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A NOVEL SULFENYLATION REAGENT. SYNTHESIS AND REACTIONS OF N-(ARYLTHIO)ISATINS

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N-(Arylthio)isatins (1) were prepared by treatment of arenesulfenyl chloride with isatin. The compounds 1 reacted with organometallic compounds, thiols, and sodium cyanide to give sulfides (2), disulfides (3), and thiocyanates (4).

It has recently been shown that N-(arylthio)phthalimides react with thiols,$^{1,2,3)}$ hydrodisulfides,$^{2)}$ alkoxides,$^{4)}$ amines,$^{5,6)}$ arenesulfinates,$^{7)}$ and active methylene compounds$^{8,9,10)}$ to give disulfides, trisulfides, sulfenates, sulfenamides, thiosulfonates, and arylthio active methylene compounds, respectively. We have also found that N-(arylthio)phthalimides act as efficient sulfur-transfer reagents for organometallic compounds.$^{11)}$

We now wish to report the synthesis of novel sulfenylation reagents, N-(arylthio)isatins (1), and the reactions with some nucleophilic reagents.

General procedure for the preparation of 1 is as follows. To a mixture of isatin (10 mmol) and triethylamine (10 mmol) in dimethylformamide (5 ml) was added dropwise with stirring arenesulfenyl chloride (10 mmol) at the reaction temperature described in Table 1. Stirring was continued for additional 30 min and then the mixture was poured into ice water. The resultant precipitates were collected by filtration and recrystallized from ethanol. The detailed data are summarized in Table 1.

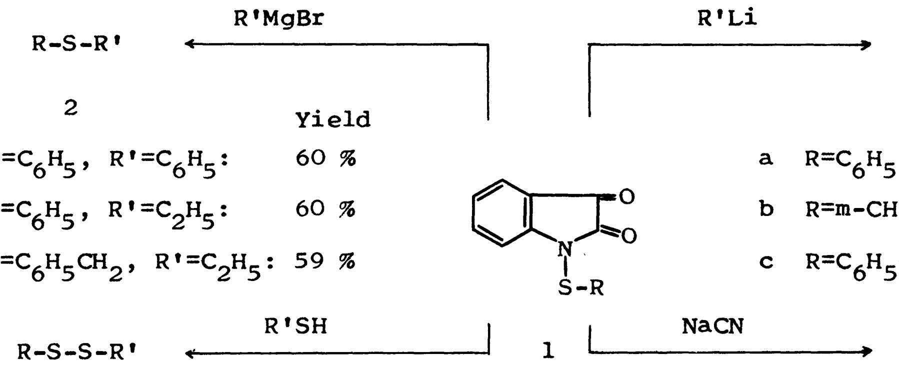
Compounds 1 were found to act as efficient sulfur-transfer reagents. Heating of 1 with two equimolar amounts of Grignard reagents or organolithium compounds in benzene under reflux for 3 hr and then pouring into a cold saturated ammonium chloride solution containing pieces of ice gave the corresponding sulfides (2) in 60 - 75% yields. Treatment of equimolar amounts of 1 and thiols in benzene for 1 hr under reflux and then concentration of the reaction mixture afforded disulfides (3) in excellent yields. Similarly, the reaction of two equimolar amounts of 1 with alkanedithiols gave bis-disulfides. Thiocyanates (4) were also obtained by vigorous stirring of a solution of 1 in chloroform with an excess of an aqueous sodium cyanide solution for 1 hr at room temperature and then by distillation of the chloroform layer under reduced pressure in good yields. The structures of these products obtained were established by microanalyses and by spectral data.

The reaction of 1 with other nucleophiles is currently under investigation.

Table 1. N-(Arylthio)isatins (1)

R	Reaction Temp. (°C)	Yield (%)	Mp(°C)	Formula	Analysis(%) Found(Calcd) C	H	N
C_6H_5-	r.t.	82	129-130	$C_{14}H_9O_2NS$	65.61 (65.40)	3.43 (3.45)	5.51 (5.51)
m-$CH_3C_6H_4$-	43	83	121-122	$C_{15}H_{11}O_2NS$	67.18 (66.91)	4.51 (4.12)	5.17 (5.20)
$C_6H_5CH_2$-	50	73	110-111	$C_{15}H_{11}O_2NS$	66.94 (66.91)	4.45 (4.12)	5.66 (5.20)
o-$NO_2C_6H_4$-	r.t.	80	240-241	$C_{14}H_8O_4N_2S$	55.86 (56.01)	2.93 (2.69)	9.69 (9.33)
p-ClC_6H_4-	50	80	193-194	$C_{14}H_8O_2NSCl$	57.90 (58.45)	2.95 (2.78)	4.97 (4.85)

r.t.: room temperature.



R-S-R' 2 (R'MgBr)

		Yield
a	$R=C_6H_5$, $R'=C_6H_5$:	60 %
b	$R=C_6H_5$, $R'=C_2H_5$:	60 %
c	$R=C_6H_5CH_2$, $R'=C_2H_5$:	59 %

R-S-R' 2 (R'Li)

		Yield
a	$R=C_6H_5$, $R'=C_6H_5$:	75 %
b	$R=m\text{-}CH_3C_6H_4$, $R'=C_6H_5$:	70 %
c	$R=C_6H_5CH_2$, $R'=n\text{-}C_4H_9$:	61 %

R-S-S-R' 3

		Yield
a	$R=C_6H_5$, $R'=C_6H_5$:	91 %
b	$R=C_6H_5$, $R'=m\text{-}CH_3C_6H_4$:	80 %
c	$R=C_6H_5CH_2$, $R'=i\text{-}C_3H_7$:	85 %

R-SCN 4

		Yield
a	$R=C_6H_5$:	90 %
b	$R=o\text{-}NO_2C_6H_4$:	78 %
c	$R=C_6H_5CH_2$:	78 %

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