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REACTIONS OF 9-PHENYLTHIOXANTHENE 10-OXIDE WITH ORGANOMETALLIC REAGENTS[1)]

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It was proved that the reaction between 9-phenylthioxanthene 10-oxide (II) and organometallic reagents proceeds through the formation of 9-phenylthioxanthenyl radical. A new method of synthesis of thiaänthracene derivative was found by the reaction of II with aryllithium.

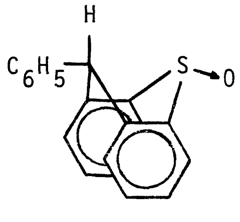
Sulfoxides that contain an active hydrogen at the α-position react with various reagents such as RCOCl,[2)] Grignard reagents[3a-3c)] and Ac_2O[4a-4c)] to give Pummerer-type products. However, the sulfoxides bearing no α-hydrogen atom, such as diphenyl sulfoxide, do not react with Ac_2O.[4b)] These also give triarylsulfonium salts by the addition of a strong acid after the reaction with aromatic Grignard reagents.[5)] No report has been found on the reaction of cyclic sulfoxides with an active hydrogen at the γ-position and organometallic reagents such as Grignard reagents or organolithiums.

In the present report, description will be made on the synthesis of 9-phenylthioxanthene 10-oxide (II) and the mechanism of the reaction between II and organometallic reagents as well as the new method of synthesis of 9,10-diphenyl-10-thiaänthracene (IV)[6)] by the reaction between sulfoxide derivative and phenyllithium.

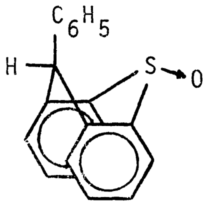
Structures of the Two Geometrical Isomers of 9-Phenylthioxanthene 10-Oxide (II)

9- Phenylthioxanthene (I)[6)] was oxidized by 35% H_2O_2 in $AcOH\text{-}CH_2Cl_2$ (1:2) at room temperature to give 9-phenylthioxanthene 10-oxide (II) in 86% yield (NMR measurement indicated that this was 1:3 mixture of cis-IIa and trans-IIb). Slow recrystallization of this mixture from MeOH gave two types of crystals, needles and prisms, which were mechanically separated with the aid of a microscope.

IIa: needles, mp 187-189°C, Found: C, 78.68; H, 4.93%. Calcd for $C_{19}H_{14}OS$: C, 78.58; H, 4.86%, IR (KBr) cm^{-1}: 1480, 1440, 1075, 1025, 945, 865, 810, 750, 700, and 685, NMR ($CDCl_3$) δ: 7.98-8.13 (2H, m, aromatic H), 6.98-7.66 (11H, m, aromatic H), and 5.13 (1H, s, C_9-H), Mass: m/e 290 (M^+) and 274 (M^+-O). IIb: prisms, mp 143-144°C, Found: 78.31; H, 5.11%. Calcd for $C_{19}H_{14}OS$: C, 78.58; H, 4.86%, IR (KBr) cm^{-1}: 1475, 1440, 1130, 1080, 1030, 940, 830, 755, 740, 725, and 695, NMR ($CDCl_3$) δ: 7.86-8.14 (2H, m, aromatic H), 6.70-7.66 (11H, m, aromatic H), and 5.53 (1H, s, C_9-H), Mass: m/e 290 (M^+) and 274 (M^+-O). The NMR studies by Ternay and his co-workers[7] on the structure of 9-methylthioxanthene 10-oxide suggests the view that the structures of IIa and IIb are as shown below.



IIa



IIb

Reactions of 9-Phenylthioxanthene 10-Oxide (II) with Organometallic Reagents

The reaction of II and phenylmagnesium bromide gave 9,9-diphenylthioxanthene (Va, 81%)[6] as a major product, and 9-phenylthioxanthene (I, 2%), 9-phenylthioxanthenol (III, 1%)[6], and 9-phenylthioxanthenyl peroxide (VI, trace)[8] as minor products. The reactions of alkyl and aryl Grignard reagents with II gave similar results. However, different reactivities against II were found between alkyl- and aryllithiums: The reaction of methyllithium with II gave only 9-methyl-9-phenylthioxanthene (Vb, 40%)[8] and I (25%) but the reaction of phenyllithium with II gave 9,10-diphenyl-10-thiaänthracene (IV) in 10% yield: mp 149°C (decomp.), Mass: m/e ($I^{\%}$rel.), Found: 350 (30, M^+), 273 (80), 213 (100), 197 (55), and 154 (45). Calcd for $C_{25}H_{18}S$: 350 (M^+), in addition to I (1%), Va (54%), and VI (trace). This mass spectrum shows that IV is a monomer.[9] The formation of IV implies a new method of synthesis of thiabenzenes.

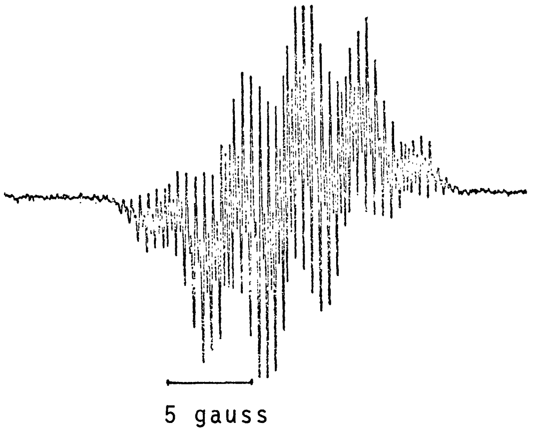


Fig. 1 ESR Spectrum of 9-Phenylthioxanthenyl Radical (VII)

The same ESR spectra were observed for the reactions between II and organometallic reagents. The ESR spectra were in agreement with that of 9-phenylthioxanthenyl radical (VII)[8] as shown in Fig. 1.

From the above data, the mechanism of the reactions between II and organometallic reagents is explained as shown in Chart 1.

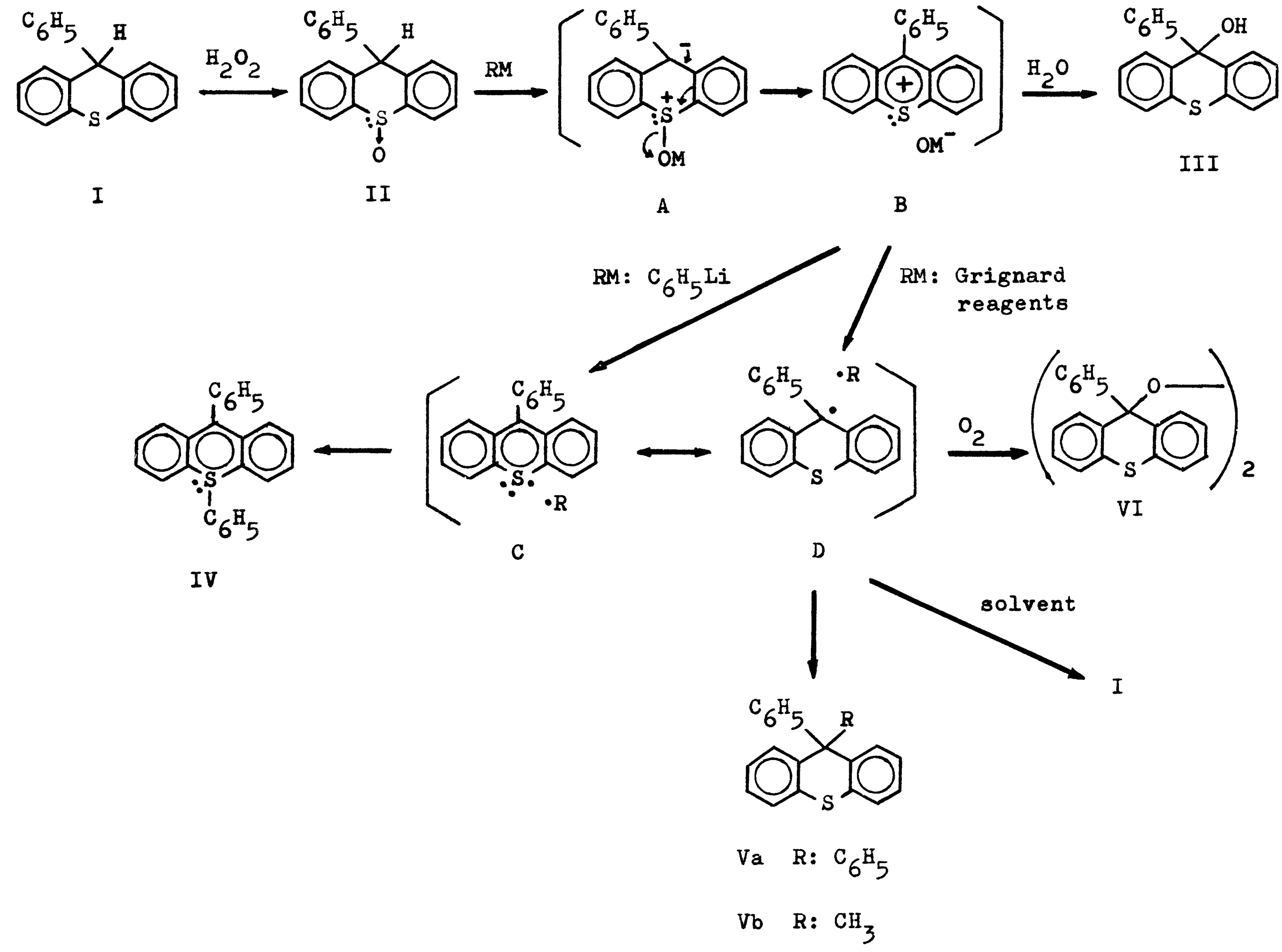


Chart 1

The zwitter ion A, which was formed as an intermediate in the reactions between II and organometallic reagents, changes to B. Then B is subjected to one-electron reduction by organometallic reagents and gives 9-phenylthioxanthenyl radical (C↔D) and •R. C or D couples with •R to give IV or V, respectively. D also reacts with solvent to produce I and with oxygen to form VI. III is formed by the hydrolysis of B.

Further studies on the title reactions are now way.

REFERENCES AND NOTES

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9) This mass spectrum was obtained below 130°C of sample temperature (Ionizing Energy: 70 ev). The sample temperature in mass spectrum measurement of thiabenzenes should be below the melting point (decomposition point) of thiabenzenes. Otherwise, many ion peaks appeared in the mass spectrum at m/e's, which were larger than that of the molecular ion peaks (M$^+$) of thiabenzenes. These ion peaks are attributable to the polimerization of degradation products of thiabenzenes. Also a number of ion peaks quite different from the fragment ion peaks of thiabenzenes appeared. Both the strength and the number of these ion peaks increased as the sample temperature was raised (See. C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, J. Org. Chem., **36**, 791 (1971). Mass spectrum of IV: m/e (I$^{\%}$rel.) 623 (10), 546 (20), 426 (10), 350 (39, M$^+$), 273 (93), 197 (100), and 154 (31) for inlet at 150-200°C, 70 ev).

The studies are now under way on the thermal decomposition of thiabenzene derivatives in mono-, bi-, and tricyclic systems and their reactions with various chemical reagents. The results will be published elsewhere in the near future.

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