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Studies on the catalysis of the reaction of organotin phenoxides with diethyl azodicarboxylate by lithium perchlorate

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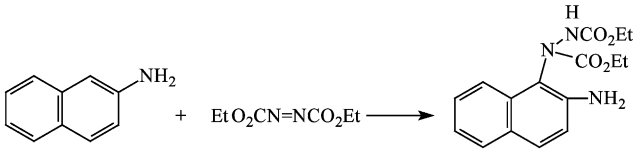
Abstract

Organotin phenoxides react at room temperature with diethyl azodicarboxylate in diethyl ether, in the presence of lithium perchlorate, give the corresponding ring-aminated phenols in excellent yield.

Keywords: Organotin phenoxides; Diethyl azodicarboxylate; Lithium perchlorate

1. Introduction

Amino groups are usually introduced into phenols by nitration under acid conditions, followed by reduction. We have been seeking milder methods for amination and were attracted by the report by Diels and Back [1] that diethyl azodicarboxylate (DEAD) reacts with 2-naphthylamine at the 1-position at room temperature:



(1)

Phenols do not react with DEAD under these conditions, but we have been able to cause the reaction to take place at room temperature by making use of the principles that (a) metals frequently act as surrogates for hydrogen with an increase in reactivity [2] and (b) many reactions are accelerated in the presence of high concentrations of lithium perchlorate [3–7].

Leblanc and coworkers [3] have shown that electron-rich arenes react with bis(2,2,2-trichloroethyl)azodicarboxylate in 3 M lithium perchlorate-diethyl ether or acetone solutions to produce *para*-substituted aryl hydrazide at 65 or 75 °C, respectively. However, it is known that heating of solutions of $LiClO_4$ in Et_2O or acetone may be hazardous.

The use of *O*-metallation of alcohols or enols to enhance the reactivity towards electrophiles such as aldehydes or alkyl or acyl halides is a familiar process [2] and we suspected that the *O*-metallation of phenols could be exploited to enhance the rate of electrophilic substitution in the ring. The polarity of the $M^{\delta+}-O^{\delta-}Ar$ bond would be expected to promote the reaction with enophiles such as DEAD, whatever the detailed structure of the metal phenoxide (which may be associated in solution), or the mechanism of the substitution (see below). We have chosen to work with organotin phenoxides (Bu_3SnOAr) because it is easy to introduce or remove the organotin group and because of the pronounced polarity of the Sn–O bond [8].

Lithium perchlorate is very soluble in ether and, under these conditions, has been used to catalyse a wide variety of reactions such as Diels–Alder and other cycloadditions and aldol and Michael reactions [3–7], and we have shown that it strongly accelerates the rate of metalloene reaction between allyltin compounds and enophiles, including DEAD [9,10]. We have hence used lithium perchlorate in the present work, but barium or magnesium perchlorate or lithium trifluoromethanesulfonate would be the alternatives [7]:

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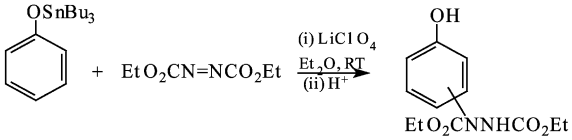
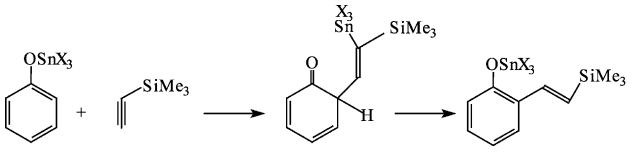


(2)

Previously, Yamaguchi [11] found that the reaction of phenol with trimethylsilylacetylene at the *o*-position is catalysed by $SnCl_4$–BuLi. He believes that the reaction occurs through the tin phenoxide and this can be written as



(3)

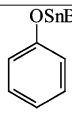
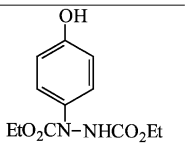
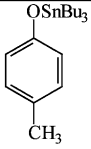
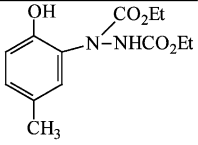
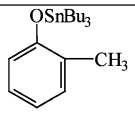
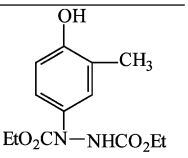
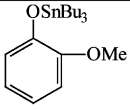
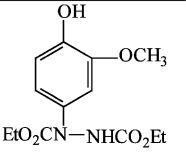
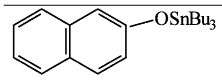
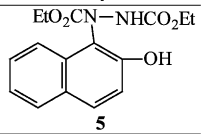
2. Results

The tributyltin phenoxides were prepared by azeotropic dehydration of a mixture of phenol and tributyltin oxide (TBTO) in toluene [12]. The tin phenoxides and DEAD were added to a 4 M solution of $LiClO_4$ in diethyl ether at 298 K. For measuring the half-lives of the reactions, the concentrations of the reagents were 0.0254 M and the absorbance of DEAD at 410 nm was monitored. On a preparative scale, the reaction was followed by TLC or NMR and the products were isolated by chromatography, which also served to remove the Bu_3Sn group.

Table 1 shows the half-lives of the reactions and the structure of the products, which are obtained, in essentially quantitative yields. No reaction occurred between the parent phenols and DEAD under these conditions; the presence of $LiClO_4$ reduces the half-lives of the reactions of tin phenoxides by a factor 7–27.

Many of the reactions that depend on the enhanced reactivity of the SnOR group over that of the HOR group (e.g. the addition to isocyanates) can be carried out using HOR and a catalytic amount of TBTO or other equivalent reagent that will stannylate the alcohol or phenol [2]. It, therefore, appeared likely that these ring aminations could similarly be carried out catalytically and indeed the reactions occur equally well when alcohol and DEAD are used together with 10 mol% of TBTO, thus avoiding the need to prepare the tin phenoxide. The cycle of reactions that is involved is shown in Eq. (4) and some examples of the reaction in Table 2:

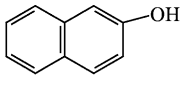
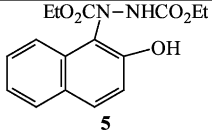
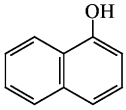
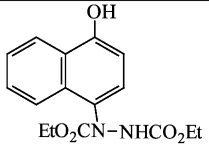
Table 1
Amination of tributyltin phenoxides by DEAD

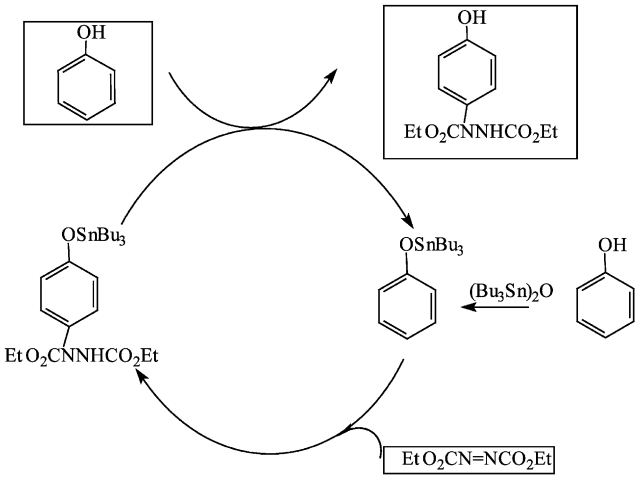
Tin phenoxide	No $LiClO_4$ $t_{1/2}$ [s]	4M $LiClO_4$ $t_{1/2}$ [s]	Product
	1050	135	 **1**
	7500	270	 **2**
	1520	200	 **3**
	6600	250	 **4**
	5760	609	 **5**

3. Discussion

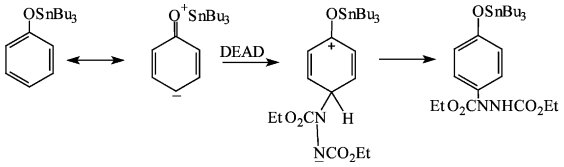
The mechanism of the reaction when amination occurs in the *para*-position to the stannyloxy group may well be a simple electrophilic substitution via a Wheland intermediate:

Table 2
Amination of naphthols with DEAD, catalysed by TBTO (10 mol%)

Naphthol	4M $LiClO_4$ $t_{1/2}$ [s]	Product	Yield %
	621	 **5**	100
	124	 **6**	100

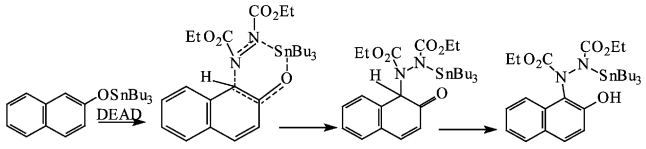


(4)



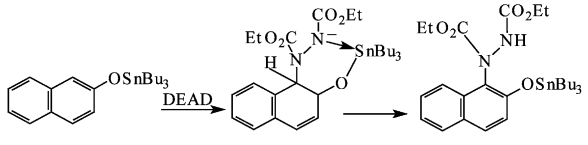
(5)

The reaction of 1-naphthylamine (Eq. (1)), however, has been written in the form of an ene reaction [13] and two reasonable mechanisms, apart from the above electrophilic substitution, can be proposed for the *ortho*-amination of 2-(tributylstannyloxy)naphthalene. First, it could follow a metalloene mechanism:



(6)

Second, the tin could act as a Lewis acid in stabilising the Wheland intermediate by coordination to anionic nitrogen:



(7)

In an attempt to obtain further evidence of the mechanism, we studied the behaviour of 2-methoxynaphthalene and 2-trimethylsiloxynaphthalene under our usual conditions, neither compound would be expected to take part in an ene reaction nor involve a Lewis acid-stabilised transition state, and if reaction did occur it would argue in favour of a conventional electrophilic aromatic substitution. However, neither compound showed any reaction with DEAD in the presence of $LiClO_4$ at room temperature for some weeks and the mechanism of the reaction must still be regarded as an open question.

Hydrazocarboxylate esters can readily be hydrolysed and then reduced to amines, hence our reaction provides a means for introducing the amino group and its derivatives into a phenolic ring under very mild conditions.

4. Experimental

NMR spectra were recorded using a Varian Gemini 200 BP spectrometer. UV spectra were recorded on a Specord spectrometer (Carl Zeiss Jena) using 10 mm cells. Studied tributyltin phenoxides and 2-(tributylstannyloxy)naphthalene were prepared by the azeotropic dehydration of a mixture of the appropriate alcohol and bis(tributyltin)oxide in toluene [12]. 2-Trimethylsiloxynaphthalene was prepared according to the procedure given by Akhatar and McCullough [14].

The addition products were purified by gradient chromatography using a mixture of light petroleum (b.p. 30–40 °C) and ethyl acetate.

Typical examples of metalloene-like reactions are as follows: tributyl-2-naphthyloxy-tin (65.8 mg, 0.152 mmol) and DEAD (24 μl, 0.152 mmol) were added to 4 mol dm^{-3} solutions of $LiClO_4$ in diethyl ether (1 cm^3). The progress of the reaction was monitored by TLC (using light petroleum–diethyl ether mixture (4/1, v/v) as eluent) and by NMR spectroscopy which showed that diethyl *N*-(2-hydroxynaphthyl)-*N*′-tributylstannylhydrazodicarboxylate was formed in a quantitative yield. Isolation of the product by chromatography gave (**6**) (2-hydroxy-1-naphtyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester which was identified by NMR spectroscopy and elemental analysis.

Kinetic measurements with DEAD were carried out in a 1 cm^3 UV cell. The concentration of DEAD and tributyltin derivative was equal to 0.0254 mol dm^{-3}. The progress of the reaction at 298 K was monitored by measuring the absorbance at 410 nm for DEAD. We measured times corresponding to the decrease of the initial absorbance by 50%. The reaction products were characterised by the following values of chemical shifts:

1) (4-Hydroxy-1-phenyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester: m.p. 132–134 °C. $C_{12}H_{16}N_2O_5$ requires: C 53.73, H 6.01. Found: C 53.64, H 5.94. $\delta_H(CDCl_3)$: 1.297 (6H, t, $J = 6.9$ Hz), 4.222 (4H, q, $J = 6.9$ Hz), 6.720 (2H, d, $J = 8.3$ Hz), 6.741 (1H, brs), 7.222 (2H, d, $J = 8.3$ Hz), 7.266 (1H, brs).
2) (2-Hydroxy-5-methyl-1-phenyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester: m.p. 122–124 °C. $C_{13}H_{18}N_2O_5$ requires: C 55.31, H 6.43. Found: C 55.16, H 6.40. $\delta_H(CDCl_3)$: 1.278 (6H, dt, $J = 7.2$

and 2.6 Hz), 2.254 (3H, s), 4.237 (4H, dq, $J = 7.2$ and 2.6 Hz), 6.748 (1H, d, $J = 7.1$ Hz), 7.013 (2H, m), 8.727 (1H, brs).

3) (3-Methyl-4-hydroxy-1-phenyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester-oil. $C_{13}H_{18}N_2O_5$ requires: C 55.31, H 6.43. Found: C 55.42, H 6.47. $\delta_H(CDCl_3)$: 1.238 (6H, t, $J = 6.9$ Hz), 2.148 (3H, s), 4.206 (4H, q, $J = 6.9$ Hz), 6.61 (1H, d, $J = 8.3$ Hz), 6.878 (1H, brs), 6.995 (1H, d, $J = 8.3$ Hz), 7.107 (1H, s), 7.453 (1H, brs).
4) (3-Methoxy-4-hydroxy-1-phenyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester: m.p. 120–121 °C. $C_{13}H_{18}N_2O_6$ requires: C 52.34, H 6.08. Found: C 52.49, H 6.12. $\delta_H(CDCl_3)$: 1.259 (6H, dt, $J = 7.1$ and 1.7 Hz), 3.871 (3H, s), 4.185 (4H, q, $J = 7.1$ Hz), 5.636 (1H, brs), 6.929 (1H, d, $J = 8.7$ Hz), 7.026 (2H, m), 7.263 (1H, brs).
5) (2-Hydroxy-1-naphthyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester: m.p. 178–180 °C. $C_{16}H_{18}N_2O_5$ requires: C 60.37, H 5.70. Found: 60.22, H 5.66. $\delta_H(CDCl_3)$: 1.166 (6H, dt, $J = 35.9$ and 7.1 Hz), 4.227 (4H, dq, $J = 27.2$ and 7.1 Hz), 7.257 (1H, m), 7.377 (1H, m), 7.521 (2H, m), 7.702 (1H, brs), 7.800 (2H, d, $J = 8.5$ Hz), 9.482 (1H, brs).
6) (1-Hydroxy-4-naphthyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester: m.p. 150–151 °C. $C_{16}H_{18}N_2O_5$ requires: C 60.37, H 5.70. Found: C 60.20, H 5.65. $\delta_H(CDCl_3)$: 1.152 (6H, dt, $J = 6.9$ and 4.4 Hz), 4.162 (4H, dq, $J = 6.9$ and 4.4 Hz), 6.624 (1H, d, $J = 8.2$ Hz), 7.481 (2H, m), 7.830 (2H, m), 8.160 (1H, m), 9.827 (1H, brs).

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