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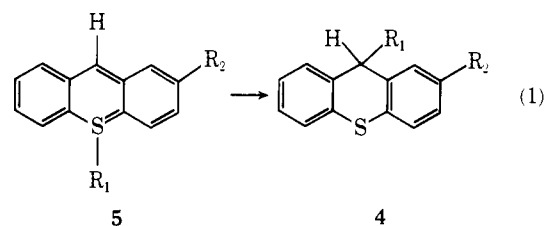
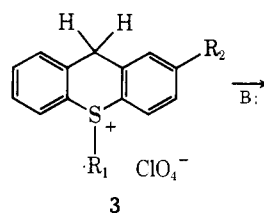
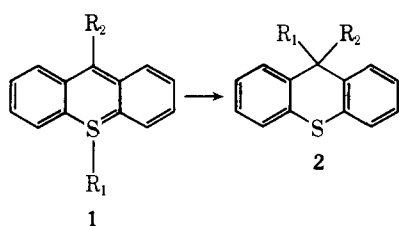
Rearrangement Kinetics of 10-Aryl-10-thiaanthracenes

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Abstract: A variety of 10-arylthioxanthanium salts have been deprotonated to yield 10-aryl-10-thiaanthracenes, whose rates of rearrangement to the corresponding 9-substituted thioxanthenes have been studied. The ylidic character of the intermediate thiaanthracenes is manifested by the upfield shift of the 9-proton, by solvent and substituent effects on the rates of rearrangement, and by generation of a stable thiaanthracene, the anion of 10-*p*-hydroxyphenyl-10-thiaanthracene. The small ΔS^\ddagger for the rearrangements of 2-chloro-10-(2,5-xylyl)-10-thiaanthracene and 10-(*p*-anisyl)-10-thiaanthracene is consistent with the intramolecularity of the reaction.

All previously known thiaanthracenes [1] have been shown to be "notably unstable compounds which readily undergo rearrangement to thioxanthenes[2] and which can only be observed as transient reaction intermediates."¹ The present study was initiated with the principal aim of determining the effects of substitution pattern in 1 on the rate of rearrangement to 2.



- a, $R_1 = \text{phenyl}; R_2 = \text{H}$
 b, $R_1 = 2,5\text{-xylyl}; R_2 = \text{H}$
 c, $R_1 = \text{phenyl}; R_2 = \text{Cl}$
 d, $R_1 = 2,5\text{-xylyl}; R_2 = \text{Cl}$
 e, $R_1 = p\text{-anisyl}; R_2 = \text{H}$
 f, $R_1 = 2,4,6\text{-trimethoxyphenyl}; R_2 = \text{H}$
 g, $R_1 = 2,4\text{-dimethoxyphenyl}; R_2 = \text{H}$
 h, $R_1 = 2,4\text{-dimethoxyphenyl}; R_2 = \text{methoxy}$
 i, $R_1 = 2,4\text{-dimethoxyphenyl}; R_2 = \text{Cl}$

Results and Discussion

Rearrangement Reactions. Deprotonation of thioxanthanium salts (type 3) had previously been found to yield the corresponding 9-substituted thioxanthenes (type 4),^{1,2} and it had been shown¹ that this reaction proceeds by the rearrangement of an intermediate thiaanthracene (type 5) (eq 1). 10-Arylthioxanthanium salts 3a-i were prepared by standard methods^{1,3} and were deprotonated using dimsyl anion⁴ in dimethyl sulfoxide (Me_2SO). The rearrangement reaction of the deprotonated species was monitored using ¹H NMR and visible spectroscopy (see below). All the reactions initially produced an intense red color, due to a transition near 500 nm which is characteristic of thiabenzenes in general.¹ The ¹H NMR spectra of these red solutions exhibited a resonance attributable to the 9-proton of 5, typically at δ 5.7.⁵ The upfield shift of this proton relative to an aromatic system is in agreement with that observed for other thiabenzenes and thus with the ylidic character of this ring system.¹ The red color was discharged in synchrony with the disappearance of this resonance, and a resonance attributable to the 9-proton of 4 ($\delta \sim 5.3\text{-}5.7$) simultaneously became more intense. Yields in the rearrangement reaction are listed in Table I.

Rate Determinations. The visible spectra of thiaanthracenes (5) all feature absorptions near 500 and 385 nm. In order to put the stability of thiaanthracenes on a quantitative basis, the rate of decomposition (rearrangement) in Me_2SO was measured by monitoring the absorbance (A) at the long wavelength peak as a function of time, with the implicit assumption that the rate of deprotonation is much greater than the rate of rearrangement. Plots of $-\ln A$ vs. time were linear over at least 2 half-lives ($\tau_{1/2}$)⁶ and there appeared to be no dependence of the rate constant on initial concentration, in harmony with first-order kinetics. Rate constants (k) were determined by least-squares analysis of the data. Results are listed in Table II.

For one particular run, monitoring the maximum at 385 nm for 5d yielded the same rate constant over the first half-life

Table I. Yields of Thioxanthenes from the Deprotonation of 10-Arylthioxanthenium Salts

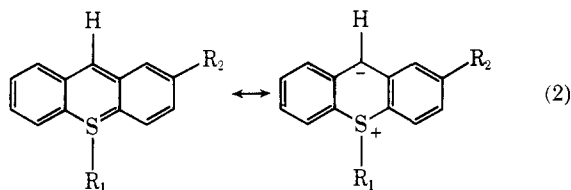
Compound	% yield of 4 ^a	Compound	% yield of 4 ^a
3a	90 ^b	3f	82
3b	90 ^b	3g	85
3c	98	3h	91
3d	71 ^{b,c}	3i	96
3e	98		

^a Yields were determined ($\pm 2\%$) by GLC using 9-*p*-tolylthioxanthene as an internal standard unless otherwise indicated. Detector response factors were determined on authentic samples of the rearrangement products. ^b Studied in ref 1. ^c Isolated yield.

($k_{385} = 1.21 \times 10^{-3} \text{ s}^{-1}$) as derived from the 510-nm peak ($k_{510} = 1.24 \times 10^{-3} \text{ s}^{-1}$). Similar agreement was found for 5e ($k_{378} = 7.9 \times 10^{-4} \text{ s}^{-1}$; $k_{500} = 8.1 \times 10^{-4} \text{ s}^{-1}$). That the rates of decay of the two absorption maxima in each thiaanthracene are the same indicates that the two absorptions arise from the same species. However, monitoring the peak near 385 nm is generally less convenient due to spectroscopic interference from decomposition (rearrangement) products, and our rate studies for the other compounds in this series were therefore restricted to the transition near 500 nm.

The rate of rearrangement of thiaanthracenes was observed to be markedly faster in a less polar solvent (90% toluene/10% Me₂SO).⁷ Rearrangement of 5d was 2.4 times faster and that of 5e was 2.5 times faster in a 90% toluene/10% Me₂SO mixture (Table III) than in Me₂SO (Table II) at 22 °C. These observations are consistent with the ylidic character of thiabenzene,¹ since a more polar solvent stabilizes a charge-separated species, and stabilization of the ground state of the reactant results in an increase in the activation energy, and thus in a decrease in the rate of rearrangement.

Substituent Effects. The effect of structure on reactivity (Table II) lends added support to the portrayal of thiaanthracenes as cyclic sulfonium ylides (eq 2).¹ Ortho and/or para



methoxy and/or para chloro substituents show a stabilizing effect of up to 500 times that of the parent, 10-phenyl-10-thiaanthracene (5a). Stabilization of a sulfonium ylide should be possible by delocalization (or by inductive stabilization) of

Table III. Rates of Rearrangement in 90% Toluene/10% Me₂SO

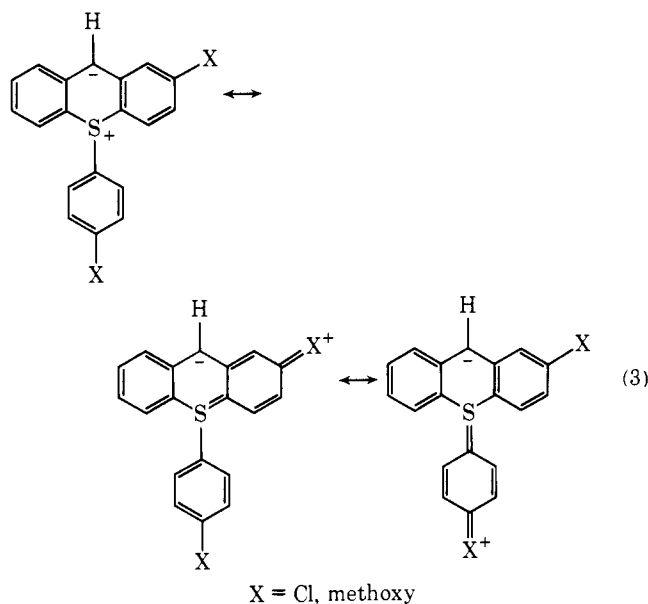
Compd	T, °C	k × 10 ⁴ , s ⁻¹
5d ^a	32.0	102.7
	21.5	29.7
	9.5	6.19
	0.0	1.77
	32.0	72.1
5e ^b	22.0	20.4
	10.0	4.90
	3.0	1.88 ^c
	-0.5	1.30 ^c

^a Rate constants were determined over the first 4 half-lives.

^b Rate constants were determined over the first half-life. Unless otherwise noted, linearity was maintained over at least 4 half-lives.

^c Deviation from linearity was substantial after the first half-life.

the positive charge on sulfur and/or of the negative charge on carbon.¹ The studies described above indicate a stabilizing effect brought about by delocalization of the positive charge through π donation⁸ (eq 3).



A Stable Thiaanthracene Anion. The observed stabilization led us to a search for an even better electron-donating substituent R₁ (eq 2), such as *p*-hydroxy- and *p*-dimethylaminophenyl.^{9,10} Difficulties were encountered in the synthesis of the 10-(*p*-dimethylaminophenyl)thioxanthenium salt by routes

Table II. Rates of Rearrangement (Eq 1) in Me₂SO at 22 ± 1 °C

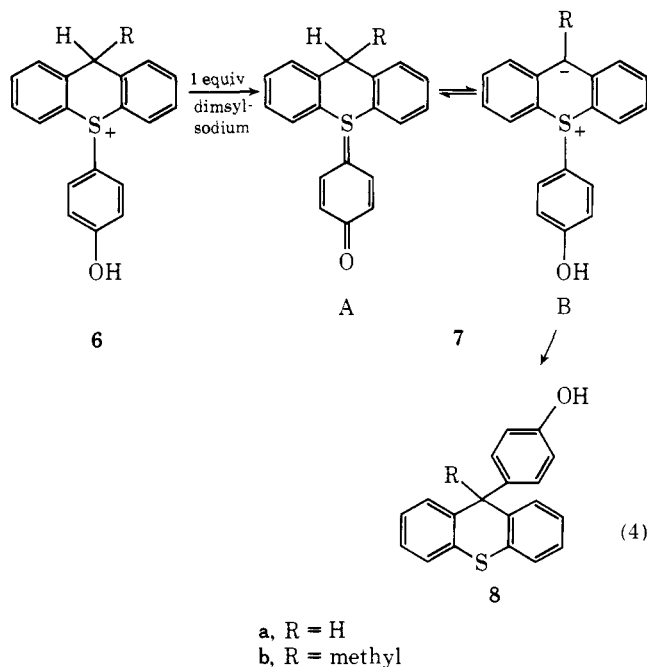
Compd	λ_{max} , nm	k × 10 ³ s ⁻¹ (no. of runs) ^a	$\tau_{1/2}$, min	No. of $\tau_{1/2}$ ^b
5a	388, 497	13 ± 4 (10)	0.9	2.1-3.9
5b	386, 510	8.4 ± 1.5 (6)	1.4	2.2-3.4
5c	391, 496	3.5 ± 1.5 (4)	3.3	2.0-2.7
5d	385, 510	1.27 ± 0.03 (3)	9.1	2.7-4.3
5e	378, 500	0.81 ± 0.09 (5)	14.2	2.0-4.5
5f	387, 530	0.61 ± 0.04 (5)	18.9	1.3-4.4
5g	382, 507	0.17 ± 0.02 (4)	68	1.3-3.5
5h	388, 492	0.033 ^c	350	2.2
5i	386, 502	0.023 ^c	505	0.3

^a Errors are the standard deviation from the average value. ^b Number of half-lives over which the data were analyzed, after which time absorbances were too small to be meaningful or deviation from linearity became substantial (generally due to a decrease in decomposition rate toward the end). ^c Value uncertain due to inhomogeneity of solution during the monitoring of the decomposition. Values are for the run which maintained linearity (homogeneity) the longest.

employed³ in the synthesis of **3** (all in acid media). Our studies were therefore restricted to 10-(*p*-hydroxyphenyl)thioxanthonium perchlorate (**6a**) and 9-methyl-10-(*p*-hydroxyphenyl)thioxanthonium perchlorate (**6b**), which were synthesized and deprotonated using dimsyl anion⁴ in Me₂SO.

Deprotonation of **6a** with 1 equiv of base afforded a deep red solution (**7a**), λ_{\max} (log ϵ) 500 nm (4.0), 340 (4.4), whose ¹H NMR spectrum featured resonances at δ 4.58 (br s, 1), 7.25 and 6.43 (AA'BB', apparent A₂B₂, q, 4, splitting = 9.5 Hz), and 8.0–7.5 (m, 8). Deprotonation in Me₂SO-*d*₆ resulted in H-D exchange at the 9 position, as evidenced by a decrease in intensity and broadening of the resonance at δ 4.58. The solution slowly decolorized (first $\tau_{1/2}$ ~ 6 h by ¹H NMR at probe temperature) and the discharge in color was accompanied by a change in the ¹H NMR spectrum (δ 5.51 (br s, 1), 6.94 and 6.67 (AA'BB', apparent A₂B₂, q, 4, splitting = 9 Hz), 8.2–7.2 (m, 8)). The 9-methyl derivative (**6b**) was similarly deprotonated. The rearrangement products (**8a** and **8b**) were isolated as their methyl ethers (**4e** and **9**, respectively) and the yields determined by GLC (**4e**, 70%; **9**, 91%).

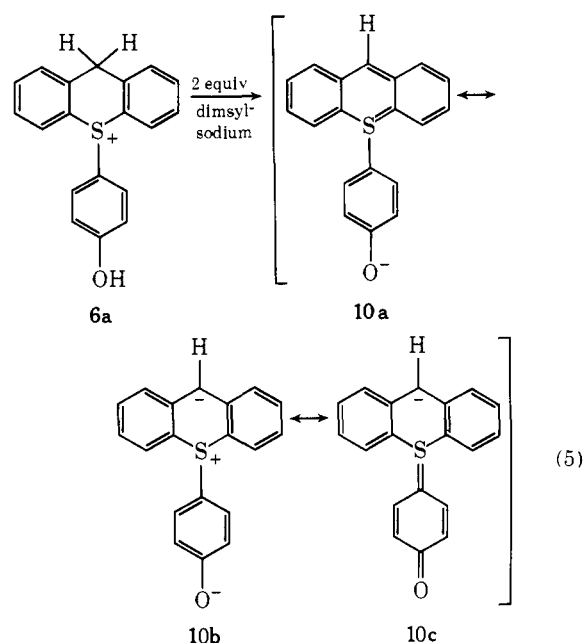
The red solution formed by deprotonation of **6a** was quenched with one equivalent of D₂SO₄, resulting in regeneration of the sulfonium salt with 78% D in the 9 position and 22% D in the hydroxylic position. This result clearly demonstrates the prototropic equilibrium, shown in eq 4, between a



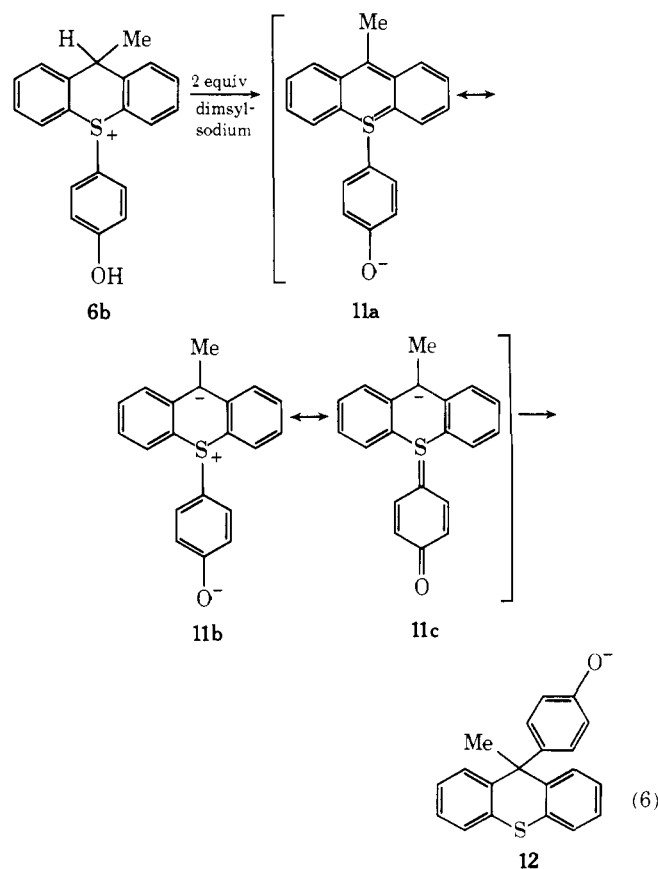
“keto” form A and an “enol” form B.¹¹ The H-D exchange in Me₂SO-*d*₆ and the broadness of the signal at δ 4.58 can also be explained by this equilibrium, which causes exchange of the diastereotopic 9-protons and of the hydroxy proton. The chemical shift lies between that of the 9-proton in other 10-aryl-10-thiaanthracenes (δ ~5.7), which resemble B, and that of the 9-protons in thioxanthene (δ 3.80 in CS₂)¹² or in 10-(*p*-hydroxyphenyl)thioxanthonium perchlorate (**6a**) (δ 4.17 and 4.55), which resemble A.

Deprotonation of **6a** with 2 equiv of base produced (eq 5) a thiaanthracene anion (**10**) with remarkable stability. Its ¹H NMR spectrum in Me₂SO (δ 5.48 (s, 1, 9-proton), 7.47–5.85 (m, 12)) did not show any appreciable change over a period of 40 days at room temperature. *This is the first example of a stable thiaanthracene derivative.* Deprotonation in Me₂SO-*d*₆ resulted in H-D exchange at the 9 position, as evidenced by a decrease in intensity of the resonance at δ 5.48. The stability of **10** is due to extensive delocalization of the positive charge on sulfur, i.e., to the importance of contributions from ca-

nonical structure **10c**, or the unimportance of contributions from **10a**, the canonical form which formally represents a thiaanthracene structure. The stability of thiaanthracene **10** is thus seen to result from its non-thiaanthracene character!



The thiaanthracene anion (**11**) derived from **6b** was not as stable as the parent compound **10**, and rearranged (eq 6) to **12**, isolated after protonation and identified as its methyl ether (**9**)



(85% yield by GLC). The ¹H NMR spectrum of **11** features resonances at δ 2.08 (s, 3, 9-CH₃), 7.43–5.95 (m, 12). The pattern in the aromatic region is essentially identical with that of **10**.

It is interesting to note the marked upfield shift of the 9-proton in **10** (δ 5.48) relative to the 9-proton in anthracene (δ

Table IV. Activation Parameters for the Rearrangements of **5d** and **5e**

Compd	ΔH^\ddagger , kcal/mol ^a	ΔS^\ddagger , eu ^a	ΔG_{25}^\ddagger , kcal/mol
5d	20.5 ± 0.13	-0.5 ± 0.5	20.65
5e	19.9 ± 0.3	-3.3 ± 1.1	20.87

^a Errors are standard deviations derived from least-squares analysis.

8.58 in Me₂SO),¹³ and of the 9-methyl protons in **11** (δ 2.08) relative to the methyl resonance in 9-methylanthracene (δ 3.06 in Me₂SO).¹⁴ A similar upfield shift ($\delta \sim 5.7$) was observed for other thiaanthracenes (**5**) and is indicative of negative charge on the 9-carbon and of the ylidic character of thiaanthracenes.

Mechanism of the Rearrangement. The dependence of the rate constant on temperature was studied for the rearrangements of **5d** and **5e** (Table III). A solvent mixture (90% toluene/10% Me₂SO) was employed, which made it possible to carry out measurements at lower temperatures. Rates and temperatures were fitted by least-squares analysis to the Eyring equation¹⁵ in order to determine the activation parameters (Table IV). The small negative ΔS^\ddagger for **5d** and **5e** is added evidence for the intramolecularity of the rearrangement,¹⁶ shown previously by crossover experiments.^{1,2e}

Thiabenzenes have been described as cyclic sulfonium ylides,¹ which can undergo thermal Steven rearrangements.^{1,2e} The ylidic character of thiaanthracenes has been demonstrated in the present work by the upfield shift of the 9-proton, solvent and substituent effects on stability, and, most significantly, by the generation of a stable thiaanthracene anion (**10**). The rearrangement of thiaanthracenes can be formally described as a six-electron, [1,4] sigmatropic shift.^{1,2e} For a [1,4] shift to occur, an ylide must be formed by deprotonation from the α -position of an allyl-like substituent or from the γ position of a vinyl-like substituent, so that a negative charge at the α position is in conjugation with the γ position. Although [1,2] shifts are more common in allylides,¹⁷ there are examples of [1,4] shifts occurring as a rearrangement pathway in ammonium allylides¹⁸ and in sulfonium allylides.¹⁹ However, when an allyl group is present, formation of the ylide usually occurs by deprotonation from the α position of one of the other, nonallylic substituents, followed by [1,2] or [3,2] *allyl* migration.¹⁷ In 10-arylthioxanthenium salts, deprotonation to form any ylide other than the thiaanthracene would require formation of a phenyl (or benzyl for **5b** or **5d**) carbanion. A [1,2] shift in thiaanthracenes can only be accompanied by loss of some benzenoid aromaticity. Thus, a [1,4] shift is the only reasonable rearrangement pathway in these systems.

Experimental Section²⁰

General Procedure for Synthesis of Thioxanthenium Salts (**3**, **6**).

Method A:^{3a} **From Sulfoxide with Concentrated Sulfuric Acid. Example:** 2-Chloro-10-phenylthioxanthenium Perchlorate (**3c**). Concentrated sulfuric acid (3 ml) was added dropwise to a stirred solution of 2-chlorothioxanthene 10-oxide¹ (0.85 g) in benzene (15 ml) at ca. 5 °C under a nitrogen atmosphere. The red reaction mixture was allowed to warm to room temperature and was stirred for 48 h. The mixture was poured onto ice and the aqueous layer was extracted with ether. The aqueous layer (almost colorless) was cooled with ice, and perchloric acid (70%, 5 ml) was added with stirring. The crystals which precipitated after cooling were collected by filtration, washed with ether, and dried under vacuum. Recrystallization from acetonitrile-ether afforded **3c** in the form of colorless plates (0.24 g, 17%).

Sulfonium salts **3a**, **3b**, and **3d** were similarly synthesized.¹

Method B:^{3b} **From Sulfoxide with Phosphorus Oxychloride and Perchloric Acid. Example:** 10-(*p*-Hydroxyphenyl)thioxanthenium Perchlorate (**6a**). Thioxanthene 10-oxide²¹ (5.62 g) was added in small portions to an ice cooled and stirred mixture of phenol (3.82 g), POCl₃

(10 ml), and perchloric acid (70%, 20 ml) under nitrogen. Slow evolution of gaseous HCl was observed. The mixture was stirred for 36 h in an ice bath and under a slow flush of nitrogen. The pink-red reaction mixture was poured into ice water and stirred for 30 min. The supernatant aqueous layer was discarded and the residual red solid was treated with ether (100 ml). The pink crystals which separated were collected by suction filtration, washed several times with ether, and dried under vacuum. The crude crystals were purified by recrystallization from acetonitrile-ether to yield **6a** in the form of colorless needles (5.24 g, 51%).

Starting either from *cis*- or from *trans*-9-methylthioxanthene 10-oxide,¹² crystals of 9-methyl-10-(*p*-hydroxyphenyl)thioxanthenium perchlorate (**6b**) were obtained in 37% yield by this method.

Using anisole in place of phenol, 10-(*p*-methoxyphenyl)thioxanthenium perchlorate (**3e**) was similarly synthesized in 53% yield.

Method C: From Sulfoxide with Phosphorus Oxychloride. Example: 10-(2,4-Dimethoxyphenyl)thioxanthenium Perchlorate (**3g**). Thioxanthene 10-oxide²¹ (1.07 g) was added to an ice cooled and stirred mixture of *m*-dimethoxybenzene (1.30 g) and POCl₃ (2.5 ml) under nitrogen. The mixture was stirred for 24 h at room temperature under nitrogen, decomposed with ice and water, and treated with ether to yield a clear two-phase mixture. The aqueous layer was extracted twice with ether and mixed with perchloric acid (70%, 5 ml) to precipitate the sulfonium salt (**3g**). The faintly violet crystalline solid was collected by suction filtration and dried under vacuum. Recrystallization from acetonitrile-ether afforded tiny colorless rods of **3g** (0.19 g, 9%).

Sulfonium salts **3f** (7.3%), **3h** (4.0%), **3i** (8.7%), and **6a** (9.2%) were similarly synthesized. 2-Methoxythioxanthene 10-oxide was prepared by diborane reduction²² of 2-methoxythioxanthene-9-one,²³ followed by oxidation with H₂O₂.¹

Physical properties and elemental analyses of these sulfonium salts are presented in Table V.

General Procedure of Deprotonation Reactions of Sulfonium Salts and Their Product Analysis.

In an NMR tube tightly sealed with a rubber septum cap and filled with nitrogen, 60–90 mg of the sulfonium salt (**3**, **6**) was dissolved in Me₂SO (or Me₂SO-*d*₆) with warming. Upon addition of 1 equiv of dimsyl- (or dimsyl-*d*₅) sodium⁴ in Me₂SO (or Me₂SO-*d*₆) to this solution, an intense red color developed instantaneously. The ¹H NMR spectrum of the solution (after centrifugation) was recorded immediately before and after addition of dimsylvodium and then at subsequent intervals until the solution became colorless and the spectrum remained invariant. The reaction mixture was then diluted with benzene and water; the aqueous layer was extracted twice with benzene, and the combined benzene extracts were washed several times with water and dried over sodium sulfate.

The crude product obtained on evaporation of the benzene was weighed and analyzed by GLC (see below) without any purification. In order to facilitate GLC analysis, the two *p*-hydroxyphenyl compounds (**7a** and **7b**) were converted to their methyl ethers (**4e** and **9**, respectively) by conventional methods (dimethyl sulfate, anhydrous potassium carbonate, and acetone) and then analyzed as such.

General Procedure for the Independent Synthesis of Rearrangement Products (**4**). Example: 9-(*p*-Methoxyphenyl)thioxanthene (**4e**).

p-Methoxyphenyllithium was prepared²⁴ by addition of 56 mmol of *n*-butyllithium in hexane (Alfa, 1.7 M) to a cooled solution of 10.43 g (56 mmol) of *p*-bromoanisole in 100 ml of anhydrous ether at -78 °C (dry ice-acetone bath) under a nitrogen atmosphere. After 30 min, 5.95 g (28 mmol) of thioxanthene-9-one in 150 ml of dry tetrahydrofuran (THF) was added. The reaction was held at -78 °C for ~3 h and then quenched with water. The orange solution turned yellow upon warming to room temperature. The layers were separated and the aqueous layer was extracted with chloroform. The organic extracts were combined, dried, and concentrated to yield a colorless oil (TLC of this oil showed it to be mainly one component with a trace of ketone).

The crude alcohol was dissolved in 100 ml of dry ether, cooled to -78 °C, and treated (dropwise) with a mixture of 7 ml of 70% HClO₄ in 20 ml of glacial acetic acid. The thioxanthylium perchlorate precipitated immediately as a red orange solid; this precipitate was filtered, washed with ether until the filtrate was colorless, and dried under vacuum.

The crude, dried perchlorate salt was suspended in 150 ml of dry THF, and solid NaBH₄ (2.5 g) was added slowly. (If this reduction was carried out in methanol or ethanol a mixture of the desired product and the 9-aryl-9-alkoxythioxanthene was obtained.) After 5 min the

Table VI. Thioxanthenes: Physical Properties^a

Compd	Molecular formula	Mp, °C	Elemental analysis, %		¹ H NMR spectrum (solvent)	Mass spectrum (inlet temp, °C) mass peak (% base peak)
			Calcd	Found		
4c	C ₁₉ H ₁₃ SCI	120-121	C, 73.90 H, 4.24 S, 10.38	74.15 4.23 10.60	(CDCl ₃) 5.26 (s, 1) 6.80-7.50 (m, 12)	(120 °C) 310 (25), 309 (17), 308 (66), 307 (11), 233 (38), 232 (24), 231 (100), 195 (10), 135.5 (11)
4e	C ₂₀ H ₁₆ OS	153-154	C, 78.91 H, 5.30 S, 10.53	78.66 5.52 10.50	(CDCl ₃) 3.70 (s, 3) 5.30 (br s, 1) 6.60-7.50 (m, 12)	(155 °C) 305 (24), 304 (100), 303 (26), 197 (26), 196 (47), 164 (12), 151 (13)
4f	C ₂₂ H ₂₀ O ₃ S	211-212	C, 72.50 H, 5.53 S, 8.80	72.30 5.32 9.02	(CDCl ₃) 3.60 (s, 6) 3.82 (s, 3) 5.55 (br s, 1) 6.25 (s, 2) 6.70-7.50 (m, 8)	(200 °C) 365 (26), 364 (100), 363 (29), 330 (27), 197 (14)
4g	C ₂₁ H ₁₈ O ₂ S	103-104	C, 75.42 H, 5.43 S, 9.59	75.09 5.61 9.68	(CDCl ₃) 3.72 (s, 3) 3.86 (s, 3) 5.71 (s, 1) 6.30-6.60 (m, 2) 6.99-7.60 (m, 9)	(105 °C) 335 (23), 334 (91), 333 (23) 317 (13), 302 (34), 198 (16) 197 (100), 196 (11), 165 (11)
4h	C ₂₂ H ₂₀ O ₃ S	Oil	Exact mass calcd 364.113308 found 364.113123		(CCl ₄) 3.52 (s, 6) 3.68 (s, 3) 5.48 (s, 1) 6.09-7.34 (m, 10)	(250 °C) ^b 365 (18), 364 (100), 363 (21) 349 (10), 348 (33), 332 (24) 227 (56), 182 (15), 184 (10) 121 (12), 119 (39), 117 (40)
4i	C ₂₁ H ₁₇ O ₂ SCI	142.5-143.5	C, 68.38 H, 4.65 S, 8.69	68.33 4.77 8.75	(CDCl ₃) 3.78 (s, 3) 3.89 (s, 3) 5.64 (s, 1) 6.32-7.55 (m, 10)	(135 °C) ^b 370 (40), 369 (29), 368 (100), 367 (19), 354 (11), 338 (18), 334 (26), 308 (17), 233 (30), 232 (15), 231 (77), 111 (11)
9	C ₂₁ H ₁₈ OS	166.5-167.5	C, 79.21 H, 5.70 S, 10.07	79.06 5.88 9.86	(CDCl ₃) 2.00 (s, 3) 3.75 (s, 3) 6.75 (s, 4) 7.13-7.53 (m, 8)	(160 °C) 319 (16), 318 (100), 305 (12), 304 (62), 303 (75), 259 (16), 211 (79), 159 (14), 129 (13), 57 (14), 43 (10)

^a 4a, 4b, and 4d have been previously reported.¹ ^b Mass peaks below 100 are not reported.

dilution) could also be monitored. The rate constants derived (see below) for the samples before and after dilution were essentially the same (e.g., for 5e at 2.64×10^{-3} M, $k = 8.1 \times 10^{-4} \text{ s}^{-1}$ and at 0.53×10^{-3} M, $k = 9.1 \times 10^{-4} \text{ s}^{-1}$; for 5f at 3.1×10^{-3} M, $k = 6.1 \times 10^{-4} \text{ s}^{-1}$ and at 3.1×10^{-4} M, $k = 6.1 \times 10^{-4} \text{ s}^{-1}$).

Determination of Rate Constants. Visible absorption spectra were recorded on solutions in standard cells ($l = 1.00$ cm) fitted with a rubber septum cap. All containers were flushed with nitrogen prior to use. Solutions were transferred and measured by syringe. A positive pressure of nitrogen was kept on the cell while recording spectra. Absorption maxima (λ_{max}) were determined by scanning repeatedly over the maxima from both directions. Once λ_{max} had been determined, subsequent data were obtained by recording at this particular wavelength (absorbance (A) vs. time).

Plots of $-\ln A$ vs. time appeared to be linear, generally for at least 2 half-lives.⁶ A rate constant (k) was determined for each run by a linear least-squares treatment of the data. The correlation coefficient (ρ) was 0.994 or better for each run. The individual rate constants for all kinetic runs for each compound were averaged and the standard deviation computed. Values for $\log \epsilon$ were calculated from the least-squares fit by extrapolation of A to time = 0. Typical values of $\log \epsilon$ were 3.5 for the 500-nm transition and 3.7 for the 385-nm transition. However, it was found that, for a given sample, values varied substantially (e.g., for 5g the following values were obtained: $\log \epsilon$ (507 nm) 3.76, 3.62, 3.34, and 3.58 (average 3.57); $\log \epsilon$ (382 nm) 4.06, 3.92, and 3.49 (average 3.82)).

Temperature Dependence. The temperature was regulated with a Lauda constant temperature circulator, Model KB-20. The cell was placed in a jacketed cell holder. For low temperature runs the cell cavity was flushed with dry air to prevent fogging on the faces of the

cell. The cell temperature at 0 °C was checked on a dry run and was found to deviate by less than 0.5 °C over a 4 h period. The solvent used for the temperature dependence runs was 90% toluene (distilled from sodium under nitrogen atmosphere)/10% Me₂SO. Similar experimental conditions were applied as described for the kinetic studies (see above). A solution of 3d (1.45 ml of 9.6 mg/10 ml) or 3e (1.5 ml of 8.6 mg/10 ml) was first added to the cell and the temperature was allowed to stabilize. The dimethylsodium solution (2.34×10^{-3} M) was externally cooled to about the same temperature. Base (1 equiv) (1.35 ml for 3d; 1.3 ml for 3e) was then syringed into the cell and the solutions were mixed. The concentrations were such that the initial absorbance was about 8 absorbance units; in this way, the rearrangement could be monitored at a wavelength ca. 70 nm above λ_{max} (i.e., at ca. 570 nm), and the period of measurement was thus extended over an additional 2 half-lives before the maximum came onto scale.

Rate constants (k) at each temperature (T) were determined by linear least-squares treatment of $-\ln A$ vs. time over the first 4 half-lives for 5d and over the first half-life for 5e. In each case the correlation coefficient (ρ) was 0.999 or better. Linearity was maintained over at least 4 half-lives except for the two lower temperature runs for 5e. The activation parameters were determined by a linear least-squares fit to the Eyring equation¹⁵ ($\ln k/T$ vs. $1/T$). Error limits are standard deviations derived from this least-squares treatment.

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Dipole Stabilized Carbanions: *N*-Methyl Carboxamides

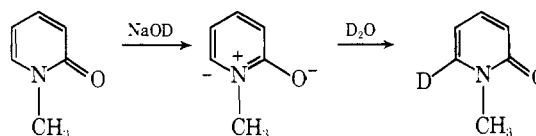
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Abstract: The mechanism of the reaction of *N,N*-dimethylbenzamide (1) with lithium 2,2,6,6-tetramethylpiperidide to give *N*-methyl-*N*-phenacylbenzamide (2) has been investigated by a double labeling experiment. The labeling results are consistent with the initial formation of a formally dipole stabilized carbanion which is subsequently benzoylated by **1**. A mechanism involving a homoenolate anion intermediate which undergoes ring opening prior to benzoylation is ruled out by the same evidence. Related conversions of *N*-methyl-*N*-phenylbenzamide (**5**) to 2-anilinoacetophenone (**6**) and *N*-phenyl-*N*-phenacylbenzamide (**7**) and of *N*-methyl-3,3-diphenyl-2-piperidone (**8**) to *N*-methyl-*N*-(4,4-diphenylbutyl)-2-(3,3-diphenyl-2-piperidonyl)acetamide (**9**) are reported. Circumstantial evidence is presented which suggests that these reactions involve the *N*-methyl syn to the carbonyl oxygen and are lithium dependent. The reaction of *N,N*-diethylbenzamide (**15**) with lithium 2,2,6,6-tetramethylpiperidide gives *o*-benzoyl-*N,N*-diethylbenzamide (**16**) due to metalation of the ortho carbon.

Carbanionic species bearing a formal negative charge adjacent to a heteroatom have recently been found to be exceedingly useful synthetically; such species have been considered theoretically interesting for some time.^{1–15} A demonstration that mesomeric dipole stabilization can be important in the direct formation of a formal α -nitrogen carbanion was provided some years ago by our report of C-6 hydrogen-deuterium exchange of some pyridones in basic deuterium oxide at 100°.² The case is illustrated for *N*-methyl-2-pyridone.

In recent years a number of α -nitrogen carbanions have been reported which could be dipole stabilized, although other effects may be important in various cases.³ Specifically, an intermediate or product can be envisioned for which at least one



canonical form has a positive charge on a nitrogen adjacent to the carbon bearing the negative charge in the hydrogen-deuterium exchanges^{2–8} and/or metalations^{3,8–14} of carboxamides,^{2,4} a vinyllogous carboxamide,² a vinyllogous carbox-sulfoxamide,⁷ isonitriles,⁹ imidates which are part of azaheteroaromatic systems,^{6,11} phosphoramides,^{5,10} isothiocyanates,¹² azoxy compounds,¹³ nitrosoamines,^{3,8} and azine 1-oxides.^{5,14} Such stabilization may also be important for some