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NEW DEOXYGENATION REACTIONS OF SULFOXIDES, SELENOXIDES AND PRIMARY NITROALKANES TO SULFIDES, SELENIDES AND NITRILES

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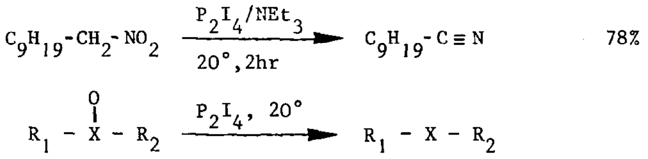
The title reactions are performed at room temperature for short periods using P_2I_4. The resulting products are formed in particularly high yield.

Diphosphorous tetraiodide, a cheap, stable, easily prepared and handled red-gold crystalline derivative [1,2] is a valuable deoxygenating reagent already successfully used for the synthesis of alkyl iodides from alcohols [1] and ethers [3b], olefins from epoxides [2,3], diols [3a,4], β-hydroxyselenides [5] and β-hydroxysulfides [5] and nitriles from oximes [2].

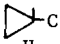
We find that P_2I_4 is particularly useful for the deoxygenation of sulfoxides, selenoxides and primary nitroalkanes producing respectively sulfides, selenides and nitriles in very high yield (Scheme). The reactions occur rapidly (<2 hr) at room temperature and the desired products are easily separated from the water soluble inorganic by-products.

SCHEME



$$C_9H_{19}\text{-}CH_2\text{-}NO_2 \xrightarrow[20°,\,2hr]{P_2I_4/NEt_3} C_9H_{19}\text{-}C\equiv N \qquad 78\%$$

$$R_1 - \overset{O}{\overset{|}{X}} - R_2 \xrightarrow{P_2I_4,\ 20°} R_1 - X - R_2$$

R_1	R_2	X	Yield % (time in hr)
C_3H_7	C_3H_7	S	78(0.5)
C_6H_5	CH_3	S	81(0.5)
CH_3	$C_{10}H_{21}$	Se	94(1)
CH_3	$C_{11}H_{23}CHCH_3$	Se	94(1)
CH_3	C_9H_{19}	Se	95(1)
C_6H_5	$C_{11}H_{23}CHCH_3$	Se	97(1) at −78°C

The synthesis of nitriles can be performed in the presence of triethylamine to avoid the acidic media and in case of phenylselenoxides the transformation can even be performed at −78°C avoiding thus the easy selenoxide elimination reaction [6].

Particularly interesting is the quantitative deoxygenation of the cyclopropylselenoxide which occurs without any cyclopropane ring opening.

Due to these observations, the results just disclosed can be successfully compared to the methods existing for sulfoxides[7] and selenoxides [8] deoxygenation reactions. Work is in progress to apply these reactions to functionalized derivatives.

Typical experiments

1. *Nitrodecane (187 mg, 10^{-3}m) and triethylamine (909 mg, 9.10^{-3}m) in CH_2Cl_2 (2 ml) are added at 20°C to a stirred suspension of P_2I_4 (1.26 g, $2.2\ 10^{-3}$m) in CH_2Cl_2 (5 ml). After stirring two more hours at 20°, solid K_2CO_3 is added to the red-black solution then water and the mixture is extracted with ether (4 times). Usual work up and purification by PLC (SiO_2, ether/pentane 10/90 R_f :0.50) leads to 120 mg (78%) of decanonitrile.*
2. *Dipropylsulfoxide (402 mg, 3.10^{-3}mole) in CH_2Cl_2 (3 ml) is added at 20° to a stirred suspension of P_2I_4 (934 mg x $1.65\ 10^{-3}$ mole) in CH_2Cl_2 (3 ml). The resulting red-black solution is stirred for 0.5 hr, hydrolyzed, and extracted with ether. The organic layer is washed (3 times) with a thiosulfate solution, dried and the solvent removed with a flow of nitrogen. The crude mixture (which is practically pure sulfide) is bulb to bulb distilled (E_{760} : 142°) leading to 275 mg of pure diisopropylsulfide.*

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