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REACTIONS OF t-ALKYL THIONITRATES WITH p-AMINOPHENOLS: ONE POT SYNTHESES OF N-(t-ALKYLTHIO)-p-BENZOQUINONEIMINES

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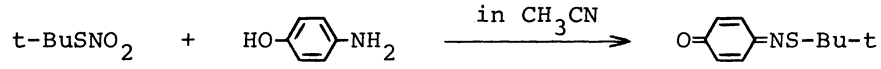
Various N-(alkylthio)-p-benzoquinoneimines were readily synthesized by treating corresponding p-aminophenols with t-alkyl thionitrates.

In the course of our studies on the synthetic applications of thionitrates, we now have found that the reactions of t-alkyl thionitrates with various p-aminophenols readily afforded the corresponding N-(t-alkylthio)-p-benzoquinoneimines.

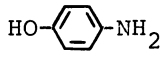
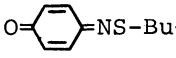
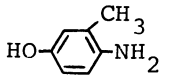
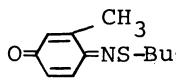
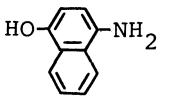
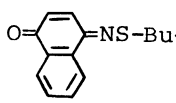
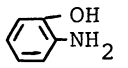
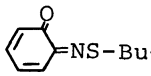
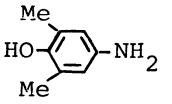
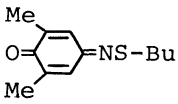
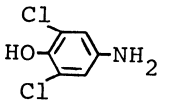
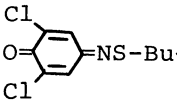
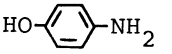
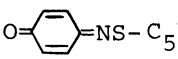
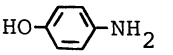
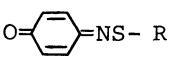
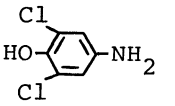
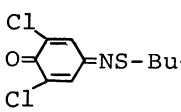
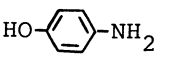
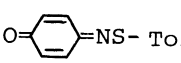


p-Benzoquinoneimines were already reported,[1] however only a few N-thio derivatives had been prepared from N-chloro-p-benzoquinoneimines and thiols.[2] Our new synthetic method for N-thio-p-benzoquinoneimines is simple and especially useful for the synthesis of N-t-alkylthio derivatives.

A typical procedure is as follows. p-Aminophenol (546 mg, 5 mmol) was added for 5 min into a stirred suspension of well-dried anhydrous copper(II) chloride (810 mg, 6 mmol)[3] and t-butyl thionitrate (1020 mg, 7.5 mmol) in anhydrous acetonitrile (15 ml). The mixture was stirred for 1 h at room temperature. Then hydrochloric acid (20%, 100 ml) was added to a suspension and the solution was extracted with ether. The ethereal extract was dried ($MgSO_4$) and evaporated. After purifying the extract on silica gel TLC (hexane:ether=10:1), bright yellow crystals of N-(t-butylthio)-p-benzoquinoneimine were obtained (390 mg, 40%).

Isolated yields and physical properties of N-thio-p-benzoquinoneimines are summarized in Table. All these new benzoquinoneimines are quite stable and have vivid yellow colors due to the strong absorption band ($\varepsilon_{max} > 10^4$)

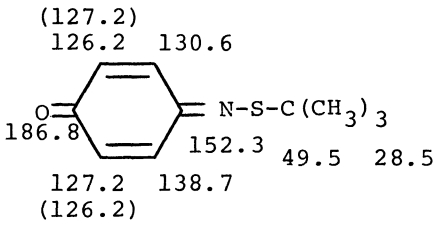
Table. Reactions of Thionitrates and Aminophenols

Aminophenols	Thionitrates	Products	Isolated Yields(%)	Physical Properties of the products		
				mp(°C)	UV(hexane) (λmax, nm)	IR (νC=O,cm^{-1})
	t-$BuSNO_2$		40 (46)[a]	77-79 (from hexane)	401 ($\varepsilon=2.7\times10^4$)	1630
	t-$BuSNO_2$		45	45-47 (from hexane)	399 ($\varepsilon=2.1\times10^4$)	1630
	t-$BuSNO_2$		15 (16)[b]	81-82 (from EtOH)	418 ($\varepsilon=1.9\times10^4$)	1642
	t-$BuSNO_2$		trace	liq.	425, 365	1620
	t-$BuSNO_2$		47	76-77 (from hexane)	405 ($\varepsilon=2.4\times10^4$)	1615
	t-$BuSNO_2$		45	62-64 (from hexane)	424 ($\varepsilon=3.4\times10^4$)	1648
	t-$C_5H_{11}SNO_2$		40	liq.	402 ($\varepsilon=2.7\times10^4$)	1632
	c)	 d)	33	liq.	405 ($\varepsilon=2.7\times10^4$)	1630
	s-$BuSNO_2$ e)		10	liq.	425 ($\varepsilon=2.2\times10^4$)	1645
	p-$TolSNO_2$ e)		6	107-109 (from EtOH)	438 ($\varepsilon=1.7\times10^4$)	1625

a) In this case $CuCl_2$ was not added. Chromatographic separation gave poor result and yield was determined by GLC. b) HCl salt was used as the starting material. c) 1,1-dimethylheptyl thionitrate was used. d) R= $CH_3(CH_2)_5C(CH_3)_2$. e) An oxidative mixture of the thiol with 2 eq. of N_2O_4 was used due to the instabilities of these thionitrates which have not been isolated in pure form at room temperature. $CuCl_2$ was not used in these cases.

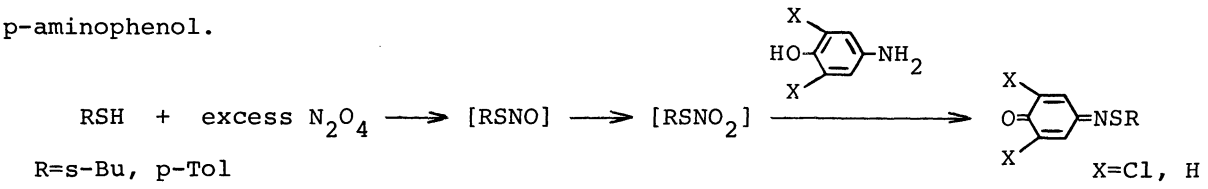
near 400 nm. Structures of the products were identified by IR, NMR, UV and MS spectroscopies. Elemental analyses of all these compounds agree well with these formulae. Carbon-13 NMR spectrum of N-(t-butylthio)-p-benzoquinoneimine was measured and the chemical shifts were determined as shown in the Figure.

Fig. ^{13}C-NMR of N-(t-butylthio)-p-benzoquinoneimine (in $CDCl_3$, ppm)



t-Alkyl thionitrates were prepared by treating corresponding thiols with excess dinitrogen tetraoxide. The following is a typical preparative procedure of t-alkyl thionitrates. Dinitrogen tetraoxide (1.5 mol)[4] in carbon tetrachloride (135 ml) was added dropwise to a stirred solution of t-BuSH (55.3 g, 0.6 mol) in dry ether (500 ml) for over 30 min at the rate that ether slowly refluxed. After addition was over, the solution was stirred further for ca. 30 min. The solution was washed with ice cold water and dried ($MgSO_4$), concentrated, and distilled (with molecular sieves) giving 67.8 g (84%) of colorless oil with stimulant odor, bp 40-41°C/6 mmHg (lit.[5] 55°C/13 mmHg). t-Pentyl thionitrate and 1,1-dimetylheptyl thionitrate are new additions in the literature and boil at 36-38°C/3 mmHg and 78-81°C/2 mmHg respectively. All these t-alkyl thionitrates were stable, however other thionitrates were not stable enough to be isolated.

An oxidative mixture of s-BuSH or p-toluenethiol with excess dinitrogen tetraoxide probably contains the corresponding thionitrate instead of thionitrite because of the formation of N-thio-p-benzoquinoneimine from the corresponding p-aminophenol.

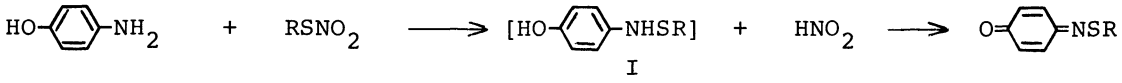


In this reaction, dinitrogen tetraoxide (30 mmol) in carbon tetrachloride (3 ml) was added to a stirred solution of s-BuSH (1.35 g, 15 mmol) at 0°C. The solution turned immediately red indicating the formation of s-butyl thionitrite and soon the red color disappeared, due undoubtedly to the formation of s-butyl thionitrate by further oxidation of s-butyl thionitrite. 4-Amino-2,6-dichlorophenol (1.78 g, 10 mmol) was then added for a few minutes and the solution was stirred for 1.5 h. The mixture was filtered[6] and the filtrate was diluted with ether, washed with aq. $NaHCO_3$ solution, dried ($MgSO_4$), evaporated and the usual TLC

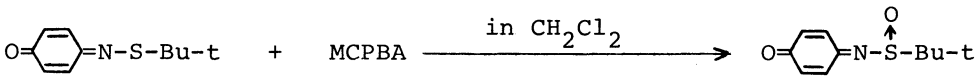
separation (hexane:ether=7:1) gave N-(s-butylthio)-2,6-dichloro-p-benzoquinoneimine (256 mg, 10%).

o-Aminophenol was also found to react with t-butyl thionitrate but gave only a small amount of the corresponding o-benzoquinoneimine derivative, accompanied with much dark colored matter which had an absorption band at 2150 cm^{-1} (probably N≡N) in IR spectrum.

The reaction is presumed to proceed via the intermediate I, which would immediately be oxidized to benzoquinoneimines with nitrous acid formed during the reaction.



When N-(t-butylthio)-p-benzoquinoneimine (1.88 mmol, 366 mg) was oxidized with an equivalent amount of m-chloroperbenzoic acid in dichloromethane (15 ml) at 0°C for 30 min, a red colored unstable sulfinyl derivative was obtained (276 mg, 70%) after column chromatography (hexane:chloroform=2:1-0:1). This sulfinyl derivative showed a strong absorption at 1080 cm^{-1} in IR spectrum, however soon decomposed (ca. 1 hr) at room temperature.



References and Notes

1) R. Adams and W.Reifschneider, Bull. Soc. Chim. Fr., 1958, 23.
2) D. N. Kramer and R. M. Gamson, J. Org. Chem., 24, 1154(1959).
3) N-(t-Butylthio)-p-benzoquinoneimine is obtained in nearly the same yield, even without copper(II) chloride as shown in the Table, but separation of the products becomes difficult. When p-aminophenol was treated with t-butyl thionitrate without copper(II) chloride, excess thionitrate was not converted to corresponding disulfide but to thiolsulfonate by undesirable oxidation. Since the thiolsulfonate formed was difficult to be removed completely unlike the disulfide by distillation or TLC from the benzoquinoneimine, copper(II) chloride is a useful reagent separating benzoquinoneimines in pure form.
4) S. Oae, Y. H. Kim, D. Fukushima and K. Shinhama, J. C. S., Perkin Trans. 1, 813(1978).
5) G.Kresze and U. Uhlich, Chem. Ber., 92, 1048(1959).
6) Brown precipitate which had absorption of 2110 cm^{-1} (probably N≡N) in IR spectrum was filtered off.

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