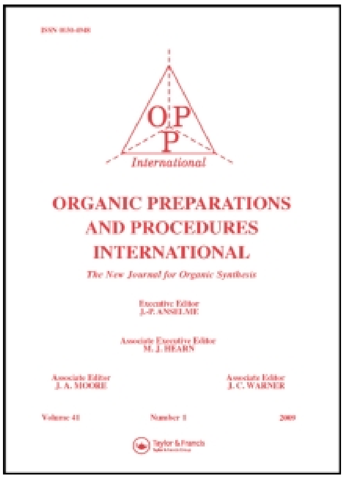

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# SYNTHESIS OF THIOKETONES AND OF TETRAARYLETHYLENES

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# SYNTHESIS OF THIOKETONES AND OF TETRAARYLETHYLENES

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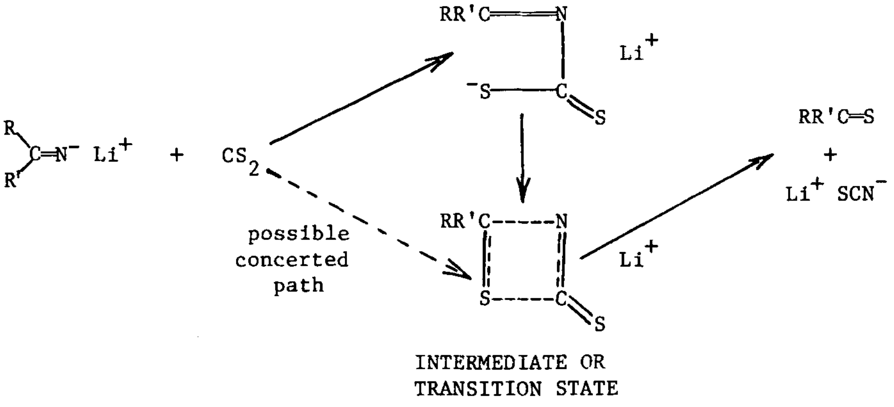
Thioketones have been synthesized by a number of methods,[1,2] most often by the simultaneous passage of hydrogen sulfide and hydrogen chloride through an ethanolic solution of the corresponding ketone. This procedure requires the use of toxic gases over a prolonged period of time, usually 24 hours. We wish to report a new route for the synthesis of diaryl thioketones[3] which avoids these difficulties and gives a high yield of thioketones.

The reaction of the lithium salt of ketimines with carbon disulfide gives a thioketone and lithium thiocyanate. The reaction can be viewed as proceeding as follows.[4]



The time required for completion of the reaction is 30 minutes and the yields obtained are good (thiobenzophenone 83%; phenyl-1-naphthyl thioketone 74%). The yields become poor (10-15%) when the magnesium bromide salt is substituted for the lithium salt, presumably due to the heterogeneous nature of the latter reaction. A similar reaction takes place with the free ketimine,[5] but the reaction requires 56 hours for completion: addition of triethylamine reduces the time to four and a half hours, the yields obtained are of the same order as those obtained with the lithium salt. However, it is often the lithium salt that is immediately at hand.

Aryl thioketones are useful as precursors for tetraarylethylenes.[2a,6] The synthetic route to aryl thioketones described here, can be used with a slight modification for a simple preparation of tetraaryl ethylenes, without isolation of the thioketones. Tetraphenylethylene was prepared in this manner in 61% yield.

## EXPERIMENTAL

Thiobenzophenone. The lithium salt of benzophenoneimine (0.02 mole) was prepared by treating 0.02 mole of phenyllithium in 200 ml. of ether, with an equivalent amount (2.06 g.) of benzonitrile dissolved in 25 ml. ether, under an atmosphere of dry nitrogen. The orange solution of the lithium salt of benzophenoneimine was next treated at room temperature with 25 ml. of carbon disulfide with stirring. Immediate reaction was apparent as shown by the disappearance of the orange color. Upon being stirred for some time, the solution turned to a greenish color, then to an intense blue after 30 minutes. The solution was washed twice with 100 ml. water in a separatory funnel,[7] separated and dried over anhydrous magnesium sulfate. Evaporation of the ether in vacuo at room temperature gave a blue oil which was chromatographed on an 18" silica gel column, using carbon tetrachloride as the eluent. The separation was carried out in a dry box under an atmosphere of nitrogen, as thiobenzophenone is sensitive to air oxidation. The mixture separated into two bands, the blue moving faster than a yellowish brown. The blue band was collected and upon evaporation of the solvent, yielded blue needles which were further purified by one crystallization from chloroform, mp. 50-52° lit. 50-52°.[8] The yield was 3.38 g. (83%).

I. R. Spectrum: C=S at 1230 $cm^{-1}$; NMR spectrum: multiplet between 7.1-8.1 .

Phenyl 1-naphthyl thioketone. The lithium salt of phenyl 1-naphthyl ketimine (0.02 mole) was prepared by treating 0.02 mole of an ethereal solution of phenyllithium (200 ml.) with an equivalent amount (3.06 g.) of 1-naphtho-nitrile dissolved in 50 ml. of ether. The reaction of the ketimine salt with carbon disulfide and isolation of the thioketone was performed in the manner described for thiobenzophenone. This gave 3.7 g. (74%) of blue crystals mp. 108-112° lit. 110°.[9]

I. R. spectrum: C=S at 1250 $cm^{-1}$; NMR spectrum: multiplet between 7.5-7.9 .

Tetraphenylethylene. To the crude oil obtained in the preparation of thiobenzophenone, was added 200 ml. of carbon tetrachloride, which dissolves all the thiobenzophenone. Lithium thiocyanate was removed by filtration and the filtrate evaporated. The crude thiobenzophenone was heated at 220° under vacuum for two hours. From the viscous brown liquid obtained, tetraphenylethylene was isolated by column chromatography on an 18" acidic alumina column with carbon tetrachloride as the eluent. The first 200 ml. were collected, evaporated to give crude tetraphenylethylene. Recrystallization from ethanol yielded 2.01 g. (60%) of white crystals mp. 217-218° lit. 224.6-224.9.[10]

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