CHEMISTRY LETTERS, pp. 1733-1736, 1981. © The Chemical Society of Japan 1981

SYNTHESES OF PHENYLAZO-1,3,5-TRIAZINES BY THE OXIDATIVE COUPLING OF HYDRAZINO-1,3,5-TRIAZINES WITH N,N-DISUBSTITUTED ANILINES

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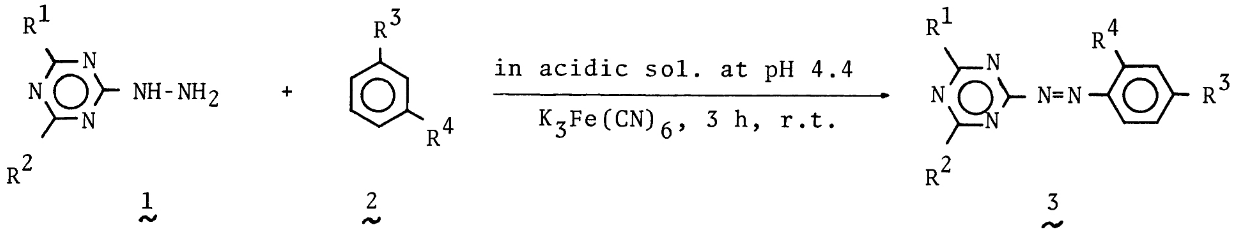
Oxidative coupling of 2-hydrazino-4,6-disubstituted 1,3,5-triazines with N,N-disubstituted anilines was studied. The oxidative coupling reaction proceeded by the use of potassium hexacyanoferrate(III) as the oxidizing agent in aqueous acetic acid solution buffered at pH 4.4 with sodium acetate at room temperature to give corresponding phenylazo-1,3,5-triazines in good yields.

Recently considerable attentions have been focused on heterocyclic azo compounds because of their excellent characteristics for dyes.[1] Although phenylazo-1,3,5-triazines(**3**) seem to have a great potential in dye chemistry, there has been little work on them because of a difficulty of the introduction of an azo group into 1,3,5-triazine ring by the usual diazotization coupling methods.

Three methods for the preparation of **3** have been reported: (i) Oxidation of β-triazinylphenylhydrazines,[2-6] (ii) dehydration condensation of hydrazino-1,3,5-triazines(**1**) with ortho quinones,[7] and (iii) oxidative coupling of **1** with aromatic amines(**2**).[8] Methods (i) and (ii) are limited in the scope by following reasons. It is difficult to prepare selectively β-triazinylphenylhydrazines by the reaction of chloro-1,3,5-triazines with phenylhydrazines,[3] and to obtain various quinone derivatives commercially. In contrast, method (iii) seems to be very useful for the synthesis of **3** because many kinds of **2** can be available easily. The oxidative coupling of **1** with **2** by potassium peroxydisulfate in dilute sulfuric acid solution had been appeared in the patent.[8] Although we have attempted the reactions of **1** and **2** according to the procedure described in the patent, no azo compounds were obtained at all.

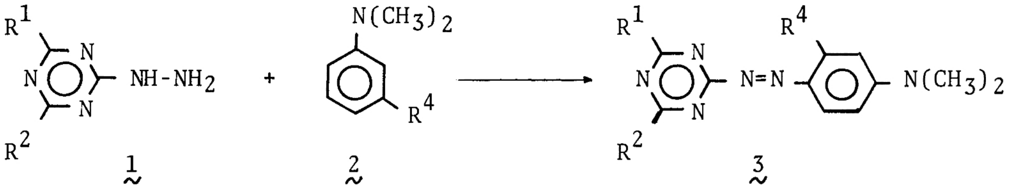
On the other hand, we found that, by the use of potassium hexacyanoferrate(III) in aqueous acetic acid solution, the oxidative coupling of **1** with **2** takes place smoothly to give **3** in excellent yields. In the present communication, we wish to report the very

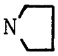
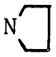
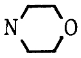
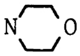
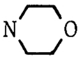
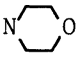


Scheme 1

useful procedure for the preparation of 3 from 1 and 2 (Scheme 1).

Table 1. Oxidative coupling of hydrazino-1,3,5-triazines with N,N-dimethylanilines[a)]



Product[b)] 3	R^1	R^2	R^4	Yield[c)] (%)	Mp(°C) (reported)	λ_{max} (nm)[d)]	ε_{max} ($\times 10^{-4}$)
3a	$N(CH_3)_2$	$N(CH_3)_2$	H	56	230-1.5 (230-1.5)[6]	431	2.85
3b	NH_2	NH_2	H	61	263-5	448	1.82
3c			H	63	230-2 (230-2)[6]	430	2.79
3d			H	97	259-60 (259-60)[6]	443	2.84
3e	$N(CH_3)_2$	C_6H_5	H	58	212-4	453	2.42
3f	$N(CH_3)_2$	Cl	H	64	174-5	477	3.47
3g	NHC_6H_5	NHC_6H_5	H	29	262-3	454	3.18
3h	OCH_3	OCH_3	H	65	198-9	480	4.06
3i	$N(CH_3)_2$	$N(CH_3)_2$	CH_3	74	188-9	431	2.73
3j	NH_2	NH_2	CH_3	70	254-5	452	2.23
3k			CH_3	64	175-6	432	2.59
3l			CH_3	91	188-9	451	2.79
3m	$N(CH_3)_2$	C_6H_5	CH_3	73	180-1	454	2.70
3n	$N(CH_3)_2$	Cl	CH_3	71	165-6	476	2.97
3o	NHC_6H_5	NHC_6H_5	CH_3	68	239-40	454	2.61
3p	OCH_3	OCH_3	CH_3	82	189-90	480	3.00

a) All the reactions were carried out under the same conditions as those for the preparation of 3a.

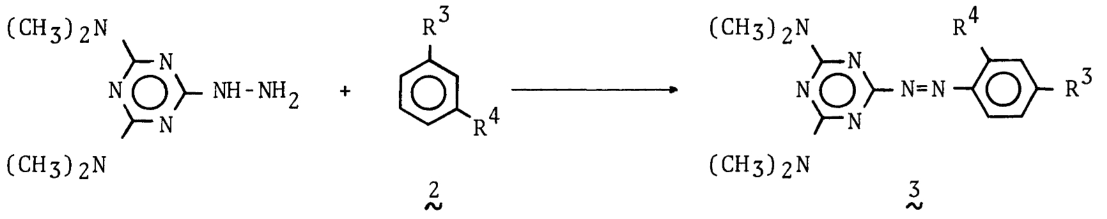
b) All the products were identified by elemental analyses and spectroscopic data (IR, NMR and MS).

c) Isolated yields.

d) In ethanol.

The typical procedure is described for **3a**: 2-hydrazino-4,6-bis(dimethylamino)-1,3,5-triazine (10 mmol) and N,N-dimethylaniline (10 mmol) were dissolved in a buffer solution(200 ml) of pH 4.4 prepared from 2N aqueous solution of acetic acid and sodium acetate. To this solution potassium hexacyanoferrate(III) (40 mmol) was added in portion wise at room temperature. After stirring for 3 h, the reaction mixture was made weakly basic with aqueous sodium carbonate and extracted with chloroform. The extracted organic layer was washed with water, dried over sodium sulfate and evaporated to dryness. The residue was recrystallized from 2-methoxyethanol to give **3a** in a yield of 56%. In this manner, the azo compounds **3b**-**3p** were obtained. The results are summarized in Table 1. The reactions proceeded smoothly and the yields of **3** were quite good. Therefore, the method seems to be applicable to a wide variety of hydrazino-1,3,5-triazines. The reaction using ammonium peroxydisulfate, lead tetraacetate, lead peroxide, ferric(III) chloride or hydrogen peroxide containing Fe(II) ion as the oxidizing agent

Table 2. Oxidative coupling of 2-hydrazino-4,6-bis(dimethylamino)-1,3,5-triazine with N,N-disubstituted anilines[a)]



Product[b)] **3**	R^3	R^4	Yield[c)] (%)	Mp(°C)	λ_{max} (nm)[d)]	ε_{max} ($\times 10^{-4}$)
3q	$N{<}^{C_2H_5}_{C_2H_4OH}$	H	48	184.5-5	439	2.58
3r	$N(C_2H_4OH)_2$	H	54	233-4	437	2.54
3s	$N(C_2H_4OH)_2$	CH_3	80	205-6	438	2.46
3t	$N{<}^{C_2H_4OH}_{C_2H_4CN}$	H	44	158-9	424	2.57
3u	$N{<}^{C_2H_4OH}_{C_2H_4CN}$	CH_3	51	200-2	421	2.45
3v	$N(C_2H_4OH)_2$	$NHCOCH_3$	86	246-6.5	468	3.17

a) All the reactions were carried out under the same conditions as those for the preparation of **3a**.

b) All the products were identified by elemental analyses and spectroscopic data(IR, NMR and MS).

c) Isolated yields.

d) In ethanol.

gave no or little **3**.

To know the adaptability of this method to other coupling components, the reactions of 2-hydrazino-4,6-bis(dimethylamino)-1,3,5-triazine with several kinds of N,N-disubstituted anilines were carried out under the conditions described above. The results are summarized in Table 2. For the coupling components **2** showed in Table 2, the reactions took place readily to give **3** in good yields. However, the reaction of 2-hydrazino-4,6-bis(dimethylamino)-1,3,5-triazine with N,N-diethyl- or N-ethyl-N-(2-cyanoethyl)-anilines gave no coupling products.

In conclusion, we succeeded in the oxidative coupling of **1** with **2** to give **3** by the use of potassium hexacyanoferrate(III) in aqueous acetic acid solution at pH 4.4. Further applications of this method to other heterocyclic systems are in progress.

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(Received September 24, 1981)