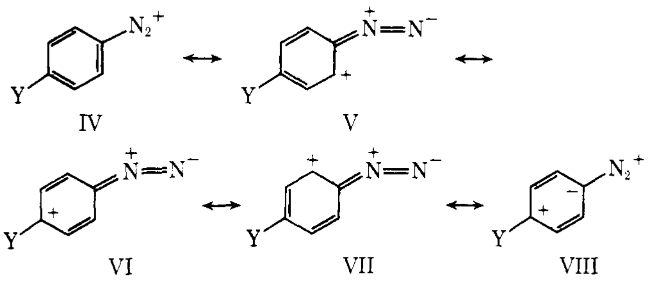


IV

Early examples of what now can be considered substitution of nucleofugal leaving groups can be found in the work of Hantsch (1896),[4a-c] Hirsch (1898),[4d] and Orton (1903)[5] but generally were given little attention. More recent examples of nucleofugal substitution were provided by the work of Meerwein[6] and Huisgen.[7] These reactions can be readily explained as nucleophilic aromatic substitutions (SNAr reactions), the diazonium group being an extremely strong withdrawing group, thus facilitating the displacement of suitable leaving groups.

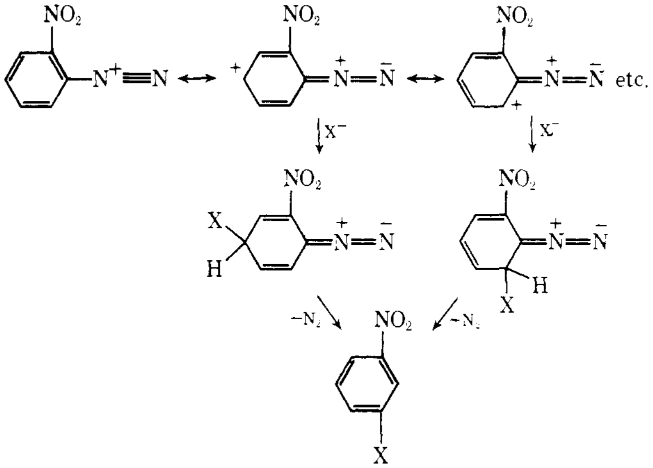
Dediazoniation of arenediazonium ions by halide ions was studied previously by Lewis[8] in aqueous media. We now report the observation of the heterolytic dediazoniation reactions of methyl-, nitro-, and α,α,α-trifluoromethylbenzenediazonium ions with halide ions in pyridinium polyhydrogen fluoride solution[9] which allow study of isomeric haloarene products. The parent benzenediazonium ion also gives halobenzenes in good yield and the novel dediazoniation reaction seems to be of general utility, also as a preparative method. When no alkali halides are added in the reaction, the benzenediazonium ions react more slowly at somewhat higher temperatures (80°) with the polyhydrogen fluoride–pyridine system to give fluorobenzenes.

The low nucleophilicity of pyridinium polyhydrogen fluoride is reflected by the observation that generally only less than 10% of fluoroarenes are formed in the reaction of arenediazonium ions with sodium chloride, bromide, or iodide present in the solvent system. There is no indication of evolution of HCl, HBr, or HI from the ionizing, but low nucleophilicity solvent. The reactions give unexpected and novel isomer distributions of haloarenes indicating the ambident nature of the arenediazonium ions, as well as the significance of intermediate aryne formation. The most striking feature of the reactions is that the heterolytic dediazoniation takes place not only at C_1 but with the halide ion attacking other ring positions than the one from which N_2 is cleaved. The ambident nature of the arenediazonium ions, which is represented by canonical structures such as (IV–VIII) and was studied directly by ^{13}C nmr spectroscopy in our laboratories,[10] explains why the nucleophile can react at several sites on the aromatic ring, other than the C_1 (ipso) carbon, followed by hydrogen shift in the dediazoniation process. Alternatively an SN1 type mechanism can also be operative in some of the studied systems. The reactions were carried out with the substituted anilines (0.02 mol) being treated in the presence of the appropriate sodium halides (0.03 mol) with sodium nitrite (0.03 mol) in 50 ml of 70% hydrogen fluoride–30% pyridine solution generally for 1 hr at 50°. Halobenzenes were isolated in the usual manner (50–80% yield) and analyzed by glc and nuclear magnetic resonance spectroscopy. Table I summarizes data of the reactions of halide ions with substituted (CH_3–, NO_2–, and CF_3–) benzenediazonium ions, formed *in situ via* diazotization of the corresponding anilines in polyhydrogen fluoride–pyridine solution.

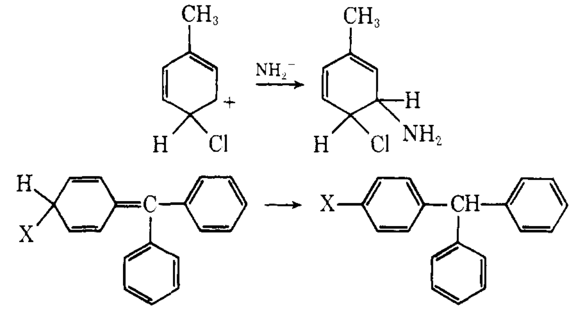


IV V VI VII VIII

Although nucleophilic dediazoniations of arenediazonium ions are generally considered of the SN1 type involving aryl cations, in recent time some evidence accumulated[3] which would seem to favor a mechanism with a bimolecular rate-determining step (SN2 type) avoiding the formation of the energetically unfavorable aryl cations. By combining this consideration, limited till now to substitution at C_1 (the ipso carbon carrying the diazonium group), with the ambident nature of aryldiazonium ions, nucleophilic halide attack at different ring positions can be rationalized. The formed cyclohexadienyl type intermediates would subsequently undergo dediazoniation with simultaneous hydrogen shift. Such nucleophilic attack on arenium ions would have its analogy in Kovacic's suggested σ-substitutions.[11]



The rearrangement step is somewhat reminiscent to that encountered in hydrogen (or halogen) abstraction reactions with the ambident triphenylmethyl cation involving ring positions and subsequent rearomatization *via* hydrogen shifts.[12]



Concerning the possible rate-limiting heterolytic C–N cleavage (SN1 type), this would lead to intermediate phenyl cations, which subsequently could also deprotonate to form arynes.[13] Addition of HX to arynes would give haloarenes. (HX addition to arynes, indeed, is known to give haloarenes[14]) (Scheme I).

The possibility of fast, intramolecular 1,2-hydrogen shifts in aryl cations prior to their quenching by halide ions (or alternatively their deprotonation to arynes) must also be considered, in order to explain formation of observed isomeric haloarenes.

The intermediate formation of arynes is indicated in experiments carried out in pyridinium polydeuterium fluoride, as in the case of the reaction of the *m*-trifluoromethylbenzenediazonium ion with chloride ion. The formed isomeric

Scheme I

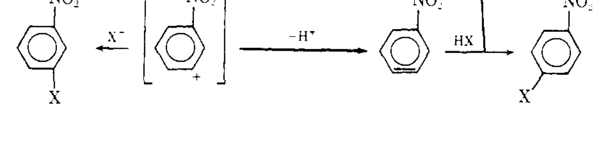


Table I. Isomeric Haloarenes Formed in Reaction of Arenediazonium Ions with Halide Ions in Pyridinium Polyhydrogen Fluoride Solution

Arenediazonium ion $R-C_6H_4N_2^+$	Halide ion	—% isomer distribution— Ortho	Meta	Para
o-CH_3	F	100	0	0
o-NO_2	F	0	100	0
o-CF_3	F	8	91	1
o-CH_3	Cl	100	0	0
o-NO_2	Cl	48	44	8
o-CF_3	Cl	57	25	18
o-CH_3	Br	100	0	0
o-NO_2	Br	92	5	3
o-CF_3	Br	30	70	0
o-CH_3	I	97	3	0
o-NO_2	I	100	0	0
o-CF_3	I	97.2	2.4	0.2
m-CH_3	F	0	100	0
m-NO_2	F	0	73	27
m-CF_3	F	0	53	47
m-CH_3	Cl	4	95	1
m-NO_2	Cl	69	31	0
m-CF_3	Cl	28	23	48
m-CH_3	Br	0	100	0
m-NO_2	Br	0	100	0
m-CF_3	Br	42	22	28
m-CH_3	I	24	67	8
m-NO_2	I	0	100	0
m-CF_3	I	0.2	98	1.7
p-CH_3	F	0	0	100
p-NO_2	F	0	65	34
p-CF_3	F	1	19	80
p-CH_3	Cl	10	10	80
p-NO_2	Cl	17	21	60
p-CF_3	Cl	0	0	100
p-CH_3	Br	0	0	100
p-NO_2	Br	0	50	50
p-CF_3	Br	30	57.5	12.5
p-CH_3	I	1	24	75
p-NO_2	I	0	0	100
p-CF_3	I	0	0	100

chlorobenzotrifluorides show (as determined by mass spectrometry) significant deuterium incorporation. This would seem possible only through a benzyne intermediate, as in control experiments pyridinium polydeuterium fluoride showed no hydrogen-deuterium exchange of the involved arenes.

Factors influencing isomeric product formation include substituent effects in both stabilizing diazonium ions (generally ortho and para substituents) and aryl cations[15] (generally meta substituents). Depending on the nature and nucleophilicity of the reactant halide ions (generally considered increasing with increasing atomic weight, *i.e.*, $F^- < Cl^- < Br^- < I^-$) and the ring substituents in the diazonium ions, the transition state of the reactions can more closely resemble starting diazonium ions (lying early on the reaction coordinate) thus proceeding through the outlined bimolecular nucleophilic substitution path or alternatively through phenyl cation type intermediates with subsequent benzyne formation.

Details of a comprehensive study of these novel nucleophilic dediazoniation reactions and an attempt to elucidate their mechanism, which can have substantial importance on our understanding of the ambident reactivity of arenediazonium ions and also preparative significance for obtaining unusual isomeric haloarene (and related aromatic) compositions, will be given in our forthcoming full paper.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged, as are stimulating discussions with Professors H. Zollinger and R. Huisgen.

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sym-Oxepin Oxide

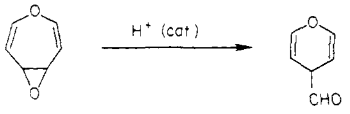
Sir:

The epoxides of aromatic systems have been the focus of considerable research due to their theoretical and biological relevance.[1] Of similar interest, but yet unreported, are the epoxides of the oxepin valence tautomers of arene oxides. We wish to report the synthesis of *sym*-oxepin oxide (4,8-dioxabicyclo[5.1.0]octa-2,5-diene) (**1**) and its facile rearrangement to 4-*H*-pyran-4-carboxaldehyde (**2**) (Scheme I).

The involvement of arene oxides in the metabolism of aromatic systems is well documented.[1b,c] Oxepin oxides may also be involved in biogenesis, either through nucleophilic opening of the epoxide or through rearrangement to the 4-*H*-pyran-4-carboxaldehyde system. Neuss, *et al.*, have suggested[2] that the oxepin oxide **3** (Figure 1) may be involved in the biogenesis of aranotin-type metabolites[3] (*genera Aspergillus* and *Arachniotus*) from phenylalanine. Further, in a postulated biosynthesis of the aflatoxins (also *genus Aspergillus*), through a C_{18}-polyhydroxynaphthacene, Büchi, *et al.*, have suggested[4] the intermediacy of the 4-*H*-pyran-4-carboxaldehyde **4**.

sym-Oxepin oxide (**1**) is of theoretical interest because of its potential for Cope rearrangement, as demonstrated for the related bicyclo[5.1.0]octa-2,5-diene[5] and *sym*-oxabicyclo[5.1.0]octa-2,5-dienes,[6] and because its reactivity might

Scheme I



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