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Direct Conversion of Arylamines to the Halides by Deamination with Thionitrite or Related Compounds and Anhydrous Copper(II) Halides

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Reactions of various arylamines with either *t*-butyl thionitrite, *t*-butyl thionitrate, or *p*-toluenesulfonyl nitrite in the presence of anhydrous copper(II) halides under mild conditions gave corresponding aryl halides in good yields. This reaction in the presence of such olefins as acrylonitrile, styrene, and acrylic acid gave the corresponding 2-aryl-1-haloethanes as the main products. *t*-Butyl thionitrite, *t*-butyl thionitrate, and *p*-toluenesulfonyl nitrite were found to be better deaminative reagents than alkyl nitrites or alkyl nitrates due to their weak sulfur–nitrogen bonds.

We reported recently that various thionitrites can be prepared simply by treating thiols with one equivalent of dinitrogen tetraoxide,[1,2] whereas *t*-BuSH can be easily converted the corresponding thionitrate with excess (over 2 eq.) dinitrogen tetraoxide in a good yield.[3]

We now have found that various arylamines (**3**) reacted readily with either *t*-butyl thionitrite (**1**) or *t*-butyl thionitrate (**2**) in the presence of anhydrous copper(II) halides under mild conditions to afford the corresponding halides (**4**) in good yields (Eq. 1).

$$\left.\begin{array}{l}\underset{\mathbf{1}}{t\text{-Bu-S-N=O}}\\ \text{or } \underset{\mathbf{2}}{t\text{-Bu-SNO}_2}\end{array}\right] + \underset{\mathbf{3}}{\text{ArNH}_2} + \underset{\text{X=Cl, Br}}{\text{CuX}_2} \xrightarrow[0\text{–}25\,^\circ\text{C}]{\text{in CH}_3\text{CN}}$$

$$\underset{\mathbf{4}}{\text{ArX}} + \text{N}_2 + \underset{\mathbf{5}}{(t\text{-Bu–})_2\text{S}_2} + \underset{\mathbf{6}}{(t\text{-Bu–})_2\text{S}_3} \qquad (1)$$

Both thionitrites and thionitrates are generally known to be unstable, however, *t*-butyl derivatives, *i.e.*, thionitrite **1** and thionitrate **2**, which can be readily synthesized quantitatively by mixing the thiol and dinitrogen tetraoxide, are stable enough to be used for these reactions. Although other nitrosyl compounds such as nitrosyl halide[4] and alkyl nitrite[5,6] have been successfully used for the same reaction, thionitrites or thionitrates are considered to be better reagents for deaminative halogenation of arylamines **3** due both to the relatively weaker S–N bond of thionitrite **1** or thionitrate **2** than the O–N bond of alkyl nitrites and also to the stronger complexation of thio-derivatives with copper salt than the oxygen and chloro analogs. Indeed, this was found to be the case. Starting with arylamines **3**, corresponding halides **4** were obtained in good yields at room temperature as shown in Table 1. Although alkyl nitrates did not give any deaminative product from arylamines even upon heating with copper(II) halides, thionitrate **2** was found to be an amazingly effective deaminative reagent. The nitroso or nitro group in thionitrite **1** or thionitrate **2** is used for the initial diazotization of arylamines **3**. The rest of the molecules was found to be converted to di-*t*-butyl disulfide (**5**) and di-*t*-butyl trisulfide (**6**), which was identified by elemental analysis, while N_2, quantitatively evolved and collected during the reaction, was identified by mass-spectroscopy. All the products were identified by comparing their IR and NMR spectra and melting or boiling points with those of authentic samples.

Treatment of arylamines **3** with thionitrite **1** and anhydrous copper(II) halides probably involves an initial formation of an intermediate diazonium salt (Eq. 2) like in the case with alkyl nitrites.[6] Trisulfide **6** was formed probably by the attack of *t*-butyldithio anion (**8**) or *t*-butyldithio radical (**9**) formed by heterolysis or homolysis of disulfide **5** on thionitrite **1** (Eq. 3).

$$\underset{\mathbf{3}}{\text{ArNH}_2} + \underset{\text{X=Cl, Br}}{\text{CuX}_2} + \underset{\mathbf{1}}{t\text{-BuS-N=O}} \longrightarrow \underset{\mathbf{3}}{\text{ArNH}_2} + [\text{CuX}_2\cdot\text{NO}]$$

$$+\ t\text{-BuS}\cdot \xrightarrow[-\text{H}_2\text{O}]{} [\text{Ar}\cdots\text{N}_2\cdots\text{CuX}_2] + [t\text{-BuS}\cdot] \longrightarrow$$

$$\underset{\mathbf{4}}{\text{ArX}} + \text{N}_2 + \text{CuX} + \underset{\mathbf{5}}{(t\text{-Bu–})_2\text{S}_2} \qquad (2)$$

$$\mathbf{5} \xrightarrow{\text{CuX}_2} \begin{array}{c}[t\text{-BuS}\text{S}^-]\\ \mathbf{8}\\ \text{or } [t\text{-BuSS}\cdot]\\ \mathbf{9}\end{array} \xrightarrow{\mathbf{1}} \underset{\mathbf{6}}{(t\text{-Bu})_2\text{S}_3} \qquad (3)$$

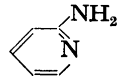
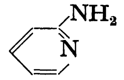
The reaction of disulfide **5** with $CuCl_2$ under the same conditions afforded both the trisulfide **6** and the di-*t*-butyl tetrasulfide (**7**). Probably, in the presence of thionitrite **1** or thionitrate **2**, the anionic intermediate *t*-BuSS⁻ or radical intermediate *t*-BuSS· reacts with the thionitrite **1** or the thionitrate **2** to give the trisulfide **6**. It is noteworthy that trisulfide **6** is formed as the major product along with a minor product *i.e.*, disulfide **5**.

$$\underset{\mathbf{5}}{t\text{-BuSS-Bu-}t} \xrightarrow{\text{CuCl}_2} \underset{\mathbf{6}}{(t\text{-Bu})_2\text{S}_3} + \underset{\mathbf{7}}{(t\text{-Bu})_2\text{S}_4}$$

$$\underset{\mathbf{1}}{t\text{-BuSNO}} \xrightarrow{\text{CuCl}_2} \underset{\mathbf{5}\ \text{trace}}{(t\text{-Bu})_2\text{S}_2} + \underset{\mathbf{6}}{(t\text{-Bu})_2\text{S}_3}$$

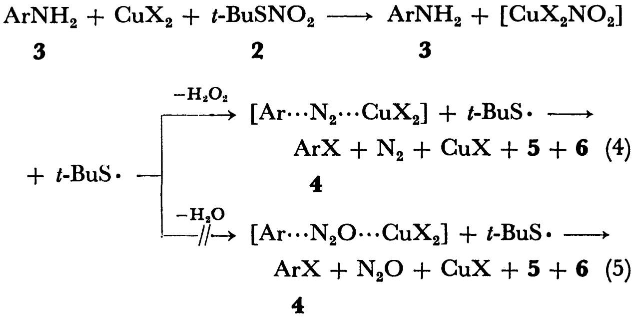
When thionitrate **2** was used instead of thionitrite **1**, nearly the same results were obtained (Table 2). If the reaction proceeds *via* a similar path as in the case of the thionitrite **1** either H_2O_2(instead of H_2O) or N_2O(instead of N_2) should be formed according to Eq. 4 or 5. However, the GC mass spectrum of gas trapped during the reaction showed only N_2 but not N_2O. A possibility of decomposition of N_2O to NO and N_2 in the mass process was ruled out by a control mass spectroscopic analysis of the authentic sample of N_2O, which showed a strong molecular peak (M^+, 44) of N_2O. Though H_2O_2 could not be confirmed, thiane and diphenyl sulfide in acetic acid was added for trapping H_2O_2

Table 1. Deamination of amines with thionitrite **1**, thionitrate **2**, or sulfonyl nitrite **14** and anhydrous copper(II) halides

Amine ($R-NH_2$)	Reagent	Reaction temp/°C	Reaction time/min	Yield of the product/%		
				RCl	RBr	Other
p-NO_2–$C_6H_4NH_2$	**1**	25	2	$98^{a,c)}$	$78^{a)}$	
p-NO_2–$C_6H_4NH_2$	**1**	0	1	$85^{a)}$		
p-NO_2–$C_6H_4NH_2$	**1**	50	0.5	$61^{a)}$		
p-NO_2–$C_6H_4NH_2$	**2**	25	2	$98^{a,d)}$	$74^{a)}$	
p-NO_2–$C_6H_4NH_2$	**2**	0	1.5	$87^{b)}$		
p-NO_2–$C_6H_4NH_2$	**14**	25	1	$89^{a)}$		
o-NO_2–$C_6H_4NH_2$	**14**	25	1	$87^{a)}$	$63^{a)}$	
p-HO_2C–$C_6H_4NH_2$	**1**	25	2	$97^{a)}$	$78^{a)}$	
p-HO_2C–$C_6H_4NH_2$	**2**	25	1.5	$86^{a)}$		
p-HO_2C–$C_6H_4NH_2$	**2**	25	1		$75^{a)}$	
p-Cl–$C_6H_4NH_2$	**1**	25	2	$78^{b)}$	$71^{b)}$	
p-Cl–$C_6H_4NH_2$	**2**	25	2	$71^{b)}$	$55^{b)}$	
p-Cl–$C_6H_4NH_2$	**14**	25	1	$76^{a)}$	$79^{a)}$	
p-Br–$C_6H_4NH_2$	**14**	25	1	$93^{a)}$	$78^{a)}$	
$C_6H_5NH_2$	**1**	25	2	$86^{b)}$	$58^{b)}$	
$C_6H_5NH_2$	**2**	25	2	$82^{b)}$	$83^{b)}$	
p-MeO–$C_6H_4NH_2$	**1**	25	2	$61^{b)}$	$36^{b)}$	
p-MeO–$C_6H_4NH_2$	**2**	25	1.5	$63^{b)}$	$57^{b)}$	
p-MeO–$C_6H_4NH_2$	**14**	25	1	$38^{a)}$	$60^{a)}$	
p-HO–$C_6H_4NH_2$	**1**	25	2	$57^{a)}$	$40^{a)}$	
p-HO–$C_6H_4NH_2$	**2**	25	1	0		$40^{g)}$
p-HO–$C_6H_4NH_2$	**2**	25	4	0		$43^{h)}$
$C_6H_5CH_2NH_2$	**1**	25	2	$18^{a,e)}$		
$C_6H_5CH_2NH_2$	**2**	25	2	$18^{a,f)}$		
	**1**	25	1.5	$35^{b)}$	$7^{a)}$	
	**2**	25	1.5	$64^{b)}$	$13^{b)}$	

a) Isolated yield. b) GC yield. c) Other side products originated from thionitrite **1** (7.5 mmol) were disulfide **5** (0.32 mmol) and trisulfide **6** (2.2 mmol). d) Other products originated from thionitrate **2** (7.5 mmol) were disulfide **5** (0.31 mmol) and trisulfide **6** (2.1 mmol). e) Benzaldehyde (13%) and benzyl alcohol (26%) were isolated. f) Benzaldehyde (32%) and benzyl alcohol (16%) were isolated. g) Compound **11** was isolated in 40% yield. h) Even in the reaction of p-aminophenol with thionitrate **2** without CuX_2, compound **11** was obtained in 43% of GC yield based on the amount of p-aminophenol.

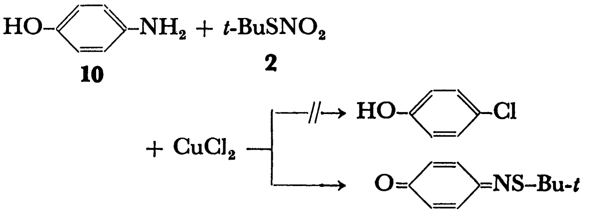
into the reaction mixture both at the begining and after the completion of the reaction. However, both sulfides were recovered quantitatively and no sulfoxide was detected. H_2O_2 formed in the reaction may be readily consumed for further oxidation of copper complex. The reaction is presumed to proceed *via* a diazonium salt intermediate as shown by Eq. 4.



$$\underset{\mathbf{3}}{ArNH_2} + CuX_2 + \underset{\mathbf{2}}{t\text{-}BuSNO_2} \longrightarrow \underset{\mathbf{3}}{ArNH_2} + [CuX_2NO_2]$$

$$+\ t\text{-}BuS\cdot \begin{cases} \xrightarrow{-H_2O_2} [Ar\cdots N_2\cdots CuX_2] + t\text{-}BuS\cdot \longrightarrow \underset{\mathbf{4}}{ArX} + N_2 + CuX + \mathbf{5} + \mathbf{6} & (4) \\ \overset{-H_2O}{-\!\!/\!\!/\!\!\rightarrow} [Ar\cdots N_2O\cdots CuX_2] + t\text{-}BuS\cdot \longrightarrow \underset{\mathbf{4}}{ArX} + N_2O + CuX + \mathbf{5} + \mathbf{6} & (5) \end{cases}$$

p-Aminophenol (**10**) did not give the corresponding halide with thionitrate **2** but gave N-(t-butylthio)-p-benzoquinone imine (**11**) in 40% yield. The reaction of p-hydroxyaniline **10** and thionitrate **2** without anhydrous copper(II) chloride also gave p-benzoquinone imine **11**, however, the corresponding S-t-butyl 2-methyl-2-propanethiosulfonate (**12**) was formed from thionitrate **2**, besides disulfide **5** and trisulfide **6**.



10 **2**

11

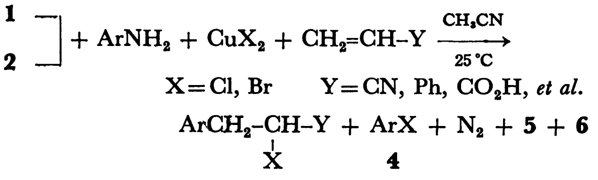
$$\mathbf{10} + \mathbf{2} \xrightarrow[25\,°C,\ 4\,h]{\text{in } CH_3CN} \mathbf{11} + \mathbf{5} + \underset{\mathbf{12}}{t\text{-}BuSO_2S\text{-}Bu\text{-}t}$$

We have also found that the 2-aryl-1-haloethanes (**13**) were readily obtained in the Meerwein arylation when various arylamines **3** were stirred with thionitrite **1** or thionitrate **2** and anhydrous copper(II) halides in the presence of such olefins as acrylonitrile, styrene and acrylic acid as shown in Table 2. In this reaction,

Table 2. Deamination with thionitrite **1** or thionitrate **2** and anhydrous copper(II) halides in the presence of olefins

$ArNH_2$	(CuX_2) X	Reagent	(CH_2=CHY) Y	Product and yield/% $\mathrm{ArCH_2\underset{X}{C}HR}$	Product and yield/% ArX
p-NO_2-$C_6H_4NH_2$	Cl	**1**	CN	48[a] (32[b])	32[a]
p-NO_2-$C_6H_4NH_2$	Cl	**2**	CN	78[a] (65[b])	11[a]
o-NO_2-$C_6H_4NH_2$	Cl	**1**	CN	29[a] (21[b])	25[a]
o-NO_2-$C_6H_4NH_2$	Cl	**2**	CN	64[a] (61[b])	36[a]
$C_6H_5NH_2$	Cl	**1**	CN	48[a] (31[b])	34[a]
$C_6H_5NH_2$	Cl	**2**	CN	50[a] (39[b])	46[a]
p-MeO-$C_6H_4NH_2$	Cl	**1**	CN	50[a] (40[b])	43[a]
p-MeO-$C_6H_4NH_2$	Cl	**2**	CN	28[a] (23[b])	19[a]
p-NO_2-$C_6H_4NH_2$	Cl	**2**	Ph	62[a] (58[b])	20[a]
p-NO_2-$C_6H_4NH_2$	Cl	**2**	CO_2Et	49[a] (35[b])	33[a]
$C_6H_5NH_2$	Cl	**2**	CO_2Et	56[a] (36[b])	22[a]
$C_6H_5NH_2$	Cl	**2**	c	40[a,d] (31[b,d])	20[a]
$C_6H_5NH_2$	Cl	**2**	CO_2H	31[a] (30[b])	20[a]
$C_6H_5NH_2$	Br	**2**	CO_2H	41[a] (38[b])	33[a]

a) GC yield. b) Isolated yield. c) Methyl methacrylate. d) $\mathrm{PhCH_2\underset{Cl}{C}(Me)CO_2Me}$.

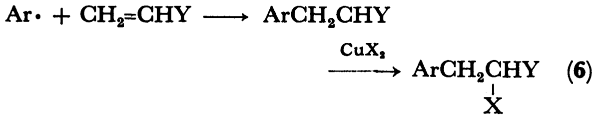


$$\left.\begin{matrix}\mathbf{1}\\ \mathbf{2}\end{matrix}\right] + \mathrm{ArNH_2} + \mathrm{CuX_2} + \mathrm{CH_2{=}CH\text{-}Y} \xrightarrow[25\,^\circ\mathrm{C}]{\mathrm{CH_3CN}}$$

$$\mathrm{X{=}Cl,\ Br} \quad \mathrm{Y{=}CN,\ Ph,\ CO_2H,}\ et\ al.$$

$$\underset{\mathbf{13}}{\mathrm{ArCH_2\text{-}\underset{X}{C}H\text{-}Y}} + \underset{\mathbf{4}}{\mathrm{ArX}} + \mathrm{N_2} + \mathbf{5} + \mathbf{6}$$

small amounts of corresponding aryl halides **4** were also formed. However, 2-aryl-1-haloethanes **13** were always the main products. Arylation of olefins proceeded more readily and gave the products in better yields with the thionitrate **2** than with the thionitrite **1**. The reaction of p-nitroaniline which has an electron-withdrawing nitro group proceeded readily giving the product nearly quantitatively, whereas, the reaction with p-methoxyaniline, which has an electron-donating methoxyl group, was somewhat anomalous and gave the adduct in a poor yield together with many uncharacterized substances. Thus thionitrite **1** and thionitrate **2** have now found to be excellent Meerwein type arylation reagents. Some of the compounds in Table 2 are quite useful compounds. For example, treatment of 2-bromo-3-phenylpropionic acid with aq. ammonia can give *dl*-phenylalanine,[7] while ethyl 2-chloro-3-(p-nitrophenyl)propionate could be used for the synthesis of chloramphenicol. Arylation of olefinic compounds is presumed to proceed *via* the Meerwein type arylation path which involves aryl radicals formed by the decomposition of diazonium salts as shown in Eq. 6.



$$\mathrm{Ar\cdot} + \mathrm{CH_2{=}CHY} \longrightarrow \mathrm{ArCH_2CHY} \xrightarrow{\mathrm{CuX_2}} \mathrm{ArCH_2\underset{X}{C}HY} \quad (6)$$

p-Toluenesulfonyl nitrite (**14**), which is a new sulfonyl derivative prepared from the corresponding sulfinic acid with N_2O_4,[16] was also found to be an excellent deaminative reagent of arylamines. This reaction requires

$$\underset{\mathbf{14}}{p\text{-}\mathrm{TolSO_2NO}} + \underset{\mathbf{3}}{\mathrm{ArNH_2}} + \mathrm{CuX_2} \xrightarrow[25\,^\circ\mathrm{C},\,1\,\mathrm{h}]{\text{in } \mathrm{CH_3CN}}$$

$$\mathrm{X{=}Cl,\ Br}$$

$$\underset{\mathbf{4}}{\mathrm{ArX}} + \mathrm{N_2} + \underset{\mathbf{15}}{(p\text{-}\mathrm{TolSO_2})_2\mathrm{NOH}}$$

a larger amount of deaminative reagent **14** than thionitrite **1** or thionitrate **2** because of the formation of a nitrogen compound, N,N'-bis(p-tolylsulfonyl)hydroxylamine (**15**). When various arylamines **3** were treated with anhydrous copper(II) halides and excess sulfonyl nitrite **14** at room temperature, evolution of nitrogen gas was observed during the period of *ca.* 30 min and the corresponding aryl halides **4** were obtained in good yields. These results are listed in Table 1.

Experimental

All the melting points and boiling points were uncorrected. Elemental analysis of sulfur was carried out by Sagami Chemical Research Center and the analyses of other elements were carried out by the Chemical Analysis Center in our University. Analytical determinations by GLC were performed on a Hitachi 163 gas chromatograph fitted with the following column (3 mm o.d. × 3 m): 10% SE-30 on Chromosorb W. ^{1}H-NMR spectra were taken at 60 MHz on a Hitachi R-24 A apparatus. IR spectra were recorded with a Hitachi 215 spectrometer. Mass spectra were recorded with a Hitachi RMU-6M spectrometer.

Synthesis of t-*Butyl Thionitrite (1).* Dinitrogen tetraoxide[1] (0.1 mol) in carbon tetrachloride (11 ml) was added to a stirred solution of t-BuSH 9.02 g (0.1 mol) in dry ether (100 ml) for a few minites at −70 °C. The solution was stirred further for several minutes and poured into the cold 5% $NaHCO_3$ aq. solution and extracted with ether. The ethereal extract was dried ($MgSO_4$) in dark at 0 °C, and the solvent was evaporated *in vacuo* giving almost pure thionitrite **1** 7.0 g (59%), which was pure enough for the reaction over several months at −20 °C with molecular sieves: bp 40—42 °C/55 mmHg (lit,[9] 36 °C/48 mmHg). IR (neat):

1490 (NO), 1360, 1298, and 1157 cm^{-1}. NMR (CCl_4): δ 1.85 (s).

Synthesis of t-*Butyl Thionitrate (2).* This reaction required a relatively large flask (2 l) fitted with a reflux condencer the end of which is open for air escape, since the reaction took place vigorously. Dinitrogen tetraoxide[1] (1.5 mol) 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 the 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 67.5 g (84%) of colorless oil which had a stimulating odor: bp 40—41 °C/6 mmHg (lit,[9] 55 °C/13 mmHg). IR (neat): 2950, 1520 (NO), 1300, 1263, 1155, and 825 cm^{-1}. NMR (CCl_4): δ 1.58 (s). Thionitrate **2** was pure enough for the reaction over several months at −20 °C with molecular sieves.

Reactions of t-*Butyl Thionitrite (1) and Primary Amines (3) with Anhydrous Copper(II) Halides.* The following is a typical run. After a solution of *t*-BuSNO 0.89 g (7.5 mmol) in dry acetonitrile (20 ml) was added onto well-dried anhydrous copper(II) chloride 0.85 g (6 mmol) under argon with vigorous stirring, *p*-nitroaniline 685 mg (5 mmol) was slowly added in a period of 5 min at 25 °C. The solution was stirred further for 2 h, and then hydrochloric acid solution (20%, 100 ml) was added. The solution, after saturated with NaCl, was extracted with ether. The extract was washed with water saturated with NaCl and dried ($MgSO_4$), concentrated. Recrystallization (from hexane) gave pure *p*-chloronitrobenzene 770 mg (quant.): mp 80—82 °C. IR and NMR spectra were identical with those of authentic samples. Other products were disulfide **5** (0.32 mmol) and trisulfide **6** (2.2 mmol). The amounts of these polysulfides were estimated by GLC and separated by distillation. Disulfide **5**: MS (70 eV), *m/e* 178 (M^+). IR spectrum was identical with that of authentic sample. Trisulfide **6**: mp 14—15 °C (lit,[10] 16.63 °C). IR (neat): 1450, 1360, and 1260 cm^{-1}; NMR (CCl_4): δ 1.36 (s) (lit.[11] δ 1.34). MS (70 eV), *m/e* 210 (M^+).

Reactions of t-*Butyl Thionitrate (2) and Primary Amines (3) with Copper(II) Halides.* The following is a typical run. Well-dried anhydrous copper(II) chloride 810 mg (6 mmol) and *p*-nitroaniline 682 mg (5 mmol) were treated with *t*-$BuSNO_2$, 1.02 g (7.5 mmol) under argon in a similar procedure to that of *t*-BuSNO, giving 780 mg (quant.) of *p*-chloronitrobenzene. Amounts of disulfide **5** (0.31 mmol) and trisulfide **6** (2.1 mmol) were also monitored by GLC and identified with IR, NMR, and MS spectral analyses after distillation.

Melting points, or boiling points, IR and NMR spectra of all halides in Table 1 were identical with those of authentic samples.

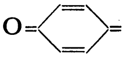
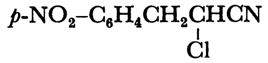
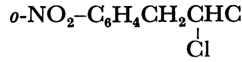
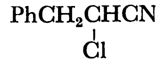
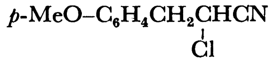
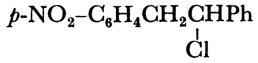
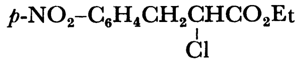
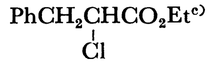
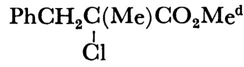
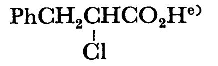
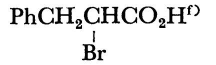
Reaction of t-*Butyl Thionitrate (2) and* p-*Aminophenol (10) with Copper(II) Chloride.* Anhydrous copper(II) chloride 810 mg (6 mmol) and *p*-aminophenol 546 mg (5 mmol) were treated with thionitrate **2** 1.02 g (7.5 mmol) for 1 h in a similar procedure to the former reaction. TLC (hexane: ether = 10: 1) gave 390 mg (40%) of *N*-(*t*-butylthio)-*p*-benzoquinone imine as bright yellow crystals: mp 77—79 °C (recrystallized from hexane). Found: C, 61.38; H, 6.60; N, 7.13; S, 16.29%. Calcd for $C_{10}H_{13}NOS$: C, 61.51; H, 6.71; N, 7.17; S, 16.42%. IR (KBr): 1630 (C=O), 1475, 1450, 1360, 1143, 861, and 705 cm^{-1}. UV (hexane) max: 401 nm. NMR (CCl_4): δ 1.45 (s, 9H), 6.13—6.50 (m, 2H), and 6.75—7.35 (m, 2H). MS (70 eV), *m/e* (rel intensity): 195 (23, M^+), 138 (76, $=NS^+$), and 57 (100, *t*-Bu^+).

TABLE 3. SPECTRAL DATA OF 2-ARYL-1-HALOETHANES

Compound	IR (neat, cm^{-1})	^{1}H-NMR (CCl_4, δ)	MS (70 eV), *m/e*, M^+
 $p\text{-}NO_2\text{-}C_6H_4CH_2\underset{Cl}{C}HCN$	1600, 1520, 1350, 857	a)	210, 213
 $o\text{-}NO_2\text{-}C_6H_4CH_2\underset{Cl}{C}HCN$[b)]	1520, 1343, 783, 722	3.53 (d, J=8 Hz, 2H), 4.87 (t, 1H), 7.14—8.15 (m, 4H)	210, 213
 $PhCH_2\underset{Cl}{C}HCN$	2240, 1497, 725, 695	a)	165, 167
 $p\text{-}MeO\text{-}C_6H_4CH_2\underset{Cl}{C}HCN$	1605, 1507, 1205, 835	a)	195, 197
 $p\text{-}NO_2\text{-}C_6H_4CH_2\underset{Cl}{C}HPh$	1550, 1490, 1320, 1180	a)	261, 263
 $p\text{-}NO_2\text{-}C_6H_4CH_2\underset{Cl}{C}HCO_2Et$	1720, 1507, 1335, 1166	a)	257, 259
 $PhCH_2\underset{Cl}{C}HCO_2Et$[c)]	1730, 1260, 1160	1.28 (t, 3H), 3.14 (dd, J=7.5 Hz, JJ=4.5 Hz, 2H)4.12 (q, 2H), 4.24 (t, 1H), 7.14 (m, 5H)	212, 214
 $PhCH_2\underset{Cl}{C}(Me)CO_2Me$[d)]	1730, 1435, 1260, 1207	1.62 (s, 3H), 3.10 (d, J=3 Hz, 2H), 4.20 (s, 3H),7.15 (m, 5H)	212, 214
 $PhCH_2\underset{Cl}{C}HCO_2H$[e)]	3400—2500, 1710, 698	3.20 (d, J=8 Hz, 2H), 4.47 (t,1H), 7.17 (m, 5H), 11.30 (br, s, 1H)	184, 186
 $PhCH_2\underset{Br}{C}HCO_2H$[f)]	3400—2500, 1710, 910	3.34 (m, 2H), 4.40 (m, 1H), 7.25 (m, 4H), 11.83 (br, s,1H)	228, 230

a) Spectral data were identical with those of literature.[8] b) Bp(bath temp) 160 °C/2 mmHg (lit,[14] 166—168 °C/4 mmHg). c) Bp (bath temp) 85—90 °C/20 mmHg (lit,[15] 85—89 °C/50 mmHg). d) Bp(bath temp) 100 °C/2 mmHg (lit,[12] 136—165 °C/15 mmHg). e) Bp (bath temp) 120 °C/2 mmHg (lit,[13] 176—177 °C/20 mmHg). f) Mp 45—47 °C (lit,[15] 48 °C).

Disulfide **5** (92 mg) and trisulfide **6** (250 mg) were also isolated by TLC and distillation.

Reaction of t-*Butyl Thionitrate (2) and* p-*Aminophenol (10) without Anhydrous Copper(II) Halide.* *p*-Aminophenol 109 mg (1 mmol) was added to a stirred solution of thionitrate **2** 202 mg (1.5 mmol) in dry acetonitrile (3 ml). The mixture was stirred further for 4 h. The amounts of the products were estimated by GLC: *p*-Benzoquinone imine **11** (0.43 mmol, 43%), disulfide **5** (0.19 mmol, 26%), thiosulfonic *S*-ester **12** (0.24 mmol, 33%). Thiosulfonic *S*-ester **12** was isolated by preparative GLC: mp 22—24 °C. IR (neat): 1290 and 1100 cm^{-1}. NMR (CCl_4): δ 1.40 (s) and 1.58 (s). MS (70 eV), *m/e* 210 (M^+). Found: C, 45.59; H, 8.61; S, 30.29%. Calcd for $C_8H_{18}O_2S_2$: C, 45.68; H, 8.62; S, 30.48%.

Reactions of t-*Butyl Thionitrite (1) or* t-*Butyl Thionitrate (2) and Arylamines (3) with Copper(II) Halides in the Presence of Olefins.* The following is a typical run. Thionitrate **2** 1.02 g (7.5 mmol) in acetonitrile (7 ml) and acrylonitrile (7 ml) were added to the well-dried anhydrous copper(II) chloride 810 mg (6 mmol). *p*-Nitroaniline 690 mg (5 mmol) in acetonitrile (5 ml) was added to the mixture in a period of 15 min with stirring. During this period, the flask was cooled by water. The mixture was kept stirring further for 30 min. Evolution of gas (110 ml) was observed during this period. Diluted aq. HCl solution (20%, 100 ml) was added to the mixture, which was then extracted with ethyl ether. The ethereal extract was dried ($MgSO_4$), and concentrated. TLC (hexane: ether=10: 1) gave 689 mg (65%) of 2-chloro-3-(*p*-nitrophenyl)propionitrile and 172 mg (22%) of *p*-chloronitrobenzene. Disulfide **5** 71 mg and trisulfide **6** 186 mg, were obtained directly by GLC.

Spectral data of the products were summarized in Table 3.

Reactions of p-*Toluenesulfonyl Nitrite (14) and Aryl Amines (3) with Copper(II) Halides.* The following is a typical run. Well-dried anhydrous copper(II) chloride 161 mg (1.2 mmol) and *p*-bromoaniline 191 mg (1.0 mmol) were treated with sulfonyl nitrite **14**[16] 444 mg (2.4 mmol) under argon in a similar procedure to that of thionitrite **1**, giving 177 mg (93% by GC) of *p*-bromochlorobenzene. Hydroxylamine **15** 340 mg (83%) was also isolated in this reaction: mp 124—125 °C (from ether), (lit,[17] 126 °C). IR spectrum of compound **15** was identical with that of an authentic sample prepared by the procedure described in the literature.[17]

References

1) S. Oae, D. Fukushima, and Y. H. Kim, *J. Chem. Soc., Chem. Commun.*, **1977**, 407.

2) S. Oae, Y. H. Kim, D. Fukushima, and K. Shinhama, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 913.

3) Y. H. Kim, K. Shinhama, D. Fukushima, and S. Oae, *Tetrahedron Lett.*, **1978**, 1211.

4) M. P. Doyle, B. Siegfried, and J. J. Hammond, *J. Am. Chem. Soc.*, **98**, 1627 (1976).

5) M. P. Doyle and B. Siegfried, *J. Chem. Soc., Chem. Commun.*, **1976**, 433.

6) M. P. Doyle, B. Siegfried, and J. F. Dellaria, Jr., *J. Org. Chem.*, **42**, 2426 (1977).

7) J. C. Westfahl and T. L. Gresham, *J. Am. Chem. Soc.*, **77**, 2910 (1955).

8) M. P. Doyle, B. Siegfried, R. C. Elliott, and J. F. Dellaria, Jr., *J. Org. Chem.* **42**, 2431 (1977).

9) G. Kresze and U. Uhlich, *Chem. Ber.*, **92**, 1048 (1959).

10) T. V. Cullum and R. A. Dean, *J. Inst. Petroleum*, **39**, 206 (1953); *Chem. Abstr.*, **48**, 4429a (1954).

11) D. Grant and J. R. Van Wazer, *J. Am. Chem. Soc.*, **86**, 3012 (1964).

12) A. V. Dombrovskii, A. P. Terentév, and A. M. Yurkevich, *Zh. Obshch. Khim.* **27**, 419 (1957); *Chem. Abstr.*, **51**, 15454g (1957).

13) S. Kaneo, *J. Pharm. Soc. Jpn*, **58**, 256 (1938).

14) A. V. Dombroskii, A. M. Yurkevich, and A. P. Terentév, *Zh. Obsh. Khim.* **26**, 3214 (1956); *Chem. Abstr.*, **51**, 8038fg (1957).

15) A. V. Dombroskii, A. M. Yurkevich, and A. P. Terentév, *Zh. Obsh. Khim.* **27**, 3346 (1957); *Chem. Abstr.*, **52**, 9020a (1958).

16) S. Oae, K. Shinhama, and Y. H. Kim, *Tetrahedron Lett.*, **1979**, 3307.

17) G. Kreze and W. Kort, *Chem. Ber.*, **24**, 2624 (1961).