temperatures were applied to the cases that the *k* at 25 °C could not be measured directly. The rate constants were determined at least in duplicate, and the deviation was within ±2%. The mean values of these data are listed in Table I.

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Preparation of Stable Thioketenes from Diazoalkanes and Carbon Monosulfide

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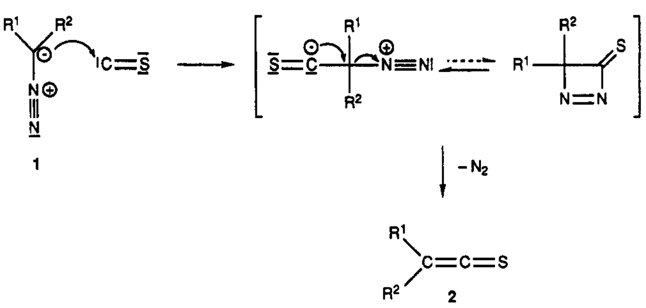
Thioketenes, which are useful building blocks in the syntheses of heterocycles,[3] are generally unstable compounds which tend to dimerize to 1,3-dithietanes or polymerize.[4] Introduction of bulky or strongly electron withdrawing groups adjacent to the thioketene functionality has a pronounced stabilizing effect, and such thioketene derivatives can often be distilled with little decomposition.[5,6]

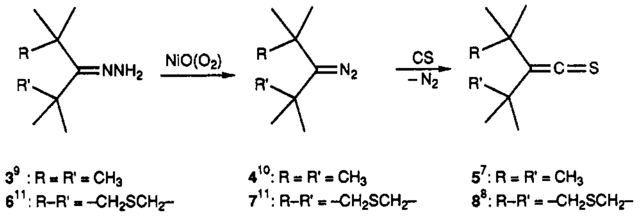
The presently available methods for the syntheses of thioketenes suffer from several drawbacks. Sterically hindered ketenes or acid chlorides can be thionated in good to excellent yields with P_4S_{10},[5,6] but since the reaction conditions are drastic in both cases (reflux in pyridine for up to 25 h), precluding syntheses of less stable thioketenes, and the syntheses of the starting ketenes or acid chlorides[6] are rather tedious, this method is of limited scope. Other methods[4] involve high-temperature pyrolyses of various precursors and are less useful for the syntheses of thioketenes on a preparative scale.

As early as 1974, K. J. Klabunde and collaborators[7] showed that bis(trifluoromethyl)diazomethane (**1**, $R^1 = R^2 = CF_3$) reacts at −196 °C with codeposited carbon monosulfide (CS) to form, in low yield, bis(trifluoromethyl)thioketene (**2**, $R^1 = R^2 = CF_3$), which was not isolated but only observed by GLC. It occurred to us that this approach might be elaborated to a versatile thioketene synthesis (Scheme I) with several advantages compared to the above mentioned methods (low reaction temperature, anhydrous and oxygen-free reaction and workup procedures). Since 1984 the use of CS as a synthetic reagent has expanded considerably, and CS can now be prepared and handled in molar quantities as exemplified by reports on insertion of CS into sulfur–chlorine, nitrogen–hydrogen, and sulfur–hydrogen bonds and cycloaddition of CS to nucleophilic alkynes.[8,9]

Scheme I



Scheme II



We have now carried out the reactions of the sterically hindered diazo compounds **4**[10] and **7**[11], with CS (Scheme II) in toluene solution at −78 °C on a preparative scale and were able to obtain the thioketenes **5**[5] and **8**[6] in 30 and 42% yield (based on **3**[12] and **6**[11]), respectively.

The low reaction temperatue (−78 °C) seems to rule out the intermediacy of the corresponding carbene (R^1R^2C) in the formation of **2** and suggests instead interaction between the LUMO of CS and the HOMO of the diazoalkane **1** (Scheme I).[7,13] There is no a priori reason to assume a ring closure to a highly strained 1,2-diazetine-3-thione prior to the nitrogen extrusion since the corresponding charged open chain should be equally capable of loss of molecular nitrogen. Interaction of **1** and CS_2 does not lead to thioketene formation.

Attempts to trap unstable **2** [(R^1,R^2) = (Ph,Ph), (H,COOEt)], generated according to Scheme I, failed, presumably because of secondary reactions between **2** and diazo compound **1**.[14] Resonance stabilized diazoalkanes such as **1** ($R^1 = R^2 = COOC_2H_5$) do not react with CS.[14]

Experimental Section

General Procedure for the CS Experiments. Carbon monosulfide was generated in a conventional vacuum line by passing CS_2 vapor through an 8-kV AC discharge. The detailed procedure has been recently described.[15,16] The gas mixture leaving the discharge tube consisting of approximately 70% CS and 30% CS_2, together with minor amounts of C_3S_2 and elemental sulfur, was

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passed directly into a reaction flask containing a stirred toluene solution of the starting diazo compound kept at −78 °C. The operating pressure in the vacuum line was 0.02–0.05 Torr, but due to the N_2 evolution a rise in pressure to 1–2 Torr was observed. The stream of CS_2 vapor was, therefore, periodically interrupted (for ca. 1–2 min every 10 min) to allow reestablishment of the high vacuum. By the end of the reaction (after ca. 2 h for the experiments in this work) the mixture and the glass walls had turned black due to formation of polymeric carbon monosulfide. When the reaction was complete, the discharge was turned off and the stream of CS_2 vapor stopped. The vacuum line was filled with nitrogen, and the reaction mixture was allowed to warm to room temperature, followed by the workup procedures described below.

Di-*tert*-butylthioketene (5). A stirred solution of hydrazone 3[12] (2.1 g, 14 mmol) in 70 mL of ether was treated with 8.0 g of nickel peroxide at room temperature Filtration and removal of the solvent in vacuo after 2 h gave crude 4[10] as an orange oil which was dissolved in 130 mL of toluene and treated with CS generated from 5.0 mL (83 mmol) of CS_2 as described above. The black reaction mixture was filtered and distilled giving 0.6 g (30%) of 5[5] as a violet oil (bp 69 °C (10 Torr)). All spectra (IR, ^{1}H and ^{13}C NMR, MS) were in agreement with the literature data.[5] The ^{1}H NMR spectrum showed a slight contamination (<5 mol%) of unreacted 4.

(Tetrahydro-3,3,5,5-tetramethyl-4*H*-thiopyran-4-ylidene)methanethione (8). A stirred solution of hydrazone 6[11] (2.3 g, 12 mmol) in 70 mL of ether was treated with 9.0 g of nickel peroxide. Filtration and evaporation of the solvent after 3 h gave 7[11] as low-melting orange crystals which were dissolved in 170 mL of toluene and treated with CS generated from 15 mL (250 mmol) of CS_2 as described above. The resulting black reaction mixture was filtered and distilled to give 1.0 g (42%) of 8[6] as a violet oil (bp 60–61 °C (0.05 Torr)). All spectra (IR, ^{1}H and ^{13}C NMR, MS) were in agreement with the literature data.[6]

Reduction of *N*-(Phenylsulfonyl)pyrroles with Sodium Cyanoborohydride in Trifluoroacetic Acid

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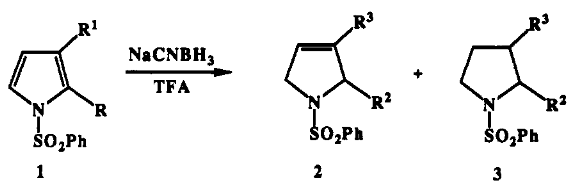
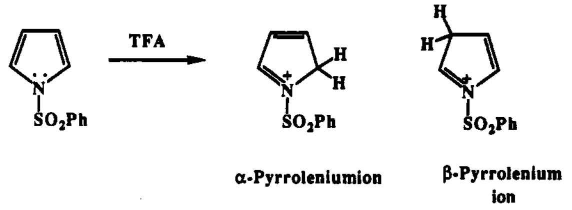
Due to the π-excessive character of the indole and pyrrole ring systems, these compounds are impervious to nucleophilic reducing species such as hydride reagents.[1,2] However, partial reduction of these heterocycles can be accomplished but only under acidic conditions via a sequence involving initial protonation (at C-3 for indoles and predominantly at C-2 for pyrroles), followed by reduction of the resultant iminium intermediates. Whereas indoles are susceptible to reduction by a variety of hydride sources under acidic conditions,[3] these methods have apparently not been successfully extended to pyrroles despite the fact that 3-pyrrolines (2,5-dihydropyrroles) represent useful synthetic intermediates.[4] To date, methods for the preparation of 3-pyrrolines by the partial reduction of pyrroles have been limited to the use of zinc in acidic media,[5] or in the case of some pyrrole-2-carboxylic acid derivatives, phosphonium iodide[6] or hypophosphorus acid[7] in hydroiodic acid. In light of our recent finding that sodium cyanoborohydride ($NaCNBH_3$) in trifluoroacetic acid (TFA)[8] represents a unique reducing system for the tandem reduction of the carbonyl group and the indole double bond of 2- and 3-acyl-1-(phenylsulfonyl)indoles to the corresponding alkyl-1-(phenylsulfonyl)indolines,[9] we have examined the analogous reaction upon *N*-(phenylsulfonyl)pyrroles and now report the first reduction of pyrroles by a hydride reducing agent (Scheme I).

Scheme I



Scheme II



The choice of the phenylsulfonyl protecting group in this study was predicated on the fact that 1-(phenylsulfonyl)pyrrole undergoes Friedel–Crafts acylation reactions with a remarkable degree of regiocontrol,[10] wherein acylation occurs at C-3 in the presence of aluminum chloride ($AlCl_3$) but predominantly at C-2 when catalyzed by boron trifluoride etherate ($BF_3{\cdot}Et_2O$) or TFA.[11] Moreover, while the analogous Friedel–Crafts alkylation reactions upon the same substrate do not occur with the same degree of regioselectivity,[12] we have recently discovered that the selectively produced N-protected acylpyrroles can be reductively deoxygenated to the corresponding alkyl derivatives[13] without reduction of the pyrrole ring or loss of the protecting group using the borane–*tert*-butylamine complex ($^{t}BuNH_2{-}BH_3$)/$AlCl_3$ reducing system.[14] By these means then, a variety of 1-

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