Dimethyl(2-phenyl-1*H*-indol-3-yl)sulfonium Chloride (4c). Freshly recrystallized (from benzene) 2-phenylindole (12 g, 0.062 mol) was dissolved in 75 mL of tetrahydrofuran, and dimethyl sulfoxide (5 mL, 0.070 mol) was added. The reaction flask was placed in an ice bath, and a slow stream of hydrogen chloride gas was passed through the reaction mixture until no further precipitation was observed. The precipitate was filtered and washed with toluene to produce 12.5 g of **4c** (69%) as a light gray powder, mp 148–151 °C (lit. mp 158–160 °C).

3-(Methylthio)-2-phenylindole (3c). Sulfonium chloride **4c** (2.45 g, 8.5 mmol) was heated under nitrogen at 130–150 °C for 1 h to give a dark-purple oily substance. This crude product was chromatographed on a 50-g silica gel column using benzene for elution. Pale-yellow crystals formed after evaporation of the benzene in vacuo and addition of carbon tetrachloride/hexane. The product was filtered and washed with hexane to yield 1.6 g of **3c** (81.2%), mp 97–100 °C (lit.[6] mp 106–107 °C).

3-(Dimethylsulfonio)-2-phenylindolide (1c). To sulfonium chloride **4c** (1.07 g, 3.7 mmol) in 30 mL of methanol was added 5 g of ion-exchange resin (Bio-Rad, AG1-X8, 100–200 mesh in OH^- form). The mixture was stirred at room temperature for 1 h. The ion-exchange resin was filtered and washed with chloroform, and the combined solvent was removed in vacuo at 20 °C or below. Pale-yellow crystals formed upon the addition of ether. The collected product **1c** was recrystallized from $CHCl_3$/ether to yield 0.82 g (87%) of **1c**, mp 148–151 °C (lit.[6] mp 165–169 °C). For characterizing data see the figures and tables and ref 2.

Diethyl(1*H*-indol-3-yl)sulfonium Iodide (6, X = I). To 1.77 g (10 mmol) of 3-(ethylthio)indole[27,28] in 0.25 mL of dimethylformamide was added 1.75 g (11 mmol) of ethyl iodide. The container was tightly stoppered and allowed to stand for 2 weeks. Ether was added to precipitate the product which was filtered and washed well with ether: 1.2 g (36%), mp 108–110 °C. For characterizing data see the figures and tables.

3-(Diethylsulfonio)indolide (5). To sulfonium iodide **6**, 0.5 g in 10 mL of methanol, was added 2.5 g of ion-exchange resin (Bio-Rad, AG1-X8, 100–200 mesh in OH^- form) in 10 mL of methanol. The mixture was stirred at room temperature for 1 h. The ion-exchange resin was removed by filtration and washed with dichloromethane. The combined organic solvent was removed in vacuo at 20 °C and the resulting solid was triturated with dichloromethane. Hexane was added to the dichloromethane-soluble portion to the cloud point. After standing for 2 h, the resulting colorless crystals were filtered to yield 0.2 g (76%) of 3-(diethylsulfonio)indolide (**5**), mp 68–71 °C. For characterizing data see the figures and tables.

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Registry No. 1a, 54087-15-9; **1b**, 68996-46-3; **1c**, 56656-05-4; **3a**, 40015-10-9; **3b**, 40015-18-7; **3c**, 40015-25-6; **4a** (X = I), 54087-14-8; **4b** (X = I), 72610-11-8; **4c** (X = I), 72610-12-9; **4c** (X = Cl), 56656-03-2; **5**, 72610-13-0; **6** (X = I), 72610-14-1; 2-methylindole, 95-20-5; thiourea, 62-56-6; *S*-(2-methyl-3-indolyl)isothiouronium iodide, 72610-15-2; 2-phenylindole, 948-65-2; dimethyl sulfoxide, 67-68-5; ethyl iodide, 75-03-6; 3-(ethylthio)indole, 1484-16-8.

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Photoinduced Decomposition of Peracetic Acid in Xylenes. Orientation in Aromatic Substitution of Methyl and Hydroxyl Radicals[1]

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The photolysis of peracetic acid (**1**) in *o*-, *m*- or *p*-xylenes (**2**) has been carried out using 2537-Å or >2900-Å light at 20–22 °C. The yields of ethyltoluenes (**3**), trimethylbenzenes (**4**), and dimethylphenols (**6**) are higher at 2537-Å than those at >2900-Å photolysis, but the reverse is true with the yield of methylbenzyl alcohol (**5**). The isomer distribution of trimethylbenzenes (**4**) formed from *o*- (**2a**) or *m*-xylene (**2b**) suggests that an attack of methyl radical at the position meta to the methyl group is favored with 2537-Å light, while an attack at the ortho position is preferential with >2900-Å light. On the other hand, the isomer distribution of dimethylphenols (**6**) at 2537 Å suggests that an attack of hydroxyl radical is favored at positions ortho and para to the methyl group. These orientations of radical attack are briefly discussed.

In the gas-phase photolysis of azomethane in toluene, methyl radical may abstract a hydrogen atom from the methyl group and/or add to the ring, ethylbenzene being a major nongaseous product in this system. On the other hand, in the liquid phase photolysis, *o*-xylene is a major product.[2] As we reported previously, the photolysis of peracetic acid in toluene with 2537-Å light gives xylenes in the order meta > ortho > para and ethylbenzene as major products, but the photolysis with >2900-Å light gives benzyl alcohol as a major product along with xylenes in the order ortho > meta > para,[3] which is consistent with that in the thermal decomposition of acetyl peroxide[4] and di-*tert*-butyl peroxide.[5]

The activation energy for hydrogen atom abstraction on the side chain of xylenes by methyl radical formed from acetone was reported to be 7.4 ± 0.2 for *p*-xylene, 7.8 ± 0.3 for *o*-xylene, and 8.5 ± 0.3 kcal/mol for *m*-xylene at 100–200 °C.[6] The difference was explained by the hyperconjugation effect in *p*- and *o*-xylenes.

We discuss in the present paper the effects of hyperconjugative electron release and wavelength of light on the

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Table I. Product Yields in Photolysis of Peracetic Acid (1) in Xylenes (2)[a]

xylene	concn range of 1, 10^2 M	light, Å	product, % EtC_6H_4Me 3		$MeC_6H_4CH_2OH$ 5	$Me_2C_6H_3OH$ 6	$(MeC_6H_4CH_2-)_2$ 7
ortho (2a)	3.4-30.7	2537	24.3	8.9	15.1	6.0	17.0
ortho (2a)	3.4-30.7	>2900	9.3	6.2	36.9		45.1
meta (2b)	5.8-34.2	2537	20.3	9.1	10.4	6.3	18.9
meta (2b)	5.8-34.2	>2900	7.4	6.9	30.0		46.6
para (2c)	6.0-33.5	2537	23.5	8.4	13.5	6.1	16.7
para (2c)	6.0-33.5	>2900	10.2	5.9	32.3		43.4

[a] These values are the average of four runs.

product yields and also on the isomer distribution of trimethylbenzenes and dimethylphenols obtained in the photolysis of peracetic acid in xylenes.

Results and Discussion

A xylene solution ((4.81–30.4) × 10^{-2} M) of peracetic acid (1) was irradiated in a quartz cell with a 30-W low-pressure Hg lamp or in a Pyrex cell with a 300-W high-pressure Hg lamp through a water jacket (20–22 °C). The products in the solution were analyzed by GLC after the removal of 1 by Me_2SO reduction. The aromatic products obtained in the photolysis of 1 in *o*-, *m*-, and *p*-xylenes (**2a–c**) are listed in Table I.

Here, product yield (%), i.e., ([product]/[decomposed 1]) × 100 (or 200, bibenzyl alone), is an average of four runs with (5–30) × 10^{-2} M peracid.

The methylation of the side chain of xylenes gave the corresponding *o*-, *m*-, and *p*-ethyltoluenes (**3a–c**), while the methylation of **2a** at the aromatic ring gave two isomers of trimethylbenzene, i.e., the 1,2,3 and 1,2,4 isomers (**4a** and **4b**), the methylation of **2b** gave three isomers, i.e., **4a**, **4b**, and the 1,3,5 isomer (**4c**), and the methylation of **2c** gave **4b** alone.

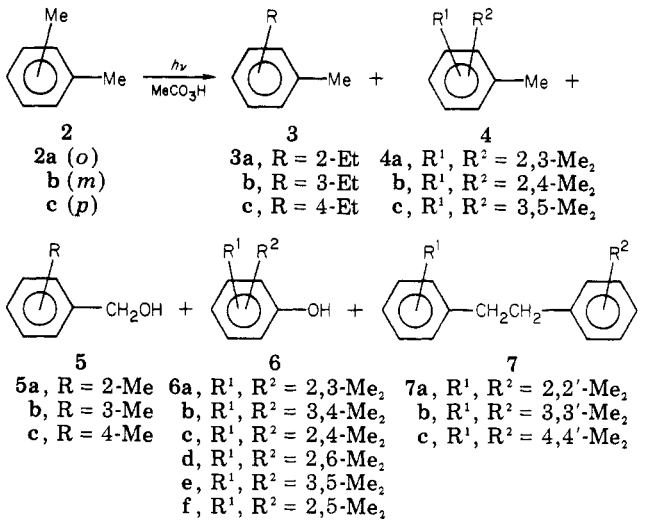
The hydroxylation of the side chain of xylenes gave the corresponding 2-, 3-, and 4-methylbenzyl alcohols (**5a–c**). By hydroxylation of the ring, *o*-xylene (**2a**) gave two isomers, 2,3- and 3,4-dimethylphenols (**6a** and **6b**), *m*-xylene (**2b**) gave three isomers, 2,4-, 2,6-, and 3,5-dimethylphenols (**6c–e**), and *p*-xylene (**2c**) gave 2,5-dimethylphenol (**6f**) alone. The yields of these phenols were always only a trace at >2900 Å with any of isomeric xylenes. Coupling products, 2,2′-, 3,3′-, and 4,4′-dimethylbibenzyls (**7a–c**), were obtained from the corresponding xylenes (Scheme I).

The yield of bibenzyls **7** listed in Table I includes that of diphenylmethanes $MeC_6H_4CH_2C_6H_3Me_2$ (**8**) formed by the addition of $MeC_6H_4CH_2\cdot$ to xylene, and the content of **8** in the yield of **7** (last column in Table I) was measured by NMR analysis of a mixture of **7** and **8**, which was collected by column chromatography with Florisil, because the separation of GLC peaks of **7** and **8** was unsatisfactory. The content of **8** in the yield of **7** was 15–25% for **2a**, 10–20% for **2b**, and 10–20% for **2c**. The yield of **8** increased with decreasing concentration of **1**.

In this photolysis of peracetic acid (1), the product yields were independent of time below 80% conversion and there was no effect of the concentration of 1 on the product yields under these conditions except for the yield of dimer **7**, which showed ca. 10% increase with decreasing concentration of peracid. This increase may be due to lowering the extent of coupling of $MeC_6H_4CH_2\cdot$ with Me· and/or HO·; i.e., a decrease in the concentration of Me· and HO· favors the addition of $MeC_6H_4CH_2\cdot$ to xylene (**2**) by avoiding loss by coupling with Me· and HO·.

As is apparent in comparing the yields of **3–6** in Table I, the preference for side-chain substitution (**3** and **5**) decreases in the order **2a** > **2c** > **2b**, while the preference for ring substitution (**4** and **6**) is reversed. This order agrees with the activation energy for H-atom abstraction from the side chain of xylenes (**2a**, 7.8 ± 0.3; **2b**, 8.5 ± 0.3; **2c**, 7.4 ± 0.2 kcal/mol);[6] that is, H-atom abstraction from the side chain of **2a** (ortho) and **2c** (para) is favored by electron-releasing hyperconjugation. On the other hand, the yields of ring substitution products (**4** and **6**) are comparable with all isomeric xylenes.

Scheme I



The yield of side-chain methylation (**3**) at 2537 Å is remarkably higher than that at >2900 Å for all xylenes, while the reverse order is observed for the yield of side-chain hydroxylation (**5**). Similar results were observed in other hydrocarbons, e.g., toluene,[3] ethylbenzene,[7] etc. This phenomenon is explicable by the wavelength effect as reported previously; i.e., excited xylene at 2537 Å transfers its energy to the peracid (2) which then gives radicals (3) and/or forms an exciplex with peracid (4), while no excitation of xylene occurs at >2900 Å, but the peracid is excited and then decomposes to Me·, CO_2, and HO· (6).[3,7]

$$ArCH_3 \xrightarrow{h\nu\ (2537\ Å)} [ArCH_3]^* \quad (1)$$

$$[ArCH_3]^* + CH_3CO_3H \rightarrow ArCH_3 + [CH_3CO_3H]^* \quad (2)$$

$$[CH_3CO_3H]^* \rightarrow CH_3CO_2\cdot + HO\cdot \rightarrow CH_3\cdot + CO_2 + HO\cdot \quad (3)$$

$$[ArCH_3]^* + CH_3CO_3H \rightarrow [ArCH_3\cdot CH_3CO_3H]_{ex} \quad (4)$$

$$[ArCH_3\cdot CH_3CO_3H]_{ex} \rightarrow ArCH_2CH_3 + H_2O + CO_2 \quad (5)$$

$$CH_3CO_3H \xrightarrow{h\nu\ (>2900\ Å)} CH_3CO_2\cdot + HO\cdot \rightarrow CH_3\cdot + CO_2 + HO\cdot \quad (6)$$

Ar = MeC_6H_4

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Table II. Isomer Distribution in Photochemical Methylation of Xylene Ring[a]

substrate	concn range of 1, 10^2 M	light, Å	distribution of $C_6H_3Me_3$, % 4a	4b	4c
2a	3.4-30.7	2537	46	54	
2a	3.4-30.7	>2900	63	37	
2b	5.8-34.2	2537	31	46	25
2b	5.8-34.2	>2900	41	46	13
2c	6.0-33.5	2537		100	
2c	6.0-33.5	>2900		100	

[a] Average of four runs.

Table III. Isomer Distribution of Hydroxylation of Xylene Ring with 2537-Å Light[a]

substrate	concn range of 1, 10^2 M	distribution of $Me_2C_6H_3OH$, % 6a	6b	6c	6d	6e	6f
2a	3.4-30.7	57	43				
2b	5.8-34.2			54	32	14	
2c	6.0-33.5						100

[a] Average of four runs.

Therefore, the concentration of $MeC_6H_4CH_2\cdot$ formed via H-atom abstraction by HO· or Me· at >2900 Å is higher than that at 2537 Å, where no HO· or Me· is freed in (4) and (5). In fact, the yield of dimer **7** at >2900 Å is much higher than at 2537 Å.

Hence the yield of the side-chain methylation product **3** at 2537 Å is higher than that at >2900 Å owing to exciplex decomposition (5) rather than coupling (7); the yield of **3** at >2900 Å is lower, since (7) alone is the main pathway.

$$ArCH_2\cdot + Me\cdot \rightarrow ArCH_2Me \quad (7)$$

On the other hand, the yield of side-chain hydroxylation (**5**) at >2900 Å is much higher than that at 2537 Å. This may be due to an increase of induced decomposition of peracid (8)[8] at >2900 Å, since the concentration of $MeC_6H_4CH_2\cdot$ is higher at >2900 Å than at 2537 Å, as stated above.

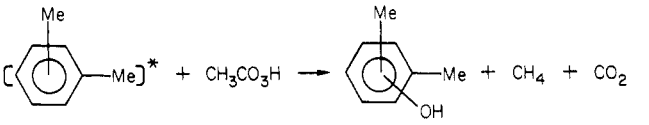
$$ArCH_2\cdot + CH_3CO_2OH \rightarrow ArCH_2OH + CH_3CO_2\cdot \quad (8)$$

$$ArCH_2\cdot + HO\cdot \rightarrow ArCH_2OH \quad (9)$$

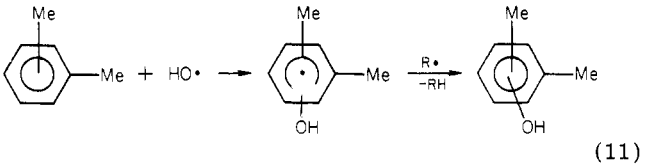
Orientation of Radical Attacks. As stated above, an attack of Me· on the ring of **2a** gives two isomers (**4a** and **4b**), and an attack on **2b** gives three isomers (**4a–c**). Similarly, the aromatic hydroxylation of **2a** gives two isomers (**6a** and **6b**), and the hydroxylation of **2b** gives three isomers (**6c–e**). The distribution of these products is shown in Tables II (methylation) and III (hydroxylation).

Here, no or only a trace of **6** is obtained at >2900 Å, so that the orientation is uncertain. Thus, the higher yield of phenols **6** at 2537 Å than at >2900 Å may be due to the participation of excited aromatics (10) similar to (5) and/or the preferential induced decomposition (8) at >2900 Å may eventually lower the yield of dimethylphenols **6** relative to that at 2537 Å.

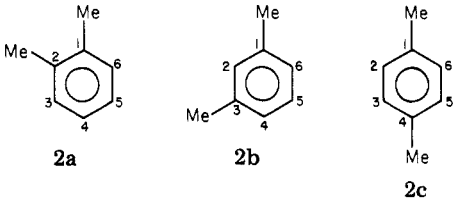
Position 3 in **2a** is affected electronically by *o*- and *m*-methyl groups and position 4 is affected by *m*- and *p*-methyl groups. Three different positions (positions 2, 4, and 5) exist in **2b**, but the four positions in **2c** are electronically equivalent.



(10)



(11)



The ratios of methylation at >2900 Å [**4a** (substitution at 3):**4b** (at 4) = 63:37 for **2a** and **4a** (at 2):**4b** (at 4):**4c** (at 5) = 41:23:13 for **2b**] and the ratio of hydroxylation at 2537 Å [**6a** (at 3):**6b** (at 4) = 57:43 for **2a** and **6d** (at 2):**6c** (at 4):**6e** (at 5) = 32:27:14 for **2b**] are consistent with the electron distribution of xylenes,[9] but the methylation at 2537 Å is different from expectation [**4a** (at 3):**4b** (at 4) = 46:54 for **2a** and **4a** (at 2):**4b** (at 4):**4c** (at 5) = 31:23:25 for **2b**].

The unexpected orientation of methylation at 2537 Å may be tentatively explained as follows: the difference of the reactivity between HO· and Me· gives the different orientation; i.e., the reactivity of HO· is higher by several orders than that of Me·.[10] According to Hammond's rule, the reaction by HO· gives a reactant-like transition state but by Me· gives a product-like one. Therefore, HO· gives the orientation on the basis of the electron density of the reactant, but Me· gives that on the basis of the stability of the product and/or that of the transition state which shows preferentially meta orientation.[10] But this effect alone cannot explain the observed orientation at 2537 Å.

Alternative explanations for the orientation at 2537 Å are the following: reaction between R· and photoexcited aromatics, which has a different electron distribution from that of nonexcited aromatics (12);[11] reaction via the exciplex (13), in which an electron transfer[12] from aromatic to peracid [$ArCH_3 \rightarrow CH_3CO_3H$] at 2537 Å may occur and may lead to different substitution patterns than mere homolytic additions; ortho attack of HO· forming a cyclohexadienyl radical followed by a more favorable attack of Me· on position 5 with simultaneous dehydration (14). The details are still under investigation.

Experimental Section

Apparatus. GLC analyses were performed on a Yanagimoto gas chromatograph with FID, Model G 180. NMR spectra were recorded on a Hitachi R-24B spectrometer using Me_4Si as an internal standard. A Halos low-pressure 30-W Hg lamp and a Halos high-pressure 300-W Hg lamp were used as light sources. All experiments were carried out in a cylindrical quartz vessel (2 × 15 cm) or a cylindrical Pyrex vessel (2 × 15 cm).

Materials. Peracetic acid and *o*-, *m*-, and *p*-ethyltoluenes were prepared as described previously.[8] A water-free peracetic acid–xylene solution was prepared as described previously[8] and ira-

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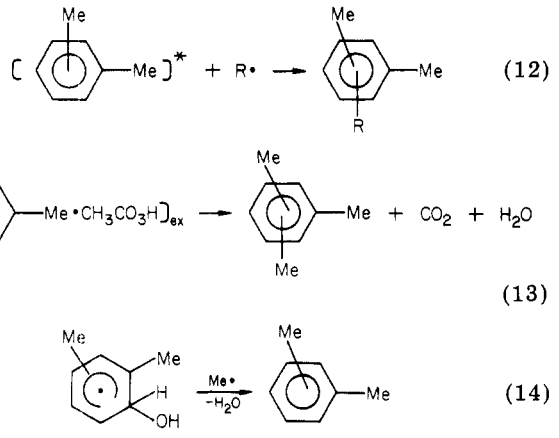

diated immediately after the estimation of peracid concentration. *o*-Methylbenzyl alcohol (**5**) was prepared by bromination of *o*-xylene followed by alkaline hydrolysis:[12] 46%; bp 112–3 °C (15 mm); mp 35–37 °C; NMR ($CDCl_3$) δ 2.26 (s, 3 H, Me), 2.35 (s, 1 H, OH), 4.51 (s, 2 H, CH_2), 7.09 (s, 4 H, aromatic). *m*-Methylbenzyl alcohol (**5b**) was prepared analogously: 38%; bp 117–8 °C (17 mm); NMR ($CDCl_3$) δ 2.27 (s, 3 H, Me), 2.80 (s, 1 H, OH), 4.46 (s, 2 H, CH_2), 7.04 (s, 4 H, aromatic). *p*-Methylbenzyl alcohol (**5c**) was obtained by reduction of *p*-tolualdehyde:[13] 63%; bp 98–100 °C (15 mm); mp 60–62 °C; NMR ($CDCl_3$) δ 2.31 (s, 3 H, Me), 2.43 (s, 1 H, OH), 4.52 (s, 2 H, CH_2), 7.13 (s, 4 H, aromatic). All other reagents were of commercial guaranteed grade.

Photolysis of a Mixture of Peracetic Acid and Xylene. A xylene solution ((4.81–30.4) × 10^{-2} M) of peracetic acid was photolyzed in a quartz vessel (20 × 150 mm) with a 30-W low-pressure Hg lamp or in a Pyrex vessel (20 × 150 mm) with a 300-W high-pressure Hg lamp through a water jacket (20–22 °C). After an estimation of the peracid remaining in the solution, a constant amount of Me_2SO–benzene was added to the photolysate to avoid contamination by the peracid in GLC thermolysis. The products in the solution were analyzed by GLC with FID (Bentone 34-DIDP, PEG 20M-Silicon DC 550, and Uniport HP). The error limit for GLC analysis was within ±5% for the value of product yields; i.e., the true value is in the range of 47.5–52.5% for a 50% yield.

The ratio of bibenzyls, $MeC_6H_4CH_2CH_2C_6H_4Me$ (**7**), to diphenylmethanes, $MeC_6H_4CH_2C_6H_3Me_2$ (**8**), was determined as follows: The solution, treated as stated above, was condensed under reduced pressure (below 30 mm) at 40–50 °C and the condensate was chromatographed on a column packed with Florisil with benzene as a developing solvent. The first eluate was a mixture of **7** and **8**, and benzene was evaporated under vacuum. Its condensate was analyzed by NMR. The ratio of **7** to **8** was determined by the methylene group signals (δ 2.8–2.9 for **7** and δ 3.8–3.9 for **8**).

Registry No. 1, 79-21-0; **2a**, 95-47-6; **2b**, 108-38-3; **2c**, 106-42-3; **3a**, 611-14-3; **3b**, 620-14-4; **3c**, 622-96-8; **4a**, 526-73-8; **4b**, 95-63-6; **4c**, 108-67-8; **5a**, 89-95-2; **5b**, 587-03-1; **5c**, 589-18-4; **6a**, 526-75-0; **6b**, 95-65-8; **6c**, 105-67-9; **6d**, 25134-01-4; **6e**, 108-68-9; **6f**, 95-87-4; **7a**, 952-80-7; **7b**, 4662-96-8; **7c**, 538-39-6; **8**, 32518-89-1.

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A New Synthetic Use of Nucleoside N^1-Oxides

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The use of adenosine N^1-oxide derivatives to prevent intramolecular cyclization during nucleophilic displacement reactions on the sugar moiety is described. This new synthetic use of N^1-oxides is illustrated by the synthesis of 5′-*O*-(*p*-toluenesulfonyl)-2′,3′-*O*-isopropylideneadenosine N^1-oxide (**6**) and subsequent displacement of the 5′ substituent with iodide or azide under conditions which lead exclusively to $N^3 \rightarrow 5'$ intramolecular cyclization in the absence of the N^1-oxide. Similarly, reaction of 2′,3′-*O*-isopropylideneadenosine N^1-oxide with methyltriphenoxyphosphonium iodide produces 5′-iodo-5′-deoxy-2′,3′-*O*-isopropylideneadenosine N^1-oxide (**7**) with no observable cyclization. In addition, 2′,3′-anhydroadenosine N^1-oxide (**17**) is shown to be stable under conditions that lead to complete $N^3 \rightarrow 3'$ intramolecular cyclization in the unprotected 2′,3′-anhydroadenosine (**14**). Reduction of the N^1-oxide to produce the parent nucleoside is readily achieved by using hexachlorodisilane or by hydrogenating over Raney nickel. The mechanistical rationale and implications for additional nucleoside transformations are discussed.

The introduction of novel functionalities into the sugar moiety of nucleoside derivatives is usually accomplished by nucleophilic displacement of suitable leaving groups with an appropriate nucleophile.[1] In various "one-step" syntheses for the introduction of azide or halogen into the sugar ring, the reaction proceeds via a reactive intermediate which again undergoes nucleophilic displacement.[2-4] When performing such sugar transformations in the adenosine series, one of the major problems has been the concomitant formation of intramolecular cyclization products[1,2,5-7] between N^3 and the sugar moiety. These derivatives have little synthetic usefulness, and various methods have been used to preclude their formation. Jahn has shown that N^6-acylated adenosine 5′-tosylates are effective substrates for nucleophilic displacement reactions,

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