J = 7.5, 7.5), 7.27 (m, 5 H), 7.49 (m, 4 H), 7.57 (dddd, 2 H, J = 1.3, 1.3, 7.5, 7.5), 8.0 (dd, 2 H, J = 1.3, 8.0); MS (m/e, relative intensity) 518 (M^+, 2), 303 (32), 289 (2), 193 (28), 136 (30), 123 (70), 105 (100), 77 (21).

(3a*R*,4*R*,5*R*,6a*S*)-5-(Benzoyloxy)hexahydro-4-((2*R*)-2-(phenylsulfinyl)-(3*S*)-3-hydroxy-4-phenoxybutyl)-2*H*-cyclopenta[*b*]furan-2-one (13). To a stirred solution of $NaIO_4$ (0.115 g, 0.53 mmol) in water (2 mL) was added sulfide **12a** (0.27 g, 0.52 mmol) in methanol (8 mL), and the mixture was heated to 40–42 °C. After 24 h methanol was removed to give a viscous crude, which was dissolved in water. The product was extracted with CH_2Cl_2. Prep TLC (hexanes/ethyl acetate, 1:5.7) gave 0.20 g (70%) of sulfoxide **13** as a foam: mp 78–79.5 °C; NMR showed that **13** was a mixture of diastereomers (1:1); $[\alpha]^{25}_D$ = −64.9° (c = 0.69); IR (KBr) 3435, 1768, 1713, 1277 cm^{-1}; ^1H NMR δ 1.5–3.6 (9 H), 3.7–4.7 (3 H), 4.8–5.4 (2 H), 6.6–7.3 (5 H), 7.3–8.1 (10 H); MS (NH_3) (m/e, relative intensity) 552 ($(M + NH_4)^+$, 20), 535 ($(M + H)^+$, 3), 428 (17), 427 (49), 426 (100), 334 (7), 269 (18), 268 (52), 159 (16). Anal. Calcd for $C_{30}H_{30}O_7S$: C, 67.39; H, 5.65; S, 6.00. Found: C, 67.12; H, 5.78; S, 5.69.

(3a*R*,4*R*,5*R*,6a*S*)-5-(Benzoyloxy)hexahydro-4-((3*R*)-3-hydroxy-4-phenoxy-1(*E*)-butenyl)-2*H*-cyclopenta[*b*]furan-2-one (1). A solution of sulfoxide **13** (0.14 g, 0.26 mmol) in toluene (3 mL) with a few crystals of $CaCO_3$ was refluxed for 24 h. The mixture was allowed to cool to room temperature and diluted with water. The product was extracted with ethyl acetate and purified by preparative TLC (hexanes/ethyl acetate, 2:3) to give 80 mg (80%) of **1** as a white solid: mp 122–122.5 °C; $[\alpha]^{25}_D$ = −76.9° (c = 0.1); IR (KBr) 3519, 1767, 1710, 1598, 1279, 1230, 1176 cm^{-1}; ^1H NMR δ 2.27 (dd, 1 H, J = 4.3, 15.7), 2.54 (d, 1 H, J = 15.9), 2.60 (ddd, 1 H, J = 6.3, 6.3, 15.7), 2.80 (m, 1 H), 2.85 (1 H, obscured by overlapping resonances), 2.88 (dd, 1 H, J = 11.2, 18.4), 3.82 (dd, 1 H, J = 8.8, 16.8), 3.95 (dd, 1 H, J = 3.5, 9.3), 4.53 (m, 1 H), 5.09 (m, 1 H), 5.30 (m, 1 H), 5.73 (dd, 1 H, J = 4.8, 15.7), 5.83 (dd, 1 H, J = 7.3, 15.5), 6.87 (br d, 2 H, J = 8.5), 6.97 (br dd, 1 H, J = 7.2, 7.2), 7.26 (dd, 2 H, J = 7.5, 7.8), 7.43 (br dd, 2 H, J = 7.4, 7.4), 7.57 (dddd, 1 H, J = 1.3, 1.3, 7.5, 7.5), 8.0 (dd, 2 H, J = 1.3, 8.0); MS (m/e, relative intensity): 408 (M^+, 8), 301 (10), 286 (26), 179 (48), 108 (40), 105 (100), 94 (28), 77 (45). Anal. Calcd for $C_{24}H_{24}O_6$: C, 70.57; H, 5.92. Found: C, 70.20; H, 5.87.

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Reactions of Thianthrene Cation Radical with Oximes of Cinnamaldehydes and Unsaturated Aromatic Ketones in Acetonitrile

A. K. M. M. Hoque, Wang Keun Lee, Henry J. Shine,* and Da-Chuan Zhao

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409

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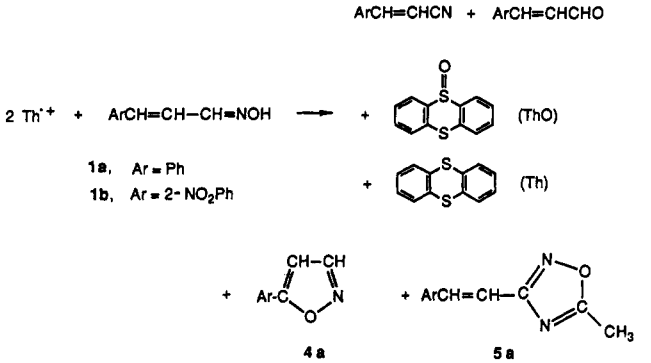
Recently we reported the reactions of aldehyde oximes (RCH=NOH) with thianthrene cation radical perchlorate ($Th^{\bullet+}ClO_4^-$) in nitrile solvents (R'CN). Among these reactions, and dependent on the nature of R, were conversions of an oxime in acetonitrile solvent into two isomeric oxadiazoles, 3-R-5-methyl- and 3-methyl-5-R-1,2,4-oxadiazole, overall dehydration to form RCN, and hydrolysis to form RCHO. The last two reactions involved prior complexation of RCH=NOH with $Th^{\bullet+}$.[1] In earlier work we found that oxidative intramolecular cyclization occurred in reactions of $Th^{\bullet+}ClO_4^-$ with arylhydrazones of chalcones and benzalacetones, with the formation of pyrazoles in excellent yields.[2] We have now completed our analogous study of the reactions of some representative unsaturated aromatic aldoximes and ketoximes.

Scheme I



Cinnamaldoxime (**1a**) underwent small and comparable amounts of intramolecular cyclization, forming 5-phenylisoxazole (**4a**), and cycloaddition to solvent, forming 5-methyl-3-styryl-1,2,4-oxadiazole (**5a**). The major fate of **1a** was conversion to cinnamonitrile. A small amount of cinnamaldehyde was formed, too (Scheme I). In contrast, 2-nitrocinnamaldoxime (**1b**) failed to undergo cyclization or cycloaddition, the only products being the corresponding aldehyde (27.7%) and nitrile (62%). In the presence of 2,4-di-*tert*-butyl-6-methylpyridine (DTBMP) **1a** failed to give **4a** and **5a** but gave only cinnamaldehyde (5.7%) and cinnamonitrile (84.5%). Correspondingly, **1b** in the presence of DTBMP gave mainly 2-nitrocinnamonitrile (83.5%) and some of the aldehyde (7.9%) (Table I). None of the cyclic products (i.e., **4b** and **5b**) was obtained. These reactions can be understood in the light of our earlier work with aldoximes.[1] That is, **1a** was oxidized, in part, to its cation radical which, in the absence of DTBMP, led to the cyclization (**4a**) and cycloaddition (**5a**) products. Complexation of **1a** with $Th^{\bullet+}$ led to aldehyde and nitrile formation, the latter pathway being enhanced by the presence of DTBMP. The failure of **1b**, with its presumed higher oxidation potential, to undergo the oxidative reactions, and instead to yield nitrile and aldehyde is also in line with our earlier experiences. These reactions can be understood with the help of our earlier mechanistic schemes.[1] In harmony with our earlier work is the balance of products, particularly for reactions in the presence of DTBMP. That is, the millimolar sum of the yields of aldehyde and nitrile (e.g., runs 1, 2, and 4) is balanced by that of thianthrene 5-oxide (ThO).

Reactions with the three ketoximes (**2a,b** and **3**) were incomplete in the absence of DTBMP. That is, about 30–40% of oxime was recovered (runs 5, 7, and 9). At the same time substantial amounts (14–24%) of ThO were obtained, attributable in good part to the reaction of workup water with unreacted $Th^{\bullet+}$. The amount of Th formed in these runs, however, was larger than can be accounted for on the basis of the amounts of products obtained. It seems that much of the $Th^{\bullet+}$ was reduced to Th without revealing the fate of the reductant. The major products of runs 5, 7, and 9 were the isoxazoles, 3-methyl-5-phenyl- (**6a**), 5-(*p*-chlorophenyl)-3-methyl- (**6b**), and 5-(*p*-methoxyphenyl)-3-methylisoxazole (**8**), formed by oxidative cyclization of the oximes. The yields, based on the amount of oxime that reacted, were substantial, namely 62% of **6a**, 63% of **6b**, and 71% of **8**. Traces of

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0022-3263/91/1956-1332$02.50/0

Table I. Products of Reaction of $Th^{\bullet+}ClO_4^-$ with the Oximes of Cinnamaldehyde (1a) and 2-Nitrocinnamaldehyde (1b) in Acetonitrile[a]

			product (mmol × 10^3 and %[b])					
run	compd	R in RCH=NOH	RCHO	RCN	isoxazole	oxadiazole	Th	ThO
1	1a	C_6H_5CH=CH	1.41	12.9	1.78	1.36	24.7	14.2
			7.0	64.5	8.9[c]	6.8[d]	61.8	35.5
2		C_6H_5CH=CH[e]	1.14	16.9			19.6	18.9
			5.7	84.5			49.0	47.3
3	1b	$O_2NC_6H_4CH$=CH	5.54	12.4			25.7	13.6
			27.7	62.0			64.3	34.0
4		$O_2NC_6H_4CH$=CH[e]	1.58	16.7			19.4	18.9
			7.9	83.5			48.5	47.3

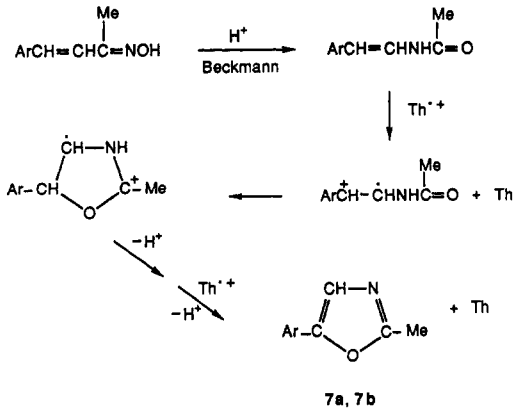
[a] $Th^{\bullet+}ClO_4^-$ (0.4 mmol), oxime (0.2 mmol) in 20 mL of CH_3CN in each reaction. [b] Percent data, second entry in each run. [c] 4a. [d] 5a. [e] DTBMP, 0.6 mmol.

Table II. Products of Reaction of $Th^{\bullet+}ClO_4^-$ with the Oximes ArCH=CHC(R)=NOH in Acetonitrile

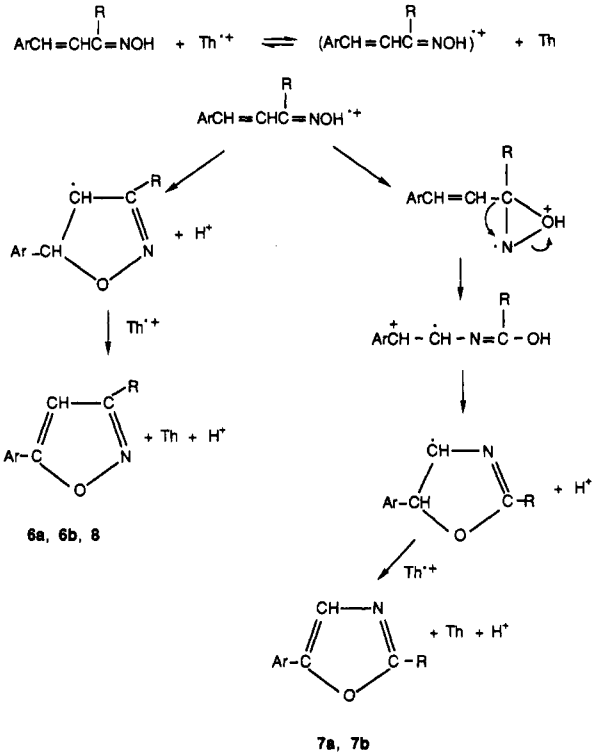
				product (mmol × 10^2 and %[a])					
run	compd	Ar	R	ketone	oxime	isoxazole	oxazole	Th	ThO
5[b]	2a	Ph	Me	1.91	5.74	5.72[c]	tr[d]	24.8	4.26
				12.7	38.3	38.1		82.7	14.2
6[b,g]		Ph	Me	0.78		13.1		28.3	1.14
				5.2		87.3		94.3	3.8
7[b]	2b	*p*ClPh	Me	1.92	4.35	6.69[e]	0.24[f]	23.2	5.33
				12.8	29.0	44.6	1.6	77.3	17.8
8[b,g]		*p*ClPh	Me	0.62		12.9	0.11	28.2	0.96
				4.1		85.8	0.73	93.9	3.2
9[h]	3	*p*MeOPh	Ph	1.57	5.95	9.96[i]		27.9	9.58
				7.9	29.8	49.8		69.8	24.0
10[g,h]		*p*MeOPh	Ph	0.64		17.6[i]		37.2	1.82
				3.2		88.0		93.0	4.6

[a] Percent data, second entry in each run. [b] $Th^{\bullet+}ClO_4^-$ (0.3 mmol), oxime (0.15 mmol) in 20 mL of CH_3CN. [c] 6a. [d] 7a. [e] 6b. [f] 7b. [g] DTBMP added. [h] $TH^{\bullet+}ClO_4^-$ (0.4 mmol), oxime (0.2 mmol). [i] 8.

Scheme II



Scheme III



2-methyl-5-phenyloxazole (**7a**) from **2a** and a small amount (1.6%) of 5-(*p*-chlorophenyl)-2-methyloxazole (**7b**) from **2b**, were found. On the other hand an oxazole from **3** was not detected. These observations are related to our earlier ones that some araldehyde oximes gave two isomeric oxadiazoles in oxidative cycloaddition to solvent acetonitrile, whereas other oximes, having relatively electron rich aromatic rings, gave only one, the anticipated, unrearranged oxadiazole.[1] The formation here of isoxazole and isomeric oxazole (e.g., **6a** and **7a** or **6b** and **7b**) requires, for oxazole formation, the rearrangement of the C=N—OH function in the oxime. There are two ways in which this rearrangement can be visualized. One is that a Beckmann rearrangement had occurred and that cyclization followed in what could be regarded as the cation radical of an *N*-acetylstyrylamine (Scheme II). The other is that rearrangement of an oxaziridine cation radical occurred (Scheme III), the formation of the oxaziridine$^{\bullet+}$ having been enhanced by positive charge localization, for example, in the case of $\mathbf{2b}^{\bullet+}$. We favor the second view since it is analogous to that in our earlier work with aryl aldehyde oximes. In that work, the formation of isomeric oxadiazoles occurred, a result that can be explained with an oxaziridine intermediate but not a Beckmann rearrangement. An acid-catalyzed Beckmann rearrangement, caused by protons liberated in product formation, is ruled out also by the result in run 8. In that run, oxazole formation (**7b**) was diminished but not eliminated by the presence of a

large excess of DTBMP. The addition of DTBMP to the reaction system caused the rapid completion of reaction. Unused oxime was not obtained and the yields of isoxazole increased in each case (runs 6, 8, and 10). At the same time, the formation of ketone was diminished, suggesting that the ketone to some extent arose from hydrolysis of a complex that had been formed between oxime and $Th^{\bullet+}$, analogous to our experience with aldoximes.[1] However, we have this time been unable to relate ketone formation quantitatively to the formation of ThO, nor have we used $H_2[^{18}O]$, as we did earlier with aldehydes, as a diagnostic aid in tracing the source of the ketone.

Experimental Section

Reactions of Oximes with $Th^{\bullet+}ClO_4^-$. A general procedure was adopted. Solid $Th^{\bullet+}ClO_4^-$ and the oxime in the mole ratio 2:1 were placed under argon in a septum-capped flask into which 20 mL of acetonitrile was injected by syringe. The mixture was stirred for 48 h. In all cases, the dark purple color of $Th^{\bullet+}$ faded with time but did not entirely disappear. When reaction was carried out in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP), the mole ratio used was 2:1:3, and the DTBMP was placed in the flask with the $Th^{\bullet+}ClO_4^-$ and oxime before solvent was added. In each of these cases the color of $Th^{\bullet+}$ disappeared completely within 5 min, but the yellow solution was stirred overnight. Thereafter, 5 mL of water was added followed by aqueous $NaHCO_3$ to neutralize $HClO_4$ that had been formed in reaction and in hydrolysis of unused $Th^{\bullet+}ClO_4^-$. The solution was extracted with 4 × 20 mL of CH_2Cl_2, and the dried ($MgSO_4$) CH_2Cl_2 solution was evaporated. The tared residue thus obtained was taken up in a standard volume of CH_2Cl_2, and the solution was analyzed by GC and GC-MS. Concentration factors for all products were determined with authentic materials. Each reaction was run twice, and the averaged yields of products are given in Tables I and II. All other experimental procedures have been described earlier.[1]

Preparation of Oximes. Oximes were prepared in standard ways from mixtures of the carbonyl compound, $NH_2OH{\cdot}HCl$, and a base in aqueous ethanol. No attempts were made to separate *E* and *Z* isomers.

Preparation of 5-Methyl-3-styryl-1,2,4-oxadiazole (5a). Cinnamaldehyde oxime (2.7 g, 18.4 mmol) in 26 mL of ice-cold 37% HCl solution, was converted into its α-chloro derivative by dropwise addition of 30 mL of commercial bleach (5.25% NaOCl). After standing for 1 h, the solution was poured into a slurry of ice (300 g) and water. The oil that separated was extracted with 30 mL of CH_2Cl_2, and the CH_2Cl_2 solution was washed twice with 30 mL of water and dried over $MgSO_4$. Removal of the CH_2Cl_2 left 2.1 g (11.6 mmol, 63%) of a yellow oil: ^1H NMR ($CDCl_3$) δ 6.85 (d, 1 H, *J* = 16 Hz), 7.30-7.44 (m, 6 H). To an ice-cold solution of the oil (2.0 g) in dry ether was added dropwise with stirring 1.5 mL of triethylamine. After 10 min the precipitate of Et_3NHCl was removed and the ether solution was washed with 200 mL of 5% H_2SO_4, 100 mL of 5% $NaHCO_3$, and 3 × 50 mL of water. It was then dried over $MgSO_4$. To the dried ether solution was added 4.5 mL of $BF_3{\cdot}Et_2O$ complex and 40 mL of dry CH_3CN. The ether was removed at 50 °C, and the remaining solution was heated under reflux for 8 h. Evaporation of the solvent under reduced pressure left 2.1 g of dark oil. This was chromatographed on a column of silica gel, with elution by ethyl acetate/hexane, 1:9. Among 15 30-mL fractions, fractions 8 and 9 were found by GC to contain the desired, but impure, oxadiazole. The fractions were purified by TLC on a silica plate with the same solvent development, to give 80 mg of yellow oil that was again subjected to TLC, giving 20 mg (0.115 mmol, 1% based on the α-chlorooxime) of a yellow solid, 98% pure by GC analysis. Crystallization from hexane gave 5 mg of **5a** as yellow needles: mp 80-81 °C; mass required for $C_{11}H_{10}N_2O$ 186.2152, found 186.0788.[3] This oxadiazole has been prepared earlier by (apparently) the dehydrochlorination and cyclization of *N*-acetyl-*N'*-chlorocinnamic acid amidine in basic solution (lit.[4] mp 78 °C).

(3) Midwest Center for Mass Spectrometry, a regional NSF facility, University of Nebraska, Lincoln, NE.

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Supplementary Material Available: Details of preparation of the oximes and of authentic samples of **4a**, **6a**, **6b**, **7a** and **8** and the ^1H NMR data for **5a** (3 pages). Ordering information is given on any current masthead page.

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A New Synthetic Route to 4-Alkylpyrenes from 2,7-Di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrenes

Akira Miyazawa,[1] Takehiko Yamato,[2] and Masashi Tashiro*,[3]

Institute of Advanced Material Study and Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-Kohen, Kasuga-si, Fukuoka 816, Japan, and Department of Industrial Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

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Introduction

It is well known that electrophilic reagents attack positions 1, 3, 6, and 8 of pyrene, but not the other positions (2, 4, 5, 7, 9, and 10). Therefore, pyrenes substituted at the latter positions must be obtained in ways other than by electrophilic substitution of pyrene itself.[4-6]

It was reported[7-9] that 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene, which is easily obtained from toluene, reacted with iodine in boiling benzene to afford 2,7-di-*tert*-butylpyrene. It was also reported[9] that positions 4, 5, 9, and 10 of the 10b,10c-dihydropyrene were reactive toward electrophilic reagents. We report a synthetic route to 4-substituted pyrenes that are not easily obtained by previously reported methods.

Results and Discussion

Electrophilic substitutions, such as nitration, formylation, acylation, and bromination, of 2,7-di-*tert*-butyl-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (**1a**) gave the 4-substituted derivatives (**1b-f**) (Scheme I).

The 4-formyl- (**1b**), 4-acyl- (**1c-d**), and 2,7-di-*tert*-butyl-4-nitro-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrenes (**1e**) were obtained from **1a** under mild conditions (Scheme I). However, bromination of **1a**, with an equimolar amount of bromine, afforded a mixture of mono- and disubstituted products and unreacted **1a**. Isolation of **1f** from the reaction mixture was unsuccessful.

4-Alkyl derivatives **1g-i** were prepared by reduction of the carbonyl derivatives **1b-d** with $LiAlH_4$-$AlCl_3$, and the

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(2) Saga University.
(3) Institute of Advanced Material Study.
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