THE REACTION OF UNSATURATED CARBONYL COMPOUNDS WITH "ACTIVATED" SULFUR[1]

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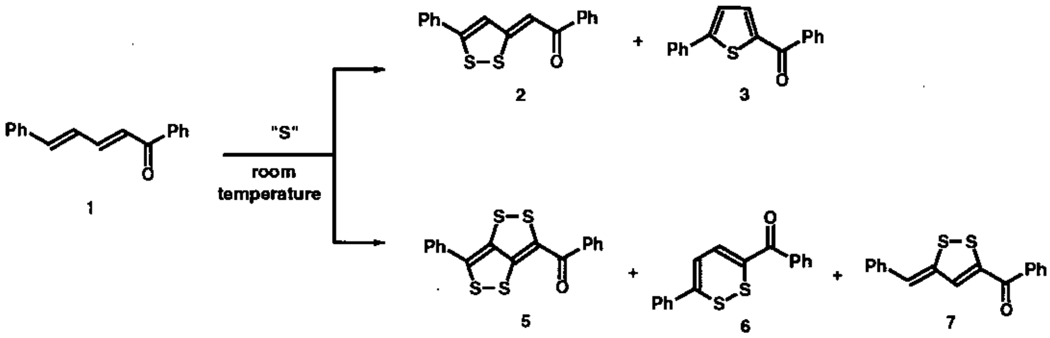
Abstract — In a reinvestigation of the sulfuration reaction of cinnamylideneacetophenone (**1**) with sulfur and triethylamine at room temperature, new products 6-benzoyl-3-phenyl-1,2-dithiolo[4,3-*c*]1,2-dithiole (**5**), 6-benzoyl-3-phenyl-1,2-dithiine (**6**) and 5- benzoyl-3-benzylidene-1,2-dithiole (**7**) were obtained along with the known products 5-phenacylidene-3-phenyl-1,2-dithiole (**2**) and 5-benzoyl-2-phenylthiophene (**3**). The reaction of dibenzylideneacetone (**8**) under the same conditions affords thiopyran-4-one (**9**). By adding Lawesson reagent to the reactant mixtures of **1** and **8**, a trithiapentalene derivative (**4**) was also formed.

The sulfuration reaction of a large number of organic compounds with sulfur under different reaction conditions has been extensively investigated in the past.[2] Much interest has been devoted to sulfurations with sulfur in the presence of secondary amines.[3] Cinnamylideneacetophenone (**1**) was reported to react with sulfur at high temperature to give 5-phenacylidene-3-phenyl-1,2-dithiole (**2**) and 5-benzoyl-2-phenylthiophene (**3**).[4] The same sulfur compounds (**2**) and (**3**), along with trithiapentalene (**4**) and fragmentation products, were previously obtained by one of us from the reaction of **1** with sulfur in refluxing morpholine.[5]

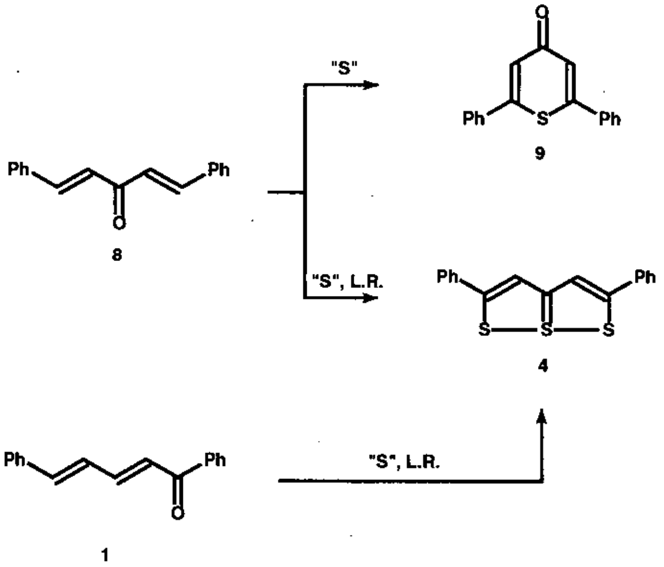
As a part of a research project on thiation processes under mild conditions, we have investigated the reaction of **1** with sulfur in the presence of triethylamine (TEA) at room temperature. Besides **2**, **3** and minor compounds, the structure elucidation of which is in progress, the new differently coloured sulfur heterocycles (**5**),[6] (**6**),[7] and (**7**),[8] were isolated (Scheme 1). Their distribution was found to be markedly affected by the nature of the solvent and reaction time.

Scheme 1



The highest yield (5%) of 6-benzoyl-3-phenyl-1,2-dithiolo[4,3-*c*]1,2-dithiole (**5**) along with **2** (5%) and **3** (9%) was isolated by allowing a mixture of **1**, sulfur and TEA in the ratio 1:14:2 in pyridine or acetonitrile for 60 h. In *N,N*-dimethylformamide (DMF) for 24 h and in dimethylsolfoxide for 7 h the yields of **5**, **2** and **3** were 3, 6 and 10%, and 3, 8, and 12%, respectively. The reaction in hexamethylphosphoramide or DMF in the ratio 1:14:8 led to the maximum yield of 12% of 6-benzoyl-3-phenyl- 1,2-dithiine (**6**) along with thiophene (**3**) (15%) after 48 h. This latter compound proved to be derived from dithiine (**6**) which showed a remarkable instability and was quantitatively converted into **3** in pyridine solution after 24 h at room temperature. By performing the reaction in

Scheme 2



acetonitrile with a reduced amount of sulfur (1:6:2) and reaction time (6 h) 5- benzoyl-3-benzylidene-1,2-dithiole (**7**) was obtained in the highest yield of 8%.

Under the same mild thiation conditions the structural isomer of **1**, dibenzylideneacetone (**8**), gave 2,6-diphenylthiopyran-4-one (**9**)[9] in a 15% yield. The formation of **9** considerably dropped when the reaction was carried out by adding 1.5 equivalents of Lawesson reagent (L.R.) to the reaction mixture, and trithiapentalene (**4**)[11] was isolated in a 40% yield (Scheme 2).

In the presence of L. R. **1** also afforded **4**. Interestingly, the yield of **4** was increased to 50% when **1** was initially allowed to react with L. R. and then, after 30 min, with sulfur and TEA.

The results clearly point out that the unsaturated carbonyl compounds (**1**) and (**8**) interact with sulfur-amine sistem to afford only products such as **2**, **3**, **5**, **6** and **7** deriving from the attack of "activated" sulfur species ("S") on their olefinic carbon atoms. The carbonyl group remains unchanged, but undergoes a thionation process leading to **4** when the L.R. is also used.

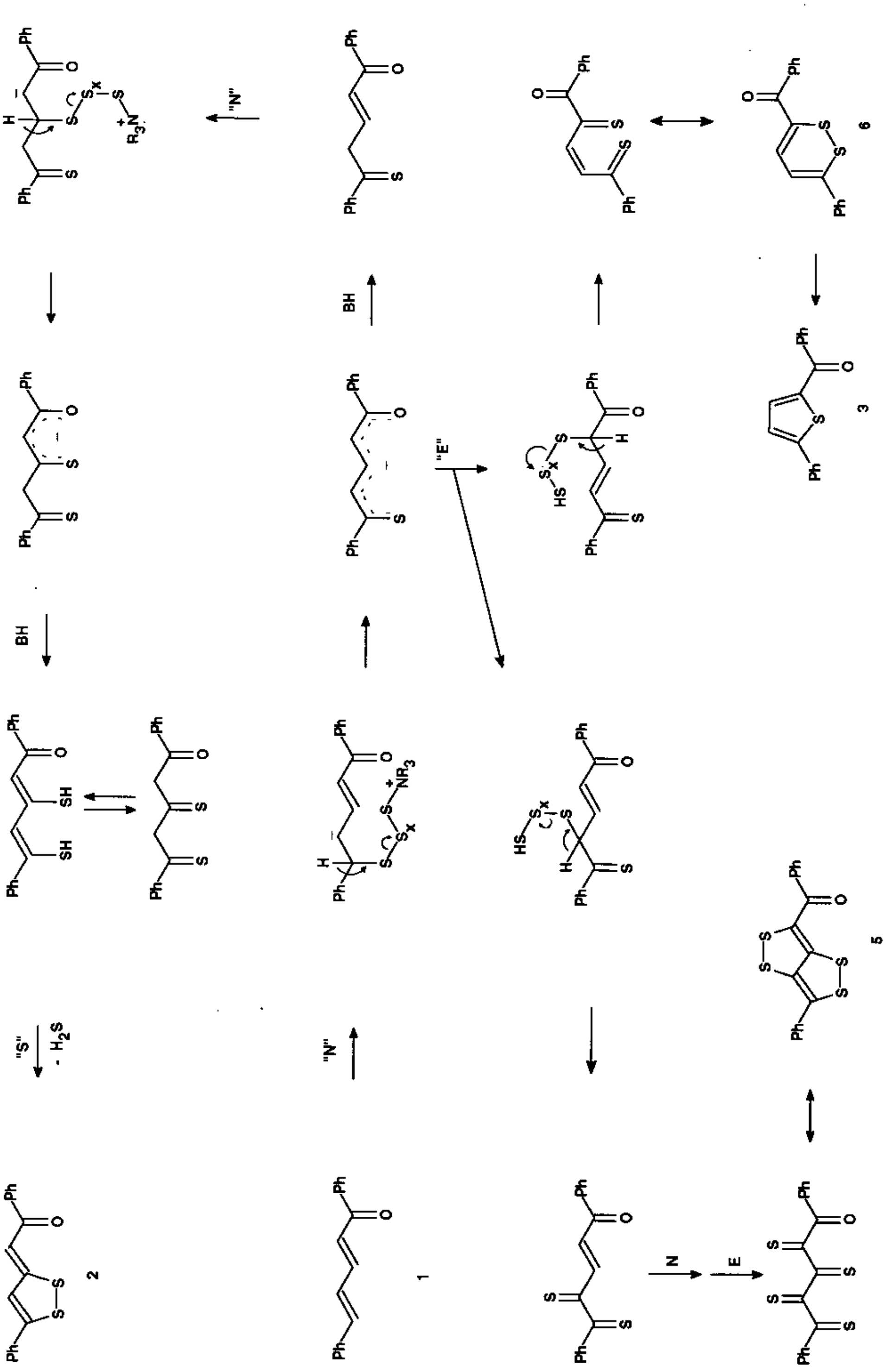
In no cases products deriving from cycloadditions of the diene moiety of **1** to di- or poliatomic sulfur species, which are thought to be present in reaction mixture of sulfur with amines,[12] were observed. Therefore, the mechanisms for the formation of known and newly isolated products require nucleophilic and electrophilic attacks by sulfur species "N" and "E" generated from the interaction of tertiary amine with sulfur:

$$S_8 + R_3N \rightleftharpoons \underset{(\text{"N"})}{R_3\overset{+}{N}\text{-S-S}_x\text{-S}^{\bullet}} \overset{BH}{\rightleftharpoons} R_3N + \underset{(\text{"E"})}{\overset{+}{S}\text{-S}_x\text{-SH}}$$

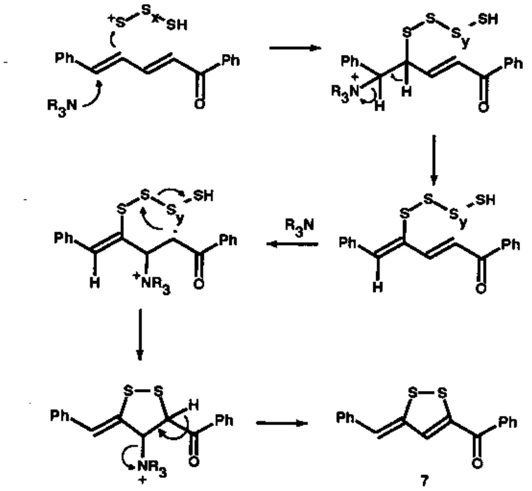
Likely, the reaction course leading to **2**, **3**, **5** and **6** starts with the initial thiation of δ-carbon atom to the carbonyl group of **1** by the nucleophilic specie "N" and proceeds with subsequent thiations of the remaining allylic carbon atoms by "E" or "N" species. The formation of **2** involves a final oxidative cyclization step by sulfur (Scheme 3). For the formation of the dithiole (**7**), an initial thiation of the α- or γ- carbon atom to the carbonyl group of 1 by the electrophilic species "E" must be invoked. It should be assisted by the tertiary amine which can interact with the β- or δ-carbon atom of **1** like a Michael reaction type (Scheme 4).

The mechanism for the formation of **9** from **8** is illustrated in Scheme 5. It involves the thiation of the two β-carbon atoms to the carbonyl group of **8**, followed by ring closure and elimination of hydrogen sufide. In the presence of thionating reagent the thiation is accompanied by the C=O —> C=S conversion and consequent formation of **4**. In the case of **1**, trithiapentalene (**4**) has been proved to be formed through the thionation of the carbonyl group of **2**,[4] but we have shown that the thionation of the carbonyl group can take place before the thiation process .

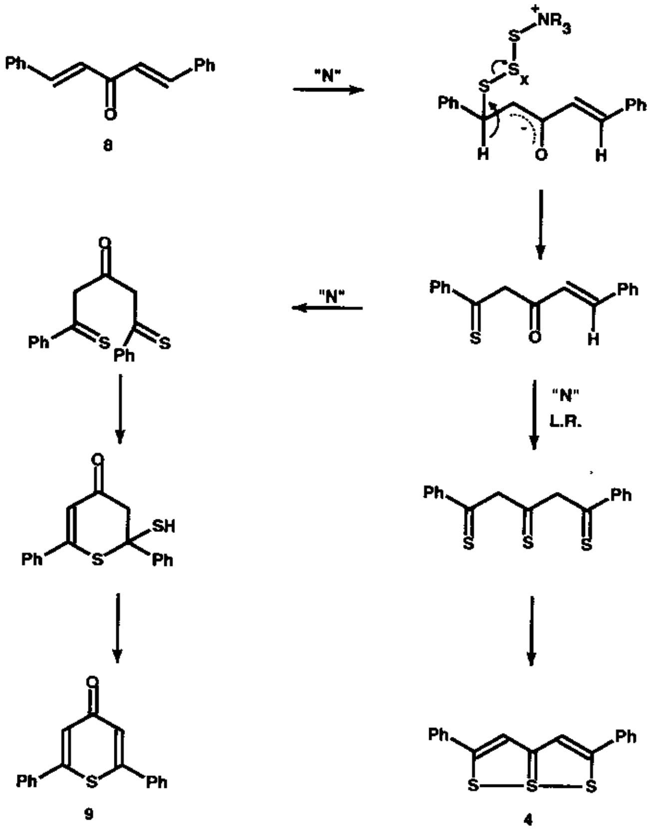
Scheme 3



Scheme 4



Scheme 5



Typically thiation reactions were conducted as follows. A mixture of **1** or **8**, sulfur and TEA was allowed under stirring at room temperature in the ratio, solvent and time above reported. The reaction mixture was then poured into ice-water. The separated solid was filtered off and treated with acetone. The excess of separated sulfur was filtered off and the filtrate was dried over anhydrous sodium sulfate and finally evaporated under reduced pressure. The resulting residue was chromatographed on silica gel. Elution with cyclohexane containing increasing amounts of ethyl acetate gave the reaction products in the order **4**, **5**, **7**, **3**, **2**, **6**.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

1. Part of this work has been presented at the 15th International Symposium on the Organic Chemistry of Sulfur, June 28-July 3, 1992, Caen, France.
2. For an extensive review on the reactions of organic compounds with sulfur see: M. G. Voronkov, N. S. Vyazankin, E. N. Deryagina, A. S. Nakhmanovich, and V. A. Usov, "Reactions of Sulfur with Organic Compounds ", ed. by J. S. Pizey, Plenum Publishing Corporation, New York (N. Y.), 1990.
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5. G. Purrello, M. Piattelli, and A. Lo Vullo, Boll. Sedute Accad. Gioenia Sci. Nat., Catania, 1967, 9, 33 (Chem. Abstr., 1969, 70, 38862).
6. 6-Benzoyl-3-phenyl-1,2-dithiolo[4,3-*c*]1,2-dithiole (**5**): mp 190 °C as blue powder from EtOH. Anal. Calcd for $C_{17}H_{10}OS_4$: C, 56.98; H, 2.79; S, 35.76. Found: C, 57.13; H, 2.70; S, 35.54. λ_{max} ($CHCl_3$) 614 nm ; ν_{max} (KBr) 1638 cm^{-1}; ^1H nmr: δ ($CDCl_3$) 7.74 (8H, m), 8.27 (2H, m) ; ms: m/z 358 (M^+), 253, 209, 189, 158, 145, 121, 105, 77.
7. 6-Benzoyl-3-phenyl-1,2-dithiine (**6**): mp 136 °C as yellow needles from EtOH. Anal. Calcd for $C_{17}H_{12}OS_2$: C, 68.92; H, 4.05; S, 21.62. Found: C, 68.93; H, 3.74; S, 21.91. λ_{max} ($CHCl_3$) 260 , 302 nm; ν_{max} (KBr) 1640 cm^{-1}; ^1H nmr: δ ($CDCl_3$) 7.32 (6H, s), 7.46-7.53 (3H, m), 7.61 (1H, d, J=7.17 Hz), 7.71-7.75 (2H, m); ^{13}C nmr: δ ($CDCl_3$) 128.50, 129.10, 129.23, 131.70, 132.60, 137.07, 138.30, 140.09, 141.38, 154.46, 186.90; ms: m/z 296 (M^+), 219, 191, 158, 147, 145, 105, 77.

8. 5-Benzoyl-3-benzylidene-1,2-dithiole (**7**): mp 144 °C as pink flakes from EtOH. Anal. Calcd for $C_{17}H_{12}OS_2$: C, 68.92; H, 4.05; S, 21.62. Found: C, 69.08; H, 4.05; S, 21.80. λ_{max} ($CHCl_3$) 496 nm; ν_{max} (KBr) 1640 cm^{-1}; ^1H nmr: δ ($CDCl_3$) 6.82 (1H, s), 7,16 (1H, s), 7.28-7.63 (8H, m), 7.76-7.80 (2H, m); ^{13}C nmr: δ ($CDCl_3$) 123.37, 127.20, 127.60, 128.73, 132.87, 136.03, 137.20, 139.16, 145.36, 146.11, 188.90; ms: m/z 296 (M^+), 219, 191, 158, 147, 121, 105, 77.

9. Physical properties of **9** are in agreement with those reported in literature.[10]

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11. Physical properties of **4** are in agreement with those reported in literature.[4]

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