2,3,7,8-tetramethoxythianthrene was observed.^{6b,12,13} Electrolysis of a nitromethane solution containing 2,3,7,8-tetramethoxythianthrene and saturated with anhydrous magnesium perchlorate at a constant potential of +1.00 V *vs.* silver|saturated silver nitrate (nitromethane) gave an apparent "*n*" value of 2.06. Thus, two electrons were removed from each molecule of 2,3,7,8-tetramethoxythianthrene to give a sapphire blue solution (λ_{max} = 710 nm)[14] of dication **1b**.

Oxidation of 2,3,7,8-tetramethoxythianthrene by perchloric acid gave the corresponding dication diperchlorate as a dark blue solid. This material dissolved in nitromethane saturated with aluminum chloride was devoid of an epr signal and its absorption in the visible was very similar to the dication solution prepared by controlled potential electrolysis. A weighed amount of the solid dication diperchlorate was added to a mixture of nitromethane and water. The aqueous phase after separation was neutralized and analyzed for perchlorate ion by use of a perchlorate ion specific electrode.[15] The amount of perchlorate ion found by this analysis was consistent with a formula of $C_{16}H_{16}O_4S_2 \cdot 2ClO_4$ for the solid. Another sample of the solid dication diperchlorate dissolved in nitromethane containing anhydrous magnesium perchlorate was titrated with a solution of 2,3,7,8-tetramethoxythianthrene (**2**) and anhydrous magnesium perchlorate in nitromethane. The amount of 2,3,7,8-tetramethoxythianthrene required to reach the endpoint determined visually by the color change was consistent with the reaction shown in eq 2. The green solution resulting

$$\mathbf{1b} + \mathbf{2} \longrightarrow 2(\mathbf{2}^{\cdot +}) \qquad (2)$$

from this titration (λ_{max} = 765 nm) unlike its precursors gave an epr signal. The epr spectrum was the same as that obtained from the 2,3,7,8-tetramethoxythianthrene cation radical formed by controlled potential electrolysis of 2,3,7,8-tetramethoxythianthrene.

Oxygen bubbled into a solution of 2,3,7,8-tetramethoxythianthrene in nitromethane saturated with aluminum chloride gave a sapphire blue solution of dication **1b**. The blue solution was not obtained in the absence of oxygen. The visible absorption spectrum of this solution was virtually the same as the blue solutions obtained by anodic or perchloric acid oxidation of 2,3,7,8-tetramethoxythianthrene. The nmr spectrum of this blue solution showed two broad singlets at δ 6.6 (12 H) and 8.4 (4 H) ppm downfield from external tetramethylsilane.[16] The nmr spectrum is easily reconciled with structure **1b**.^{16,17} The very markedly deshielded methyl groups indicate considerable delocalization of the positive charges from the rings to the oxygen atoms.

The data strongly support the thesis that oxidation of 2,3,7,8-tetramethoxythianthrene in each of the three ways studied gives the corresponding dication **1b**.

Acknowledgment. Support of this research by the National Institutes of Health, the National Science Foundation, and the Mobil Foundation is gratefully acknowledged.

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A Convenient General Method of Dehydrogenation Using the Alkyllithium–*N,N,N',N'*-Tetramethylethylenediamine Complex[1]

Sir:

Dehydrogenation is frequently the final step in the synthesis of polycyclic aromatic molecules. However, the traditional methods are seldom completely satisfactory due to the facility of competing secondary processes. We now report an efficient and convenient general method of aromatization, utilizing the alkyllithium–*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex.[2] A significant feature of the method is the intermediacy of the dianions of polycyclic hydrocarbons, the first examples of such to be generated *via* double proton abstraction, with the recent exceptions of the acenaphthylene and naphthalene[3a] dianions.[3b]

Initial experiments were conducted with *cis*-9-ethyl-10-methyl-9,10-dihydroanthracene (**1b**) selected as a challenge on the basis of its unsatisfactory behavior with other methods.[4] In a typical experiment, a solution of *n*-butyllithium (20 mmol) in hexane was introduced by syringe into a solution of **1b** (5 mmol) in dry cyclohexane (30 ml) and TMEDA (15 ml) and the resulting deep red solution of the monoanion brought to reflux, whereupon the color changed to the intense purple characteristic of the dianion. After 1 hr at reflux, the mixture was allowed to cool (5 min) and the color discharged by the addition of anhydrous cad-

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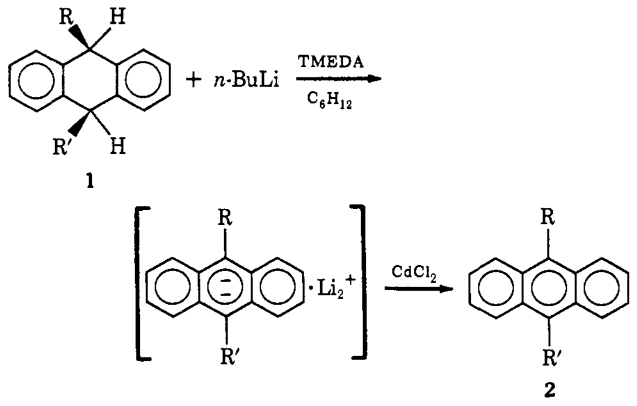
(4) Numerous attempts with other reagents (*e.g.*, sulfur, palladium on charcoal, $AlCl_3$, I_2, $FeCl_3$, $SbCl_5$, DDQ, trityl perchlorate, etc.) led to unsatisfactory yields of products difficult to purify.



a, $R = R' = H$; b, $R = CH_3$, $R' = CH_2CH_3$;
c, $R = CH_3$, $R' = H$; d, $R = CH_2CH_3$, $R' = H$;
e, $R = R' = CH_3$; f, $R = R' = CH_2CH_3$

mium(II) chloride (10 mmol). The product isolated by conventional extraction procedures was 9-ethyl-10-methylanthracene[5] (**2b**) (99%). Analogous reaction of 9,10-dihydroanthracene or its 9-methyl or 9-ethyl or 9,10-dimethyl or 9,10-diethyl derivatives proceeded similarly to afford the related anthracenes **2a,c–f** in essentially quantitative yield.

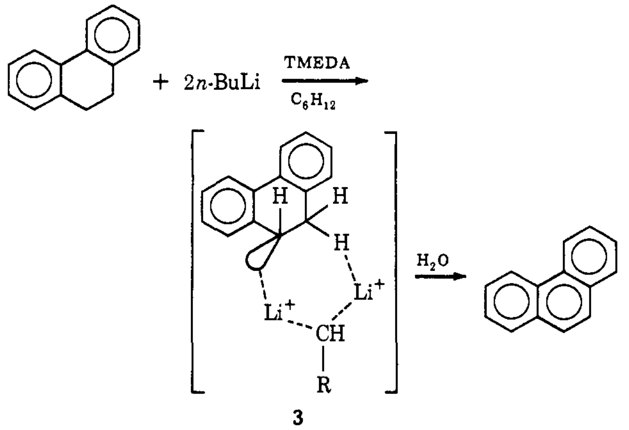
Since **1b–f** are readily obtained in high yield through alkylation of **1a** with *n*-butyllithium and the appropriate alkyl halide in THF at low temperature,[7] the overall sequence constitutes a net synthesis of the mono- and dialkylanthracenes from **1a**. This synthesis is, in our opinion, by all criteria (*e.g.*, yield, convenience, speed, purity of products) the method of choice.

Intermediacy of a dianion is supported by the necessity for an electron acceptor in the final stage.[8] Cadmium(II) chloride is reduced to metallic cadmium in the process. Other metal salts (*e.g.*, lead(II) chloride, copper(II) iodide or bromide, mercury(II) chloride, nickel(II) acetylacetonate) also serve.[9] In further agreement with a dianionic intermediate, treatment of the initial stage product with deuterium oxide leads to essentially quantitative (by nmr) incorporation of deuterium in both benzylic positions of **1b**, the latter recovered as an approximately equal mixture of cis and trans isomers.

Aromatization *via* hydride loss from a monoanion does not appear to compete to any significant extent under the conditions employed. Thus, the monoanion generated from equimolar proportions of **1b** and the lithium reagent affords on treatment with deuterium oxide **1b** containing a single deuterium and no **2b** (nmr and glpc).

Analogous reaction (1 hr) of 7,12-dihydrobenz[*a*]anthracene, acenaphthene, and bibenzyl proceeds similarly to afford benz[*a*]anthracene (97%), acenaphthylene (98%), and stilbene (67%), respectively.

On the other hand, 9,10-dihydrophenanthrene undergoes smooth dehydrogenation to phenanthrene *without added metal salt!* Here also aromatization *via* hydride loss from a monoanion does not appear likely. Thus, 2 equiv of the lithium reagent are required for quantitative conversion; with 1 molar equiv of *n*-butyllithium only starting material is recovered. Also, the reaction mixture retains an intense dark reddish brown color until it is discharged with water. On the other hand, attempted methylation of the anionic intermediate (3 molar equiv of RLi employed) with methyl bromide at 0° provided phenanthrene (94%) as the sole major product. Attempted deuteration also failed, again affording only phenanthrene (99%). These observations appear equally incompatible with a dianion. Moreover, reagents capable of oxidizing other aromatic dianions, such as copper(II) iodide and sodium benzoate, failed to discharge the color of the intermediate.



4,5,9,10-Tetrahydropyrene exhibited intermediate behavior, undergoing transformation directly to pyrene moderately well (72%) in the absence of added metal salt but more efficiently (94%) in the presence of copper(II) iodide.

Although the exact nature of the intermediate produced from dihydrophenanthrene remains uncertain, we tentatively suggest a 1:1 complex (*e.g.*, **3**)[10] between the salt of the monoanion and a molecule of the lithium reagent with both cations further solvated with one or more TMEDA molecules. Reactions of such a sterically crowded complex may be envisioned as taking place more readily on the incipient hydride center than on the sheltered carbanion orbital. The monoanionic intermediates derived from other ring systems (*e.g.*, the monoanion of **1**) probably also exist in solution in the form of complexes or aggregates with the cation and TMEDA. That such association plays an important role in allowing dianion formation is indicated by the fact that substitution of a highly polar solvent, such as hexamethylphosphoramide, for cyclohexane strongly inhibits aromatization of **1b**.

Why reactions of the 1,2- and 1,4-dihydro ring systems follow different pathways is not clear and may be a consequence of the different geometric requirements of the types of structure or the fact that 1,4-dianion forma-

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[5] All product structures were confirmed by nmr and glpc in comparison with authentic samples which, with the exception of acenaphthylene and benz[a]anthracene, were previously synthesized in our laboratory through conventional procedures.[6]

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[9] However, products were generally cleaner and yields higher with the cadmium salt.

[10] The structure of **3** is presented only as a visual aid to understanding. Recent evidence[3a] suggests the location of the lithium cation likely to be above the plane of the rings.

tion is energetically more favorable due to the lower charge repulsion to be overcome.

Research in progress is directed toward determining the scope of the method, particularly its applicability to more highly saturated molecules and to the synthesis of carcinogenic aromatic hydrocarbons and related compounds otherwise accessible only through tedious multistep procedures.

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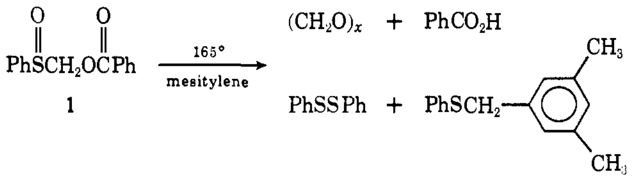
Mechanism of the Thermolysis of Benzoyloxymethyl Phenyl Sulfoxide. A New Sulfoxide Fragmentation Reaction

Sir:

Thermolysis of a sulfoxide may result in racemization, rearrangement, or fragmentation.[1-10] The most common fragmentations involve rearrangement to sulfenates followed by elimination of thiols to give aldehydes[4,5] or direct β elimination of sulfenic acids to give alkenes.[6-9] We recently reported an additional sulfoxide thermolysis reaction where methoxymethyl phenyl sulfoxide rearranged at 36° to a sulfenate, which then decomposed to phenyl benzenethiosulfinate and bismethoxymethyl ether.[11] The benzoyloxy analog (**1**),[12] however, was unreactive below 110°.

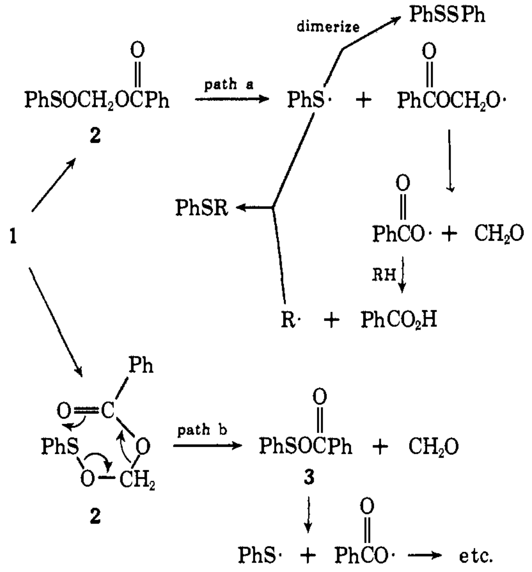
We now wish to report on the thermolysis of benzoyloxymethyl phenyl sulfoxide (**1**), for which a new sulfoxide fragmentation mechanism has been observed. An oxygen-18 labeling study indicates that the mechanism for the fragmentation does not involve a sulfenate intermediate.



Thermolysis of **1** in *cis*-decalin at *ca.* 190° for 4 days gave phenyl disulfide (61%), benzoic acid (23%), some paraformaldehyde, and considerable carbon black. After refluxing in toluene for 10 days, less than 10% of **1** was converted to products. However, on refluxing in mesitylene for 5 days, **1** was completely converted in a clean reaction to phenyl disulfide (*ca.* 10%), 3,5-dimethylbenzyl phenyl sulfide (*ca.* 80%), benzoic acid (77%), and paraformaldehyde (83%).[13]

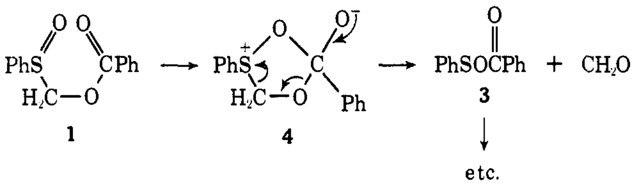
Two reaction mechanisms may be envisioned to explain the products isolated. The first (Scheme I) involves initial Meisenheimer rearrangement of **1** to benzoyloxymethyl benzenesulfenate (**2**) followed by fragmentation by either of two pathways. Path a involves homolytic cleavage of the S–O bond of **2**. Dimerization of the thiophenoxy radicals gives rise to phenyl disulfide. β-Scission of the benzoyloxymethoxy radical results in the formation of formaldehyde and benzoyloxy radical. Attack of the latter on solvent leads to benzoic acid and the sulfide. Path b involves a cyclic process leading to expulsion of formaldehyde with formation of an intermediate sulfenyl benzoate (**3**). Decomposition of **3** would give the other products. Some sulfenyl carboxylates have been isolated,[14] but **3** would be expected to decompose under the reaction conditions.

Scheme I



The second mechanism (Scheme II) involves direct attack of the sulfoxide oxygen on the carbonyl to give a cyclic zwitterionic intermediate (**4**), which could collapse with expulsion of formaldehyde to give benzene sulfenyl benzoate (**3**). A significant difference between these mechanisms is that the sulfoxide oxygen atom goes to the formaldehyde in Scheme I but to benzoic acid in Scheme II.

Scheme II



In order to distinguish between these mechanisms we have carried out the thermolysis of **1** labeled with ^{18}O

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