Desulfurization of Thioketones and Thioamides with Diphosphorus Tetraiodide

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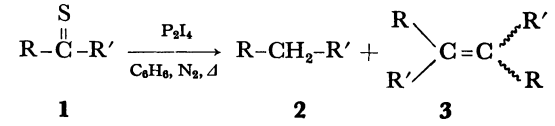
Synopsis. On heating with diphosphorus tetraiodide in benzene, thioketones undergo reductive desulfurization to afford parent hydrocarbons, while thioamides are slowly converted into nitriles.

Diphosphorus tetraiodide (P_2I_4) exhibits a high affinity for oxygen and thus acts as an excellent deoxygenating and dehydrating agent for various oxygen-containing compounds.[1] However, its ability as a desulfurizing agent has been little studied yet. Only recently, the desulfurization of episulfides to olefins has been reported.[2] In the present paper, we describe the reaction of P_2I_4 with thioketones and thioamides.

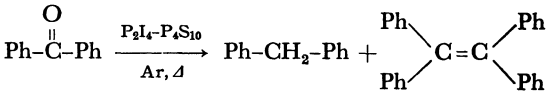
Ketones are inert to P_2I_4 in boiling benzene and only in combination with lithium aluminum hydride they are reducible to hydrocarbons.[3] In contrast, thioketones **1** have been found to be moderately reactive and on heating with P_2I_4 in boiling benzene followed by aqueous work-up, they were converted to parent hydrocarbons **2** in good to moderate yields (Table 1). The origin of protons may be sought to a trace of water which is normally present in commercial solvent employed, since the use of less amounts of solvent or thorough drying of solvent led to significantly reduced yields of the reduction products. In some cases, especially when the reactions were performed in a concentrated solution, the desulfurative dimerization of thioketones was found to compete with the reduction, giving olefins **3** as a side product. Geometry of these olefinic products was not determined.

Conventional synthesis of aromatic thioketones involves treatment of the corresponding ketones with



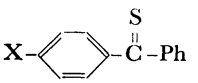
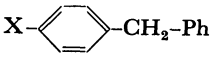
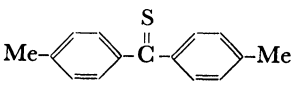
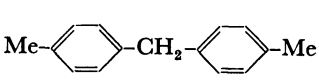
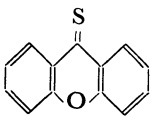
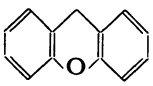
1 **2** **3**

tetraphosphorus decasulfide (P_4S_{10}). When this reaction was carried out in the presence of equimolar amounts of P_2I_4, ketones underwent reduction and reductive dimerization in parallel to give mixtures of hydrocarbons **2** and olefins **3**, usually the latter being predominant. Thus, by this treatment benzophenone was converted into diphenylmethane and tetraphenylethylene in 21 and 35% isolated yields, respectively.



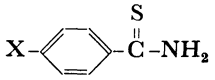
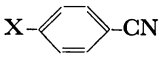
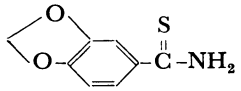
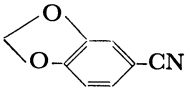
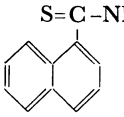
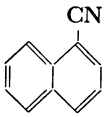
Amides are smoothly dehydrated to nitriles by P_2I_4.[4] In contrast, dehydrosulfurization of thioamides **4** with P_2I_4 proceeded quite slowly in a benzene/triethylamine mixture (10:1) under refluxing conditions, but nitriles **5** were in most cases obtained in high state of purity (Table 2). In the absence of triethylamine, little or no nitriles were formed. Uses of other solvent systems such as DMF, carbon tetrachloride, and heptane in combination with triethylamine or pyridine gave poor results. Aliphatic thioamides were more easily dehydrosulfurized as compared to aromatic ones.

TABLE 1. REDUCTIVE DESULFURIZATION OF THIOKETONES WITH P_2I_4[a]

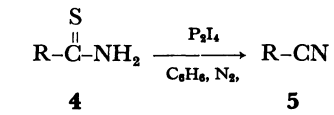
Thioketone **1**		Reaction time/h	Hydrocarbon **2**	Yield/%[b]
	X=H	6		85[c]
	Me	5		52
	Me	5[d]		26[e]
	MeO	7		34
	Cl	4		74
		5		79
		9		56

a) All reactions were carried out according to the procedure described in Experimental section, except for the case d) where the reaction was conducted in a more concentrated solution. b) Yields refer to the isolated compounds and are not optimized. All products are known and identified by comparison with authentic specimens. c) GLC yield. d) Amount of benzene as solvent was reduced to 5 ml. e) Accompanied by 16% yield of 1,2-diphenyl-1,2-bis(4-methylphenyl)ethylene.

Table 2. Dehydrosulfurization of thioamides to nitriles with P_2I_4

Thioketone **4**		Reaction time/h	Nitrile **5**	Yield/%[a]
	X=H	16		35
	MeO	12		53
	Cl	14		42
		13		56
		14		88
Ph-CH_2-C(=S)-NH_2		10	Ph-CH_2-CN	59
Ph-CH_2CH_2-C(=S)-NH_2		10	Ph-CH_2CH_2-CN	71

a) Yields refer to the isolated compounds and are not optimized. All products are known and identified by comparison with authentic specimens.



4 **5**

We may conclude that P_2I_4 is not so effective as a desulfurizing agent for thiocarbonyl compounds. However, it exhibits an interesting mode of reductive dimerization with some substrates which, depending on circumstances, may find utility for synthetic purposes.

Experimental

Materials. Thioketones were prepared from ketones and tetraphosphorus decasulfide according to the literature procedure.[5,6] Thioamides were obtained by adding hydrogen sulfide to nitriles in pyridine in the presence of triethylamine, as described in Ref. 7. Products were identified by mass, IR, and ^{1}H-NMR spectra as well as by direct comparison with authentic specimens. All products are known. Separation of hydrocarbon mixture was performed on a fraction preparative liquid chromatograph (Japan Analytical Industry Co, LC-08) using chloroform as solvent.

Reaction of Thioketones **1** *with* P_2I_4. To a solution of thioketone (1.0 mmol) in benzene (20 ml) was added P_2I_4 (1.0 mmol) and the resulting mixture was heated under reflux for appropriate hours under argon. Then the reaction was quenched by the addition of aqueous sodium hydrogensulfite and the organic phase was separated, washed with water, and dried over sodium sulfate. Removal of the solvent under reduced pressure yielded corresponding product or products, which were purified either by chromatography over silica gel or by recrystallization.

Reaction of Ketones with P_2I_4 *in the Presence of* P_4S_{10}. A mixture of aromatic ketone (1.0 mmol), P_2I_4 (1.0 mmol), and P_4S_{10} (1.0 mmol) was heated in an oil bath at around 130 °C for 3 h. After cooling the dark brown reaction mixture was extracted with ether and the extract was washed with 10% aqueous sodium sulfite and water, dried over sodium sulfate, and evaporated under reduced pressure. The residue was subjected to preparative liquid chromatography to obtain hydrocarbon component.

Reaction of Thioamides **4** *with* P_2I_4. To a solution of thioamide (1.0 mmol) in benzene-triethylamine mixture (10:1, 10 ml) was added P_2I_4 (1.0—1.5 mmol) and the resulting mixture was heated under gentle reflux for appropriate hours under nitrogen. After cooling the mixture was washed with 10% aqueous ammonium chloride, the organic phase was extracted with ether, dried over sodium sulfate, and evaporated to leave a residue, which was chromatographed over silica gel, distilled *in vacuo*, or recrystallized from appropriate solvent.

References

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2) J. R. Schauder, J. N. Denis, and A. Krief, *Tetrahedron Lett.*, **24**, 1657 (1983).

3) H. Suzuki, R. Masuda, H. Kubota, and A. Osuka, *Chem. Lett.*, **1983**, 909.

4) H. Suzuki and N. Sato, *Nippon Kagaku Kaishi*, **1981**, 392.

5) Aromatic thioketones were chosen as substrate because of their handling ease and ready availability.

6) J. W. Scheeren, P. H. J. Ooms, and R. J. F. Nivard, *Synthesis*, **1973**, 149. For a general survey of the chemistry of thiocarbonyl compounds, see F. Duus, "Thiocarbonyl Compounds," in "Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds," ed by D. N. Jones, Oxford (1979), Vol. 3, pp. 373—487.

7) A. E. S. Fairfull, J. L. Lowe, and D. A. Peak, *J. Chem. Soc.*, **1952**, 742.