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A UNIQUE SULFUR YLIDE REACTION: ON THE QUESTION OF R_4S INTERMEDIATES

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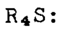
The question of the availability of the sulfur 3d orbitals for bonding in the ground state remains unanswered despite many studies.[3] In the case where the ligands are carbon, two types of such systems must be considered. Type A possesses three sigma and one pi bond to sulfur as represented by the ylides; whereas, type B possesses four sigma bonds to sulfur. Intermediates

$R_2\underset{..}{\overset{\oplus}{S}}-\overset{\ominus}{C}H_2 \longleftrightarrow R_2\ddot{S}=CH_2$

Type A



$R_4S:$

Type B

of the latter type have been postulated in the exchange of aryl groups in arylsulfonium salts with aryllithiums[4] and in the reaction of 2-methyl-1,3-dihydroisothianaphthenylium iodide with phenyllithium.[5,6] We wish to present a unique C-S insertion reaction which is best described in terms of tetravalent sulfur intermediates of types A and B. We also report a novel photochemical extrusion reaction of a thioketone discovered during the course of these studies.

Treatment of triphenylcyclopropenium bromide (Ia) with dimethylsulfoniummethylide[7] in tetrahydrofuran-hexane produced two compounds IIa and IIIa isolated after elution from a silica gel column with 10% benzene in pentane. Compound IIa[8] (m.p. 215-6°, 15% yield) possessed only aromatic absorptions in the NMR spectrum. Its mass spectrum showed an intense molecular ion at m/e 312 and appropriately intense M+1 and M+2 peaks for the presence of one sulfur atom. In conjunction with the ultraviolet spectrum (λ_{max} 242 mμ, log ϵ 4.41), these data suggested 2,3,4 triphenylthiophene as the correct structure. Comparison with an authentic sample[9] confirmed the assignment.

Elementary analyses[8] and mass spectral data indicated a formula of $C_{43}H_{30}S$ for compound IIIa (m.p. 198-200°, 25% yield). The presence of a thioketone function was suggested by the facile loss of CS in the mass spectrometer (second most intense peak at m/e 534) and a band at 1072 cm^{-1} in its infrared spectrum.[10] The presence of the cyclopropene ring was suggested by the infrared band at 1822 cm^{-1}, the strong peak at m/e 267 (base peak) in the mass spectrum (triphenylcyclopropenium ion), and the close similarity of the ultraviolet spectrum mμ (log ε), 225 (4.68), 302 (4.48), sh. 326 (4.26) to bis-triphenylcyclopropenyls.[11] On these bases, structure IIIa is assigned (see Scheme I).

Further evidence for structure IIIa derives from its photochemistry. Irradiation with a 450 watt Hanovia lamp fitted with a pyrex filter in benzene produced hexaphenylbenzene in near quantitative yield. In Scheme II, we summarize various mechanistic pathways to account for this observation. The facts that triphenylcyclopropene readily photodimerizes[12] and that quadricyclanones convert photochemically to benzene[13] suggest path b_3 as the most reasonable. To our knowledge, this photochemical rearrangement and elimination represents the first thioketone counterpart of the photochemical carbon monoxide extrusion of ketones.

Scheme I outlines a reasonable mechanistic interpretation for the formation of the thiophene and thioketone. Some preliminary evidence in support of this mechanism derives from studies of the condensation of trimethylcyclopropenium bromide[14] with dimethylsulfoniummethylide in which similar products were observed. Analysis of the gases produced revealed substantial quantities of ethane. Control experiments revealed that dimethylsulfoniummethylide accounts only for trace amounts of the ethane. Work on the mechanism of this reaction and on similar reactions is being pursued.

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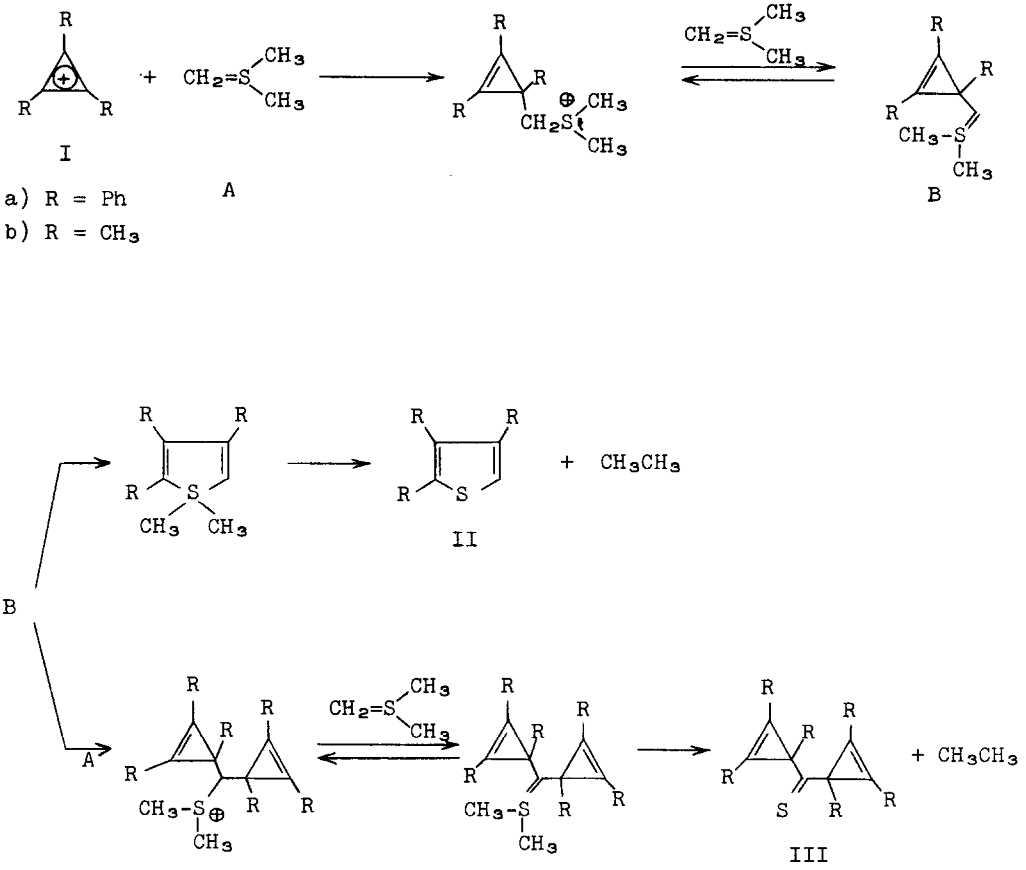
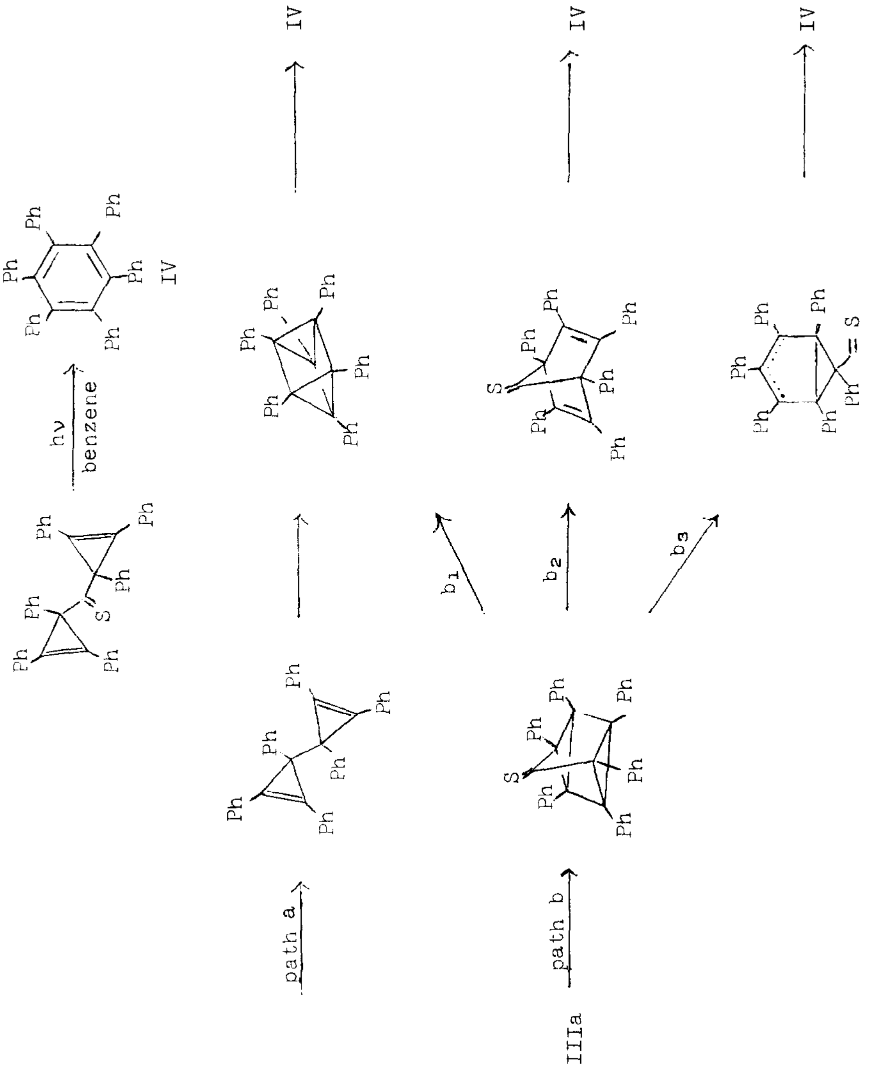
Scheme I: Reaction of Cyclopropenium Salts with Dimethylsulfoniummethylide



Scheme II: Photochemical Rearrangement of Thioketone



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