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Studies on the catalysis by lithium perchlorate of reactions of aromatic amines with diethyl azodicarboxylate and naphtalen-2-ol with 4-phenyl-1,2,4-triazoline-3,5-dione

W.J. Kinart[a,*] C.M. Kinart[b], R. Oszczeda[a] and Q.T. Tran[a]

[a]*Department of Organic Chemistry, University of Lodz, Narutowicza 68, 90-136 Lodz, Poland*
[b]*Department of Chemistry, University of Lodz, Pomorska 163, 90-236 Lodz, Poland*

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The ene-like reaction of naphtalen-1-ylamine and naphtalen-2-ylamine, and pyridin-2-ylamine with diethyl azodicarboxylate (DEAD) as well as that of naphthalen-2-ol with 4-phenyl-1,2,4-trizoline-3,5-dione is catalyzed by lithium perchlorate. Also conversion of ester function of (DEAD) to amide function in reaction with 2-aminopyridine and further rearrangement of ethyl *N*-pyridyn-2-ylcarbamoylazoformate into ethyl pyridin-2-ylcarbamate are catalyzed by $LiClO_4$.

KEY WORDS: lithium perchlorate; aromatic amines; diethyl azodicarboxylate; naphtalen-2-ol; 4-phenyl-1,2,4-triazoline-3,5-dione.

1. Introduction

Diels and Back [1] persuing a line of investigation that had been initiated earlier by Curtis, published a paper on the reactions of diethyl azodicarboxylate (DEAD). Curtis had found that one could convert the ester functions to amide functions by reaction with primary amines (Scheme 1).

$$EtO_2CN{=}NCO_2Et + 2\ RNH_2 \rightarrow RHNOC\text{-}N{=}N - CONHR + 2\ EtOH$$

Scheme 1.

Diels and Back found that although some aromatic amines confirmed to this pattern of substitution, an exception emerged in the aphtalen-2-ylamine, which gave an entirely different type of reaction, namely an addition leading to hydrazine derivative (Scheme 2).

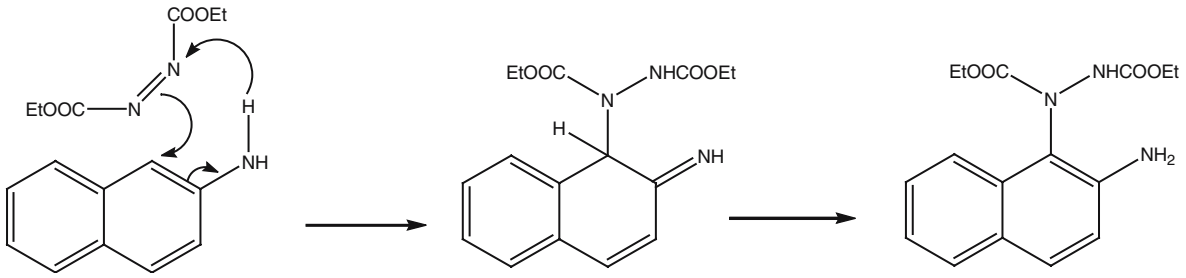
The nature of the reaction as an addition rather than a substitution was apparent just from the elemental analysis of the product but Diels and Back expanded a considerable effort to prove the structure by independent synthesis.

The transformation involves overall the addition of C—H bond of naphtalen-2-ylamine to the N=N bond of the azoester. Today we would think it likely that the mechanism passes over the enamine via a process that is formal equivalent of an ene reaction (although it may involve more than one step). Azodiesters have been recognized as reagents for amination electron rich arenes [2]. Polanc [3] demonstrated the variety of applications of arylhydrazines in organic synthesis. Recently we have shown that organotin phenoxides react at room temperature with diethyl azodicarboxylate [4] and bis(2,2,2-trichloroethyl) azodicarboxylate [5] in diethyl ether, in the presence of lithium perchlorate, give the corresponding ring-aminated phenols in excellent yield. Also the analogous catalytic effect of $LiClO_4$ (typically, 5 M solutions in diethyl ether) has been observed by us for ene and metalloene reactions of diethyl azodicarboxylate and 4-phenyl-1,2,4-trizoline-3,5-dione [6].

Diprotected monosubstituted hydrazine derivatives are versatile intermediates in the synthesis of aromatic amines [7], aryl hydrazines [8, 9], substituted hydrazine derivatives [10–12], azatides (as important peptidomimetics) [13–15], and β-strand mimics [16]. These products are used in the preparation of a wide variety of biologically and industrially valuable compounds [17, 18].

Monosubstituted hydrazines are also intermediates in the preparation of heterocyclic compounds such as pyrazoles [19], indazoles [20], imidazolinones [21], and cinnolines [22]. Moreover, 2-heteroaryl hydrazines [23] are interesting synthetic targets due to their efficiency as ligands for a variety of metal complexes. Diprotected

* To whom correspondence should be addressed.
E-mail: ckinart@uni.lodz.pl



Scheme 2.

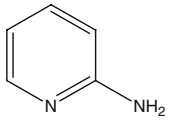
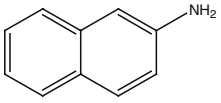
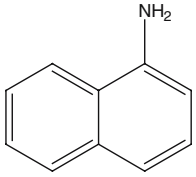
aryl hydrazines are generally prepared by electrophilic amination [4, 7, 20, 24–28] of electron-rich arens utilizing dialkyl azodicarboxylate or via the reaction of tert-butyl carbazates with boronic acids catalyzed by cuprous chloride at room temperature [29].

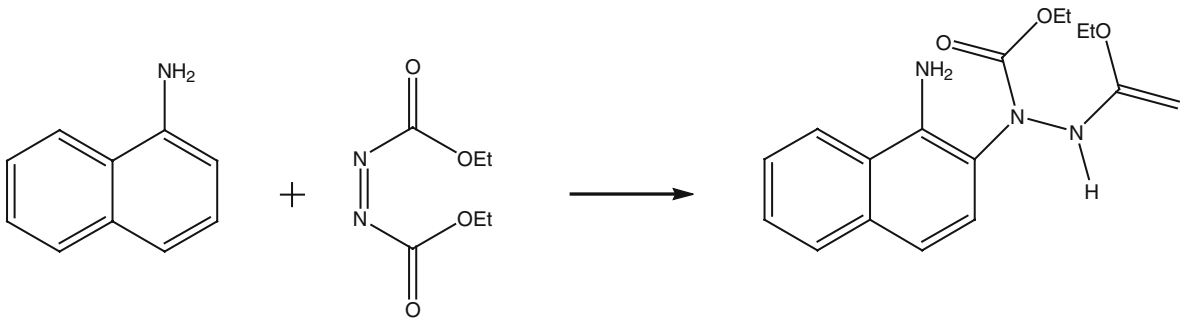
2. Results and discussion

The reaction of pyridin-2-ylamine, naphtalen-1-ylamine and naphtalen-2-ylamine with equimolar amounts of DEAD (0.152 mmol) in Et_2O and 4 mol dm^{-3} solutions of $LiClO_4$ in Et_2O, was followed visually by the fading of the color of the azo compound. Products were purified by gradient chromatography and identified by NMR spectroscopy. For more dilute solutions (0.0254 mol dm^{-3}), the rates were followed by UV–VIS spectroscopy by measuring half-lives of reactions (times corresponding to decrease of the initial absorbance by 50%). The results are shown in Table 1.

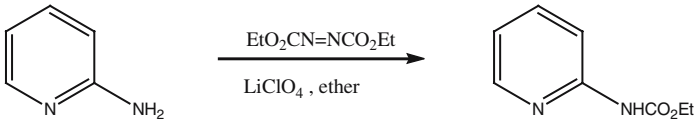
The reaction of naphtalen-1-ylamine with DEAD is given by Scheme 2 and that of naphtalen-2-ylamine by Scheme 3. Products (**1**) and (**2**) were obtained in quantitative yields (Scheme 3).

Table 1
Reactions of naphtalen-1-ylamine and naphtalen-2-ylamine with DEAD in Et_2O

Compound	$LiClO_4$ [mol dm^{-3}]	Half-life of the reaction [s]
	4	$t_{1/4}$ = 120 min
	0	–
	4	10 s
	0	5100 s
	4	30 s
	0	3480 s



Scheme 3.



Scheme 4.

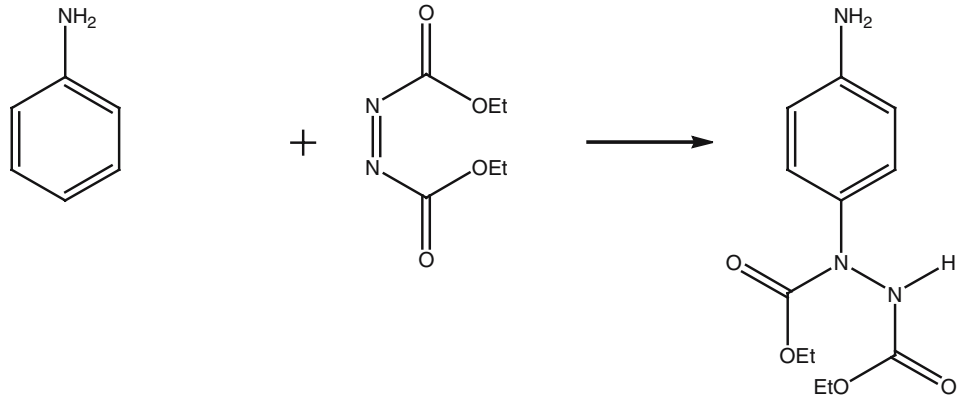
The reaction of pyridin-2-ylamine with diethyl azodicarboxylate carried out in 5 M solution of $LiClO_4$ in Et_2O leads to pyridin-2-ylcarbamic acid ethyl ester with 60% yield (see Scheme 4). When the studied reaction mixture was prepared from one molar equivalent of amine and two molar equivalents the azo compound its yield was nearly quantitative.

The above reaction is exothermic and during its progress bubbles of gas are evolved. It can be followed visually by fading of the orange color of the azo compound. No additional kinetic studies, except that of measuring of half-live of the reaction, have been carried out. However, we suspect that its mechanism may involve initial formation of ethyl N-pyridyn-2-ylcarbamoylazoformate which rearranges spontaneously in polar medium of 5 M $LiClO_4$ in Et_2O into (**3**). This reaction resembles Lossen rearrangement [30] of the *O*-acyl derivatives of hydroxamic acid leading to isocyanates when treated with bases or Wolff-Kishner reduction of ketones with hydrazine [31]. The reaction of pyridin-2-ylamine with DEAD even in 4 mol dm^{-3} solution of $LiClO_4$ in Et_2O was slow. Time corresponding to the decrease of the initial absorbance by 25% ($t_{1/4}$) for 0.025 mol dm^{-3} solution of both reagents was equal to 120 min. Recently Luning [32], in purpose to obtain new receptor molecules containing four hydrogen-bond acceptor or donor sites based on aminopyridines, synthesised pyridin-2-ylcarbamic acid ethyl ester from pyridin-2-ylamine and ethyl chloroformate [33]. Suggested by us method is faster, less toxic and cheaper. It seems also much easier than the procedure recommended by Moriconi [34] based on dehydration over Pd–C of tautomeric mixture of 2-carbethoxyimino-1,2,3,4-tetrahydropyridine and 2-carbethoxyamino-3,4-dihydropyridine obtained by the reaction of 1-trimethylsilyl-1,4-dihydropyridine with ethyl azidoformate. The reaction of aniline with DEAD is given by Scheme 5.

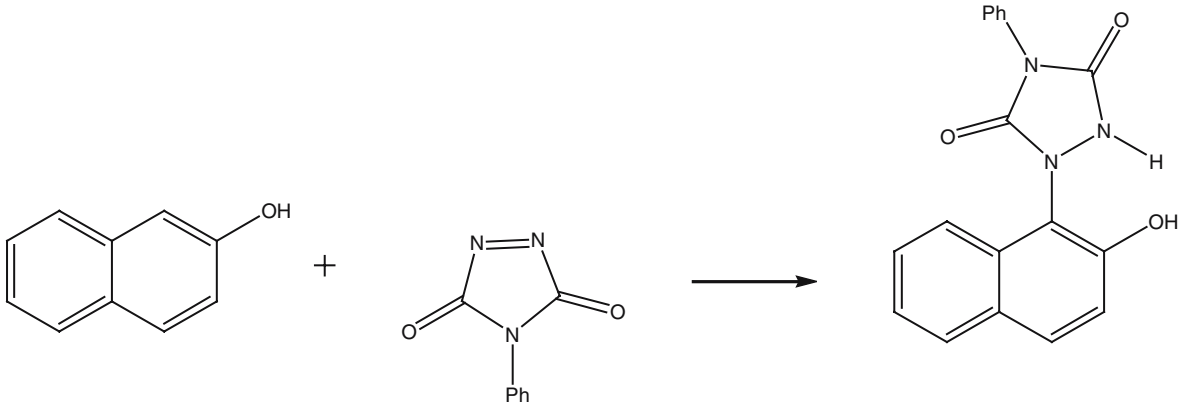
No progress of the above reaction was observed in pure Et_2O. Whereas, in 5 M solution of $LiClO_4$ in Et_2O the single addition product was formed with 30% yield.

We have carried also present studies in purpose to find out if $LiClO_4$ would catalyze reactions of 4-phenyl-1,2,4-triazoline-3,5-dione with naphtols and phenols which are very useful synthetic targets [35]. We have chosen naphtalen-2-ol as a model compound (see Scheme 6) .

The kinetic studies indicated the decrease of the half-live of the reaction of 0.0046 M solution of both reagents from 816 in pure Et_2O to 64 s in 4 M solution



Scheme 5.



Scheme 6.

of $LiClO_4$ in Et_2O. Also the yield of the reaction was improved from 40% in diethyl ether to 60% in the second solvent

3. Experimental

NMR spectra were recorded using a Varian Gemini 200BP spectrometer. UV spectra were recorded on a Specord spectrometer (Carl Zeiss Jena) using 10 mm cells. The addition products were purified by gradient chromatography using a 30% mixture of light petroleum (b.p. 30–40 °C) and ethyl acetate.

Typical examples of ene-like reactions were as follows: naphtalen-2-ylamine (21.7 mg, 0.152 mmol) and DEAD (24 μl, 0.152 mmol) were added to 4 mol dm^{-3} solution of $LiClO_4$ in diethyl ether (1 cm^3). The progress of the reaction was followed visually by fading of the orange color of the azo compound.

Kinetic measurements were carried out in a 1 cm^3, UV cell. The concentration of DEAD and naphtalen-1-ylamine, naphtalen-2-ylamine and pyridin-2-ylamine was equal to 0.025 mol dm^{-3}. The progress of the reaction at 298 K was monitored by measuring the absorbance at 410 nm. We measured times corresponding to the decrease of the initial absorbance by 50% assuming that their ratio corresponds to a certain degree with the ratio of the reaction rate constants. The analogous studies for the reaction of naphtalen-2-ol with PTAD have been carried. The concentration of reagents was equal to 0.0046 mol dm^{-3}, and the absorbance of 4-phenyl-1,2,4-triazoline-3,5-dione at 530 nm was measured.

The reactions products were characterized by the following values of chemical shifts:

(**1**) (2-amino-[1]naphtyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester m.p.198 °C. $C_{16}H_{19}N_3O_4$ requires: C 60.56, H 6.03. Found: C 60.32, H 6.00. $\delta_H(CDCl_3)$: 1.18 (6H, dt, $J=23.7$ and 6.9 Hz), 4.18 (4H, dq, $J=6.9$ and 4.0 Hz), 4.79 (2H, brs), 6.97 (1H, d, $J=9.0$ Hz), 7.24 (1H, m), 7.40 (1H, brs), 7.43 (2H, m), 7.63 (1H, d, $J=9.0$ Hz), 7.71 (1H, d, $J=8.0$ Hz)

(**2**) (1-amino-[2]naphtyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester m.p. 147 °C. $C_{16}H_{19}N_3O_4$ requires: C 60.56, H 6.03. Found: C 60.32, H 6.01. $\delta_H(CDCl_3)$: 1.21 (6H, t, $J=6.9$ Hz), 4.17 (4H, q, $J=6.9$ Hz), 5.17 (2H. brs), 7.16 (2H, m), 7.39 (2H, m), 7.70 (1H, m), 7.77 (1H, m). The comparison of NMR, MS and IR spectra of (**3**) obtained from the reaction of pyridin-2-ylamine with diethyl azodicarboxylate in 50 mol dm^{-3} solution of $LiClO_4$ in Et_2O with identical values given by Luning [35] provided the basis for it identification.

(**4**) (4-amino-[1]phenyl)-hydrazine-*N*,*N*′-dicarboxylic acid diethyl ester m.p. 138 °C. $C_{12}H_{17}N_3O_4$ requires: C 53.92, H 6.41. Found: C 53.83, H 6.38. δ_H (DMSO-d_6): 1.28 (6H, t, $J=7.1$ Hz), 3.71 (2H, br s, NH_2), 4.23 (4H, q, $J=7.1$ Hz), 6.63 (2H, d, $J=8.5$ Hz), 7.00 (1H, br s, NH) 7.18 (2H, d, $J=8.5$ Hz) The NMR Spectrum of the adduct (**5**) has been given elsewhere [35] and provided the basis of the identification report in this work.

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