**5-Cyano-2-phenyl-4-(phenylthio)-1,3-oxazine-6-thione (entry 12, 2a′)**: yellow needles (AcOEt); mp 199–200 °C; IR (KBr) 3030 (arom CH), 2210 (CN) cm$^{-1}$; NMR ($CDCl_3$) $\delta$ 7.95 (m, 2, pH), 7.65 (m, 8, Ph, SPh); mass spectrum, *m/e* 322 ($M^+$), 261 (M − COS −H). Anal. Calcd for $C_{17}H_{10}N_2OS_2$: C, 63.33; H, 3.13; N, 8.69; S, 19.90. Found: C, 63.03; H, 3.23; N, 8.55; S, 20.20.

**Registry No.** **1a**, 37614-61-2; **1a***, 87740-50-9; **1a**-$d_3$, 87740-51-0; **1a′** ($R^1$ = Et), 87740-52-1; **1a′** ($R^1$ = $CH_2Ph$), 65882-52-2; **1a′** ($R^1$ = Ph), 87740-53-2; **1b**, 87740-54-3; **1c**, 87740-55-4; **1d**, 57280-03-2; **1e**, 87740-56-5; **1f**, 87740-57-6; **1g**, 87740-58-7; **2a**, 80532-88-3; **2a***, 87740-59-8; **2a**-$d_3$, 87740-60-1; **2a′** ($R^1$ = Me; $R^2$ = $\beta$-naphthyl), 87740-61-2; **2a′** ($R^1$ = Me; $R^2$ = *p*-anisyl), 87740-62-3; **2a′** ($R^1$ = Me; $R^2$ = *o*-iodophenyl), 87740-63-4; **2a′** ($R^1$ = Et; $R^2$ = *p*-anisyl), 87740-64-5; **2a′** ($R^1$ = $CH_2Ph$; $R^2$ = *p*-anisyl), 87740-65-6; **2a′** ($R^1$ = $R^2$ = Ph), 87740-66-7; **3a**, 80532-90-7; **3a***, 87740-67-8; **3a**-$d_3$, 87740-68-9; **3a′** ($R^1$ = Me; $R^2$ = $\beta$-naphthyl), 87740-69-0; **3a′** ($R^1$ = Me; $R^2$ = *p*-anisyl), 87740-70-3; **3a′** ($R^1$ = Me; $R^2$ = *p*-chlorophenyl), 87740-71-4; **3a′** ($R^1$ = Me; $R^2$ = *o*-iodophenyl), 87740-72-5; **3a′** ($R^1$ = Me; $R^2$ = *p*-nitrophenyl), 87761-65-7; **3a′** ($R^1$ = Et; $R^2$ = *p*-anisyl), 87740-73-6; **3a′** ($R^1$ = Et; $R^2$ = *p*-nitrophenyl), 87740-74-7; **3a′** ($R^1$ = $CH_2Ph$; $R^2$ = $\beta$-naphthyl), 87740-75-8; **3a′** ($R^1$ = $CH_2Ph$; $R^2$ = Ph), 87740-76-9; **3a′** ($R^1$ = $CH_2Ph$; $R^2$ = *p*-nitrophenyl), 87740-77-0; **4a**, 80532-91-8; **4a***, 87740-78-1; **5a**, 80532-87-2; **5b**, 87740-79-2; **5c**, 87740-80-5; **5d**, 87740-81-6; **5e**, 87740-82-7; **5f**, 87740-83-8; **6a**, 87740-84-9; **6b**, 87740-85-0; methyl trithiocarbonate, 1113-26-4; cyanoacetamide, 107-91-5; *N*-methylcyanoacetamide, 6330-25-2; *N*-ethylcyanoacetamide, 15029-36-4; ethyl trithiocarbonate, 1118-64-5; methyl dithiopropionate, 5415-95-2; methyl dithiobenzoate, 2168-78-7; benzoic acid, 65-85-0; $\beta$-naphthoic acid, 93-09-4; *p*-methoxybenzoic acid, 100-09-4; *p*-chlorobenzoic acid, 74-11-3; *o*-iodobenzoic acid, 88-67-5; *p*-nitrobenzoic acid, 62-23-7.

**Supplementary Material Available:** $^{13}C$ NMR spectra of **4a** and **4a*** in $Me_2$ SO-$d_6$ (67.8 MHz) with completely coupled and off-resonance decoupled protons (2 pages). Ordering information is given on any current masthead page.

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# Evidence against 1,2-Migrations in Aryl Cations

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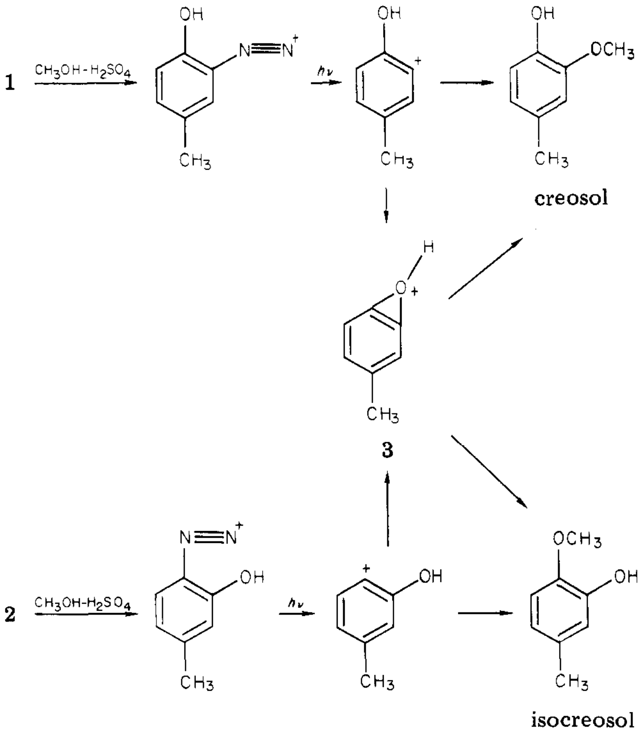
Photolytic methoxydediazoniation of 2-diazo-4-methylphenol (1) and 2-diazo-5-methylphenol (2) in 50% $CH_3OH$–$H_2SO_4$ yielded 2-methoxy-4-methylphenol (creosol) and 2-methoxy-5-methylphenol (isocreosol), respectively. The absence of detectable amounts of crossover products (within the limits of detection of 5%) in both reactions demonstrates that no 1,2-hydroxyl shift occurred in the intermediate phenylium ion nor could the hypothetical protonated benzoxirene be an intermediate in this reaction.

The dediazoniation reaction of arenediazonium ions is regarded as the one instance where a phenyl cation is a reaction intermediate.[1,2] One may reasonably ask whether there exists in the chemistry of the phenylium ion any behavior analogous to the widespread propensity to neighboring group effects among alkyl cations.[3,4]

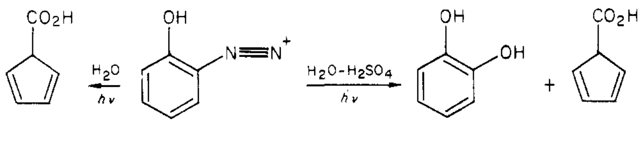
Participation by neighboring hydroxyl to form an epoxide is known in aliphatic chemistry[5] both in the case of dediazoniation[6] and in the case of carbonium ions generated from 1,2 diols,[7] although the major products in most of these cases arise from pinacol–pinacolone type rearrangements.

The formation of a bridged intermediate such as **3** suffers from several difficulties (Scheme I). First, the formation of epoxides, via aliphatic cations has, whenever studied,[8] required an anti-periplanar arrangement of the leaving group and the migrating group, which is of course not possible in the formation of **3**. The intermediate **3** would also suffer from the fact that it is the protonated form of a benzoxirene, an antiaromatic species. There is

Scheme I



Scheme II



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some evidence for the intermediacy of oxirenes,[9] though not of benzoxirenes.[10] On the other side of the ledger is the recent observation[11] that gas phase phenylium ion "tends to internally solvate its positive charge via a fast automerization involving consecutive 1,2 hydrogen shifts".

We chose to examine this question by following the lead of De Jonge,[12] who found that the photolytic decompositon of *o*-hydroxybenzenediazonium sulfate in water gave the Wolff rearrangement product, cyclopentadienecarboxylic acid, whereas in 50% $H_2SO_4$ solvent it yielded the hydroxydediazoniation[13] product, catechol, as well as the Wolff rearrangement product (Scheme II).

We prepared two diazophenols, 2-diazo-4-methylphenol (2-diazo-4-methyl-3,5-cyclohexadien-1-one, **1**) and 2-diazo-5-methylphenol (2-diazo-5-methyl-3,5-cyclohexadien-1-one, **2**), which on dediazoniation in $CH_3OH-H_2SO_4$ should give in addition to the Wolff rearrangement products two methylguaiacols, creosol and isocreosol, respectively, in the absence of a 1,2 hydroxyl shift. On the other hand, a mixture of the two methylguaiacols should be formed in each reaction if the reaction proceeded by way of such a shift and/or by way of the protonated benzoxirene intermediate **3**.

Irradiation[14] of **1** in $CH_3OH-H_2SO_4$ yielded creosol as the sole methoxydediazoniation[13] product. Decomposition of **2** under like conditions was found to yield isocreosol as the only methoxydediazoniation product. The yields of the two methylguaiacols were low (6–8%), the bulk of the material undergoing a Wolff rearrangement, as was expected from the results of De Jonge, Alink, and Dijkstra.[12] To make certain that these results were not vitiated by fractionation in the workup, samples of creosol and isocreosol were subjected to the reaction and workup conditions. The recovery was found to be satisfactory and equal in the two cases.

This absence of crossover products indicates that no detectable fraction of the methylguaiacols is formed via a benzoxirene or by way of a 1,2-hydroxyl shift. If this is indeed an $S_N1$ reaction in which the phenylium ion has an appreciable lifetime,[1d] then it appears that the energy of this cation is not higher than that of the protonated benzoxirene (**3**).

## Experimental Section

Gas chromatographic separations were performed on a Beckman GC-65 instrument equipped with a 6 ft × $^1/_4$ in. 40% SE 30 column. Infrared spectra were measured on a Perkin-Elmer 1320 spectrophotometer. NMR spectra were determined on a Varian T-60 NMR spectrometer with $Me_4Si$ as an internal standard.

**2-Diazo-4-methylphenol (1).** To a stirred solution of 2.93 g (23.8 mmol) of 2-amino-4-methylphenol and 12 mL of 6 N HCl in 25 mL of water at 0 °C was added, dropwise, 1.76 g (25.5 mmol) of $NaNO_2$ in 30 mL of water. The excess nitrous acid was destroyed with about 50 mg of urea, and the solution was neutralized by addition of solid $Na_2CO_3$ and extracted with two 50-mL portions of benzene. The benzene phase was dried over anhydrous $MgSO_4$, the benzene removed on a rotary evaporator, and the product dried at room temperature in vacuo. The yield of product was 1.26 g (39%): $\lambda_{max}$ (methanol) 418 nm ($\epsilon$ 4140); NMR ($CDCl_3$) $\delta$ 2.2 (s, 3, 4-$CH_3$), 6.6 (d, 1, $J$ = 5 Hz, 6-H), 7.0 (m, 1, 3-H), 7.2 (dd, 1, $J$ = 1 and 5 Hz, 5-H); IR (KBr) 2140 sh, 2080, 1610 $cm^{-1}$.

**2-Diazo-5-methylphenol (2).** This compound was prepared from 2-amino-5-methylphenol by the same procedure as above. The yield of product was 36%: mp 67–69 °C dec $\lambda_{max}$ (methanol) 399 nm ($\epsilon$ 3180); NMR ($CDCl_3$) $\delta$ 2.2 (s, 3, 5-Me), 6.1 (dd, 1, $J$ = 1 and 4 Hz), 6.5 (m, 1, 6-H), 7.2 (d, 1, $J$ = 4 Hz, 3-H); IR (KBr) 2160, 2120, 1605 $cm^{-1}$.

**2-Methoxy-4-methylphenol (Creosol) and 2-Methoxy-5-methylphenol (Isocreosol).** Isocreosol was prepared from 2-methoxy-5-methylaniline by the procedure of Goldberg & Turner.[15] Creosol was purchased from Pfaltz & Bauer. Gas chromatography of these two compounds under our conditions (150 °C, 6 ft × $^1/_4$ in. 40% SE 30 column) yielded nearly identical retention times. Samples of each compound were collected from the gas chromatograph and their infrared spectra (KBr) were determined. The principal differences between the IR spectra ($cm^{-1}$) of these two compounds are as follows (in $cm^{-1}$; creosol, isocreosol): –, 1440; 1360, 1330; –, 1173; 1117, 1125; 915, 938; 835, 855; 803, 790; 785, 755.

From these differences and from the examination of spectra of synthetic mixtures, it was found that 5% or more of one isomer could be detected in the presence of the other.

**Photodecomposition of 2-Diazo-4-methylphenol.** 2-Diazo-4-methylphenol (1) (0.10 g, 0.74 mmol) was dissolved in 50 g of 50% (by wt) $CH_3OH$–concentrated $H_2SO_4$ at 0 °C. This solution was placed in a water-jacketed Pyrex tube maintained at 0 °C and irradiated in a Rayonet Photochemical Reactor equipped with 3500-Å lamps. After 24 h, the solution was poured into 150 g of ice and extracted with three 50-mL portions of ether. The ether phase was dried over anhydrous $MgSO_4$ and evaporated to about 2 mL. To this solution was added 100 mg of *p*-dichlorobenzene (VPC internal standard) and the solution was subjected to vapor phase chromatography. The yield of 2-methoxy-4-methylphenol (creosol) was 7.9%. A sample of this product (1–2 mg) was collected from the gas chromatograph directly into 50 mg of KBr. The infrared spectrum of this sample was found to be that of creosol.

When a sample of creosol was subjected to the above reaction and workup conditions, the recovery was 70%. A sample of isocreosol yielded a 72% recovery.

**Photodecomposition of 2-Diazo-5-methylphenol.** 2-Diazo-5-methylphenol (2) was treated in the same manner as above, giving a 6.0% yield of isocreosol.

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**Registry No.** 1, 87842-95-3; 2, 87842-96-4; 2-amino-4-methylphenol, 95-84-1; 2-hydroxy-5-methylbenzenediazonium, 38988-22-6; 2-amino-5-methylphenol, 2835-98-5; 2-hydroxy-4-methylbenzenediazonium, 87842-97-5; 2-methoxy-5-methylaniline, 120-71-8; isocresol, 1195-09-1; cresol, 93-51-6; methanol, 67-56-1.

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