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

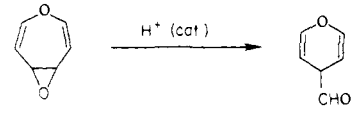
Sir:

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 1).

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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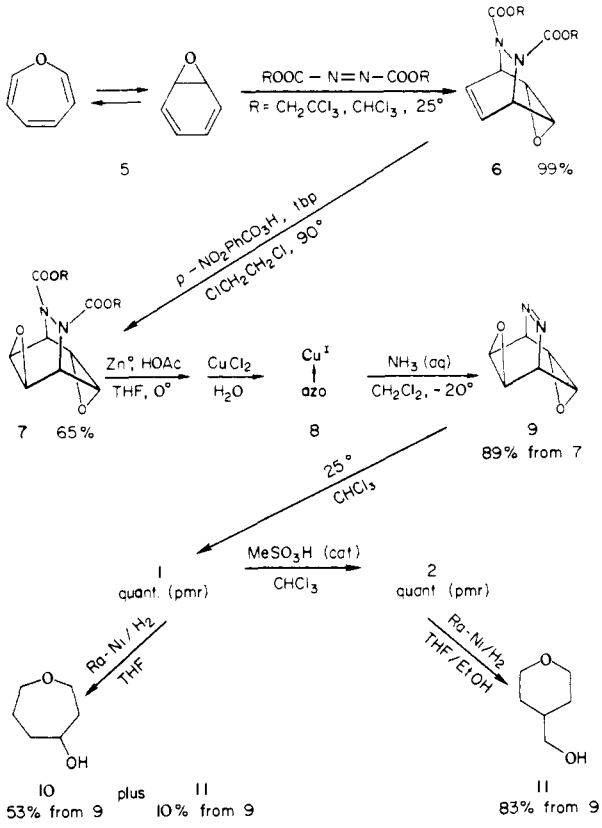
Scheme II

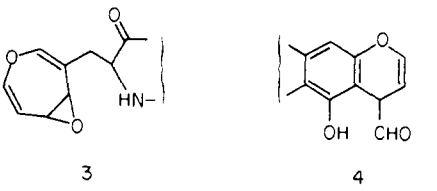


parallel that of the seldom isolated epoxides of enol ethers.[7] The latter consideration prompted us to adopt a synthetic route allowing for the generation of **1** under exceedingly mild conditions (Scheme II).

Diels–Alder addition of bis(trichloroethyl)azodicarboxylate[8] to benzene oxide–oxepin (**5**)[1a] yields the adduct **6**.[9] Epoxidation of **6** is achieved in a 1,2-dichloroethane slurry at 90° by excess *p*-nitroperoxybenzoic acid, stabilized by 1 wt % of 4,4′-thiobis(6-*tert*-butyl-3-methylphenol) (tbp),[10] giving the diepoxide **7**.[11,12] Reductive cleavage of the trichloroethylcarbamate esters of **7** followed by oxidation with Cu^{II} produces the brick red cuprous complex **8**.[13] The azo diepoxide **9**[14] is liberated from **8** at −20° by aqueous NH_3 (20%) and is isolated as a white crystalline solid by low temperature evaporation of its methylene chloride solution. Dissolution of **9** in aprotic solvents and warming to ambient temperature lead to the loss of nitrogen[15] and the quantitative (pmr) formation of **1**.[16,17] Oxepin oxide (**1**) is isolated as a white crystalline solid, melting below ambient temperature, by vacuum transfer of a methylene chloride solution, followed by low temperature evaporation of the solvent. The same air sensitivity reported for γ-pyran[18] is seen for oxepin oxide (**1**); **1** turns brown quickly after exposure to air.

The pmr of **1** shows no evidence of fluxional character up to 116°,[19] precluding a Cope rearrangement at or below this temperature, *on the pmr time scale*. Thus, the rates for Cope rearrangement follow the order bicyclo[5.1.0]octa-2,5-diene[5] > *sym*-oxabicyclo[5.1.0]octa-2,5-dienes[6] > 4,8-dioxabicyclo[5.1.0]octa-2,5-diene (**1**). Similar rate differences have been noted between *cis*-divinylcyclopropane[20] and *cis*-divinyloxirane[21] and in the bicyclo[6.1.0]nona-2,6-diene series.[22]

Treatment of **1**, in aprotic solvents with 0.1 mol % of methanesulfonic acid, leads within seconds to the quantitative (pmr) generation of aldehyde **2**[23] (Scheme I). Catalytic reduction of **1** (Scheme II) yields 53%[24] of 4-oxepanol (**10**), 10%[24] of 4-hydroxymethyltetrahydropyran (**11**) plus several unidentified minor products. Similar reduction of **2** yields 83%[24] of **11**. Both **10** and **11**, so produced, are identical in physical[25] and spectroscopic[26] properties to authentic samples.[27,28]



3 4

Figure 1. The Neuss (**3**) and Büchi (**4**) intermediates.

NOTE ADDED IN PROOF. An independent synthesis of *sym*-oxepin oxide appeared subsequent to submission of this communication: H. Klein and W. Grimme, *Angew. Chem.*, **86**, 742 (1974).

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(13) Data for **8**: ir (KBr) 1465 cm^{-1}; mp 132–135° dec.
(14) Data for **9**: compound **9** is stable at −20° in $CDCl_3$ solution and the pmr shows δ 6.08 (2 H, m), 3.50 (2 H, MM′XX′ half spectrum), and 3.40 (2 H, AA′XX′ half spectrum). ^1H decoupling: irr at δ 6.08 gives 3.50 (2 H, s), 3.40 (2 H, s); irr at δ 3.45 gives 6.08 (2 H, s); mp 51–80° dec.
(15) $t_{1/2}$ *ca.* 15 min at ambient temperature.
(16) Glassware base treated (soaked in 1 *N* NaOH, rinsed with H_2O then NH_4OH, and dried); solvents filtered through basic alumina or distilled from base.
(17) Data for **1**: ir ($CDCl_3$) 1670, 1650, 1320, 1170, 1100, 990, 840 cm^{-1}; pmr ($CDCl_3$, 100 MHz) δ 6.33 (2 H, d), 5.14 (2 H, m), 3.33 (2 H, m); cmr ($CDCl_3$, 25 MHz) δ^c(TMS) 146.4 (d, J_{CH} = 190.5 Hz), 103.7 (d, J_{CH} = 158.1 Hz), 51.2 (d, J_{CH} = 174.7 Hz); uv (CH_3CN) λ_{max} (shoulder) 227 nm, (ε 980); mass spectrum (70 eV) *m/e* parent 110, base 81.
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(23) Data for **2**: ir ($CDCl_3$) 1725, 1680, 1620, 1260 cm^{-1}; pmr ($CDCl_3$, 100 MHz) δ 9.51 (1 H, d), 6.50 (2 H, m), 4.90 (2 H, m), 3.64 (1 H, m); uv (CH_3CN) λ_{max} 246 (ϵ 590), 310 nm (ϵ 110); mass spectrum (70 eV) *m/e* parent 110, base 81. Exact mass of *p*-nitrophenylhydrazone calcd for $C_{12}H_{11}N_3O_3$, 245.0800; found, 245.0797.
(24) Yield based on **9** after isolation by preparative glc.
(25) Compared by glc coinjection (Carbowax 20M and SE-30) and by mixture melting point of phenylurethane derivatives.
(26) Compared by ir, pmr, and mass spectrum. Exact mass of **10** prepared *via* **1**: calcd for $C_6H_{12}O_2$, 116.0837; found, 116.0840. Exact mass of **11** prepared *via* **2**: calcd for $C_6H_{12}O_2$, 116.0837; found, 116.0840.
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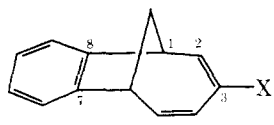
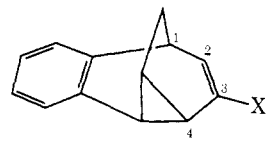
Substituent and Multiplicity Effects on Rearrangements of Some Benzo[7,8]bicyclo[4.2.1]nona-2,4,7-trienes[1]

Sir:

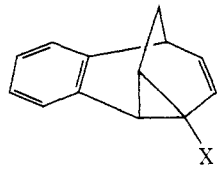
Compounds which can *a priori* react by more than one photochemical pathway can be good substrates for delineating structural effects on photochemical reactivity. Substituted benzo[7,8]bicyclo[4.2.1]nona-2,4,7-trienes (BBNT's) such as **2–4** are "four-way threats" in this respect, capable of undergoing either of two di-π-methane (DPM) rearrangements[2] to benzobarbaralanes or either of two disrotatory ring closures to exo or endo cyclobutenes. The parent triene (**1**) has only three options, since the DPM products are enantiomers. We report here some preliminary results of a systematic study of substituent effects on BBNT photochemistry. These include the rare ability of 3-MeBBNT (**4**) and parent **1** to undergo both singlet and triplet DPM rearrangement, the surprising *inability* of 3-Cl- and 3-BrBBNT (**2** and **3**) to undergo either singlet or triplet DPM rearrangement, and pronounced substituent and multiplicity effects on exo–endo cyclobutene ratios.



1, X = H
2, X = Cl
3, X = Br
4, X = CH_3

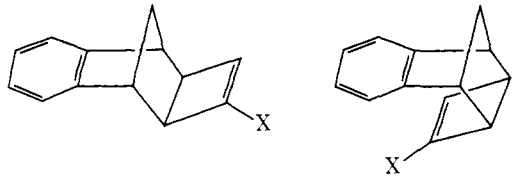


5, X = H
6, X = CH_3



exo cyclobutenes

7, X = CH_3



endo cyclobutenes

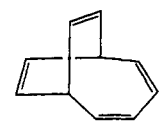
Syntheses of **1** and **2** were reported elsewhere;[3] **3** was prepared in analogous fashion, and **4** was made by reaction of **2** or **3** with lithium dimethylcuprate.[4] Direct or sensitized irradiation of "trienes" **1–4** gave rapid conversion to photoproducts (summarized in Table I),[5] which were isolated by preparative vpc or high-pressure liquid chromatography and characterized spectroscopically.[6]

Regarding first the hydrocarbons **1** and **4** in Table I, one can see that sensitized irradiation affords only DPM products, presumed to arise from triplet excited states, whereas direct irradiation gives DPM products and cyclobutenes. The latter, then, must arise only from singlet excited states, while the multiplicity responsible for DPM products from direct irradiation of **1** and **4** was uncertain. Formation of a photodimer of **1** on sensitization (triplet assumed) but not on direct irradiation suggested minimal formation of the triplet state of **1** on direct irradiation.[9] Thus it appeared that **1** has the ability, rare among bicyclic systems, to undergo DPM rearrangement *via* either the singlet or triplet excited state. The presence of three photoproducts (a fingerprint) from direct irradiation of **1** encouraged attempts to quench formation of **5**. These attempts, using up to 5 *M* piperylene or 1 *M* cyclooctatetraene, produced no detectable change in the photoproduct distribution,[10] and strengthened our conclusion that the direct irradiation **1** → **5** DPM reaction is essentially completely a singlet excited state process.

Positive "fingerprint" evidence (Table I) points also to the ability of 3-MeBBNT (**4**) to undergo either singlet or triplet DPM rearrangement. This evidence is the altered regioselectivity in formation of DPM products; the triplet excited state strongly favors formation of 3-methylbenzobarbaralane (**6**), while the singlet favors the 4-methyl isomer.[11] Clearly, the same excited state does not give rise to two different isomer distributions; again, the direct irradiation DPM reactions appear to be predominantly singlet processes.

The above gives strongly suggestive evidence that all products of irradiation of **1** and **4** come from singlet excited states. Within the singlet manifold, it is noted further that the competitive balance shown by **1** (0.67:1 ratio of cyclobutenes *vs.* DPM product) is strongly skewed in favor of cyclobutene formation (9.0:1) by introduction of the 3-methyl substituent in **4**. This high sensitivity of certain bicyclic systems to structural changes is further demonstrated by the following comparisons with literature work. Direct irradiation of trienes **8**[12a] and **9**[12b] gives only the DPM products bullvalene and benzobullvalene. In contrast, direct irradiation of **11** reportedly affords only cyclobutenes,[8a] while **10** is reported[8c,13] to parallel **1** in yielding significant amounts of DPM product as well as cyclobutenes.

The complete preference of the excited triplets of **1** and **4** for DPM rearrangement over cyclobutene ring closure parallels the behavior of **10**[8c] and **11**;[8a] a similar total DPM preference can be assumed for the triplets of **8** and **9**. By comparison with these six trienes, the sensitized photochem-



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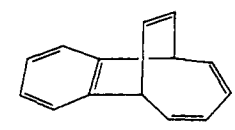
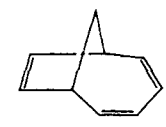


9



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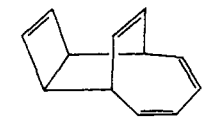

11