Dyes and Pigments **8** (1987) 449–458

Synthesis of Dyes from 1-Amino-2,4-dichloroanthraquinone

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(Received 5 January, 1987; accepted 4 March 1987)

SUMMARY

A method for the synthesis of 1-amino-2,4-dichloroanthraquinone of very high purity is described, involving chlorination with gaseous chlorine of 1-aminoanthraquinone in boiling aliphatic organic solvents.

The 1-amino-2,4-dichloroanthraquinone thus obtained was used in the synthesis of blue acid dyestuffs by condensation with various arylamines, followed by sulfonation with oleum.

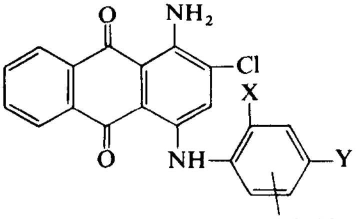
The resulting dyes had similar spectrophotometric and application properties to those of the analogous derivatives of 1-amino-2,4-dibromoanthraquinone.

1 INTRODUCTION

In the acid dyes for the colouration of wool and polyamide fibres, in blue and green shades, anthraquinone derivatives are of major importance. The dyes are mainly derivatives of 1,4-diaminoanthraquinone in which one (mainly blue dyes) or two (green or blue dyes) amino groups are substituted by phenyl groups. One of the intermediates widely used for the synthesis of anthraquinone blue dyes is 1-amino-2,4-dibromoanthraquinone. The rapid growth in the use of bromine for the production of pesticides has resulted in an increase in the cost of bromine. This has caused an interest in the production of dyes from 1-amino-2,4-dichloroanthraquinone **I** as well as in new methods for the synthesis of this compound.[1–6]

Dyes and Pigments 0143-7208/87/$03·50

We report here the results of investigations into the synthesis of 1-amino-2,4-dichloroanthraquinone of high purity and its use in the formation of blue dyes represented by the general formula **II**, where X = H, CH_3, OCH_3; Y = H, Cl, CH_3, OCH_3, OC_2H_5.



II

A study was also made on the comparative effect of introduction of the chlorine atoms instead of the bromine atom on the reactivity of the relevant intermediate compounds and on the spectroscopic properties and applicability of the dyes **II**.

2 RESULTS AND DISCUSSION

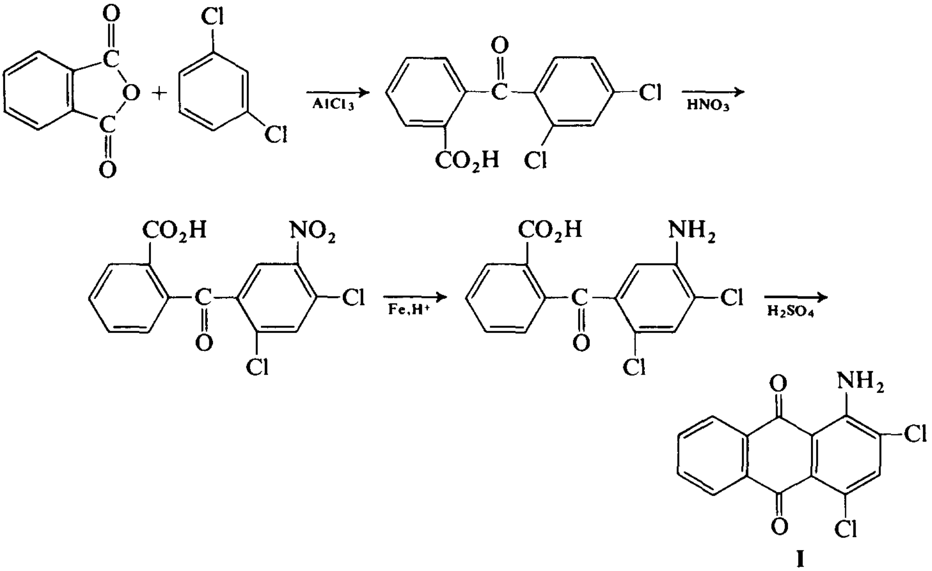
2.1 Synthesis of 1-amino-2,4-dichloroanthraquinone (I)

The literature describes some methods for the synthesis of 1-amino-2,4-dichloroanthraquinone. Thus, Gubelmann *et al.*[7] describe a synthesis as outlined in Scheme 1. This method seems to be rather expensive because of the numerous stages and large quantities of waste materials; the *m*-dichlorobenzene used is expensive and is not a readily available industrial material.

Another method is described by Tkachenko and Shteinberg.[8] It consists in protecting the amino group in 1-aminoanthraquinone with thionyl chloride, separation of the product, followed by its chlorination with sulfuryl chloride in the presence of iodine, and finally hydrolysis with water of the blocking group (Scheme 2).

The same authors[9] have also described another synthesis of **I** by the direct chlorination of 1-aminoanthraquinone with gaseous chlorine in organic aromatic solvents in the presence of sodium acetate or potassium acetate and DMF at 20°C.

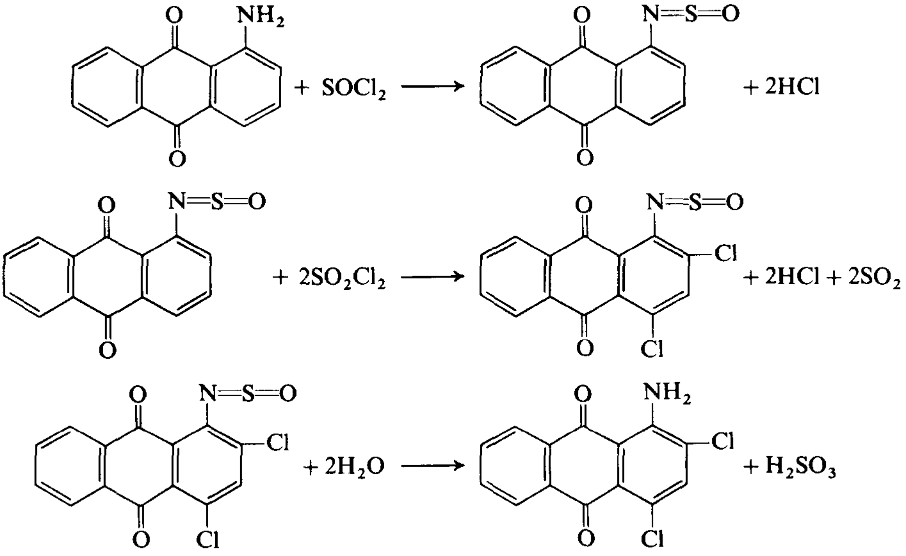
Our initial studies on methods of producing **I** followed the process described by Tkachenko and Shteinberg (Scheme 2). However, in the first stage of the synthesis, it was found that the separation of 1-aminoanthraquinone *N*-sulfoxide from the reaction medium was hindered by the



I

Scheme 1

instability of the product due to its facile hydrolysis in air. This made the second stage of the process, i.e. chlorination with sulfuryl chloride, difficult. We found it advantageous to distill excess of thionyl chloride from the reaction medium and to chlorinate the residual 1-aminoanthraquinone *N*-sulfoxide with a stoichiometric quantity of sulfuryl chloride. This procedure made it possible to carry out the reaction in an anhydrous medium. We also



Scheme 2

found that a 10% excess of thionyl chloride was sufficient for blocking the 1-aminoanthraquinone instead of the previously recommended excess of 4 moles. Under these conditions, it was found possible to obtain **I** in high purity.

The above method of producing 1-aminoanthraquinone *N*-sulfoxide made it possible for chlorination to be effected with gaseous chlorine. The best results were achieved by carrying out the reaction in tetrachloroethylene at temperatures of 50–80°C using I_2, $FeCl_3$, $SbCl_5$ or other compounds as catalysts. In this way **I** was obtained in high purity and yield.

On the basis of the above experiments, chlorination of 1-aminoanthraquinone with gaseous chlorine in tetrachloroethylene was carried out. In this case it was found out that reaction proceeded well at the boiling temperature of the solvent. At lower temperature the separation of 1-aminoanthraquinone hydrochloride interfered with the reaction. Use of refluxing temperatures enabled the evolved hydrogen chloride to be easily eliminated from the reaction medium, and this chlorination process yielded high purity **I** in practically quantitative yield (above 98%).

2.2 Synthesis of dyes

Aniline (**D-1**) and its derivatives such as *p*-toluidine (**D-2**), *o*-toluidine (**D-3**), 2,4-dimethylaniline (**D-4**), *p*-anisidine (**D-5**), *o*-anisidine (**D-6**), *p*-phenetidine (**D-7**) and *p*-chloroaniline (**D-8**), were used for condensation

TABLE 1

Some Reaction Parameters, Melting Points and R_f (TLC) of Products from Condensation of **I** (**D1**–**D8**) and 1-Amino-2,4-dibromo-anthraquinone (**D9**–**D10**) with Arylamines

Condensing amine	*Dye*	*Temperature of reaction (°C)*	*Time of reaction (h)*	*Yield (%)*	*Melting point of dye (°C)*	*TLC R_f*[a]
Aniline	**D-1**	180	25	79·3	231–233·5	0·79
p-Toluidine	**D-2**	190	5	79·8	226–228	0·76
o-Toluidine	**D-3**	190–192	42	68·7	181–182·5	0·76
2,4-Dimethylaniline	**D-4**	205–210	16	72·5	212–214	0·76
p-Anisidine	**D-5**	190–192	5	77·6	235–236·5	0·66
o-Anisidine	**D-6**	200	16	70·8	208–210	0·69
p-Phenetidine	**D-7**	210	4	78·7	203–204	0·71
p-Chloroaniline	**D-8**	205–210	18	80·8	265–266·5	0·81
p-Toluidine	**D-9**[b]	190	5	79·9	237–239	0·79
o-Toluidine	**D-10**	190–192	45	64·8	192–194	0·79

[a] Chromatoplate Silufol UV_{254}; eluent, toluene/ethyl acetate (10:1, v/v).

[b] Ref. 10.

with **I**. The reaction was carried out in the same way as described[10] for the condensation of 1-amino-2,4-dibromoanthraquinone with *p*-toluidine. The end point of the condensation was determined by chromatographic (TLC) and spectrophotometric methods.

The results of the syntheses are given in Table 1, which also gives for comparison data for similar condensations of 1-amino-2,4-dibromoanthraquinone with *p*-toluidine (**D-9**) and *o*-toluidine (**D-10**).

The course of the reaction between **I** and *p*-toluidine was studied. The formation during the condensation of small quantities of a blue dye having very similar λ_{max} to the principal product excluded the use of spectroscopic methods in directly determining the amount of the main blue dye. However, the quantity of reacted **I** ($\lambda_{max} = 475$ nm) was readily determined by spectroscopic methods. The results are shown in Fig. 1.

This indicates that the condensation of **I** with *p*-toluidine is a pseudo-first-order reaction. The decisive stage is the formation of the transition state and not the elimination of the chloride ion. Thus no significant difference in the reaction times of arylamines can be observed between **I** and 1-amino-2,4-dibromoanthraquinone. On the other hand there are large differences of reaction times for the condensation of **I** with different arylamines. This is due to differences in the nucleophilic character of the amines and also to steric effects in the case of *ortho*-substituted anilines.

For the sulfonation reaction, the above dyes directly separated after the condensation were used without further purification. The sulfonation

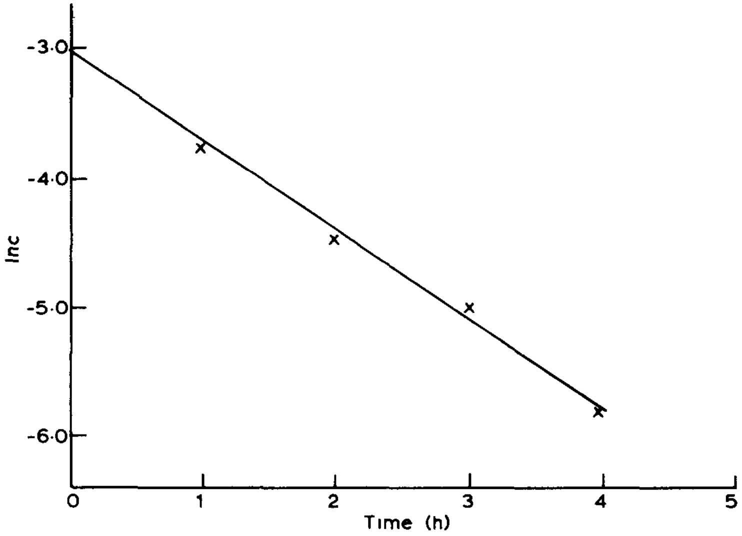


Fig. 1. The change of concentration of 1-amino-2,4-dichloroanthraquinone with time in the reaction with *p*-toluidine.

reaction was carried out in similar way to the sulfonation of the blue product obtained by condensation of 1-amino-2,4-dibromoanthraquinone with *p*-toluidine (C.I. 62100). The separated dyes were purified by crystallization of their sodium salts from water. Results are shown in Table 2.

The dyes **D-2, D-5, D-7, D-8** gave homogeneous products. The other dyes contained small quantities of a second isomer, in **D-1** to an extent of approx. 5% and in the remaining dyes minor traces.

2.3 Spectroscopic analysis

Electronic spectra of the dyes obtained by condensation of **I** with aromatic amines (**D-1–D-8**) and their sulfonated derivatives (**DS-1–DS-8**) were obtained in the Vis range using a Specord 71 (Zeiss Jena). For the unsulfonated dyes, solutions in cyclohexane and in pyridine were used, and for the sulfonate dyes 50% aq. pyridine. The results are given in Table 3.

The absorption curves of all the dyes showed two absorption maxima and were thus similar to the absorption spectra of 1,4-diaminoanthraquinone. Shifts in absorption maxima are in accord with the polar and steric effects of the substituent groups present in the phenyl rings, *ortho*-substituents for example resulting in a hypsochromic shift.

Comparing **DS-2**, containing the 2-chloro substituent, with the analogous 2-bromo derivative **DS-9**, a slight bathochromic shift of 3–4 nm is observed as well as a slight hypsochromic effect. This results in the dyeings on

TABLE 2
Some Parameters of Reaction of Sulfonation and R_f (TLC) of Acid Dyes (**DS1–DS10**) Obtained by Sulfonation of **D1–D10**

Starting product dye no.	*Concentration of oleum (%)*	*Temperature of sulfonation (°C)*	*Time of sulfonation (h)*	*Yield (%)*	*TLC R_f*[a]
D-1	5	25	3	94	0·51
D-2	5	20	3	93	0·74
D-3	5	20	3	91	0·65
D-4	5	15	3	96	0·71
D-5	2	25	2·5	95	0·53
D-6	2	25	2·5	91	0·63
D-7	2	25	2·5	54	0·58
D-8	5	40	5	96	0·73
D-9[b]	5	20	3	95	0·80
D-10	5	20	3	92	0·74

[a] Chromatoplate Silufol UV_{254}; eluent, water/acetic acid:ethyl acetate (3:4:16, by vol.).
[b] Ref. 10.

TABLE 3

Absorption Maxima of the Dyes Derived from 1-Amino-2,4-dichloroanthraquinone (**D1–D8**) and 1-Amino-2,4-dibromoanthraquinone (**D9–D10**)

Condensing amine	*Dye no.*	*Pyridine*		*Cyclohexane*		*Acid dye no.*	*Pyridine/water, 50:50 v/v*	
		λ_{max} (*nm*)	ε (*dcm*^{3} *mol*$^{-1}$ *cm*$^{-1}$)	λ_{max} (*nm*)	ε (*dcm*^{3} *mol*$^{-1}$ *cm*$^{-1}$)		λ_{max} (*nm*)	ε (*dcm*^{3} *mol*$^{-1}$ *cm*$^{-1}$)
Aniline	**D-1**	592	14 700	575	13 800	**DS-1**	592	15 900
		628	14 800	614	13 800		631	15 500
p-Toluidine	**D-2**	596	14 900	579	15 000	**DS-2**	601	16 500
		632	15 300	616	15 100		639	16 900
o-Toluidine	**D-3**	594	14 800	573	14 900	**DS-3**	598	15 700
		628	15 100	613	15 100		633	16 000
2,4-Dimethyl aniline	**D-4**	594	14 700	575	14 300	**DS-4**	592	15 500
		628	15 300	614	14 900		630	16 700
p-Anisidine	**D-5**	598	14 600	578	13 500	**DS-5**	597	15 200
		630	15 100	615	13 900		631	16 200
o-Anisidine	**D-6**	594	13 800	578	13 900	**DS-6**	598	15 000
		626	14 300	615	14 500		626	15 800
p-Phenetidine	**D-7**	599	14 700	580	14 900	**DS-7**	598	14 600
		631	15 400	615	15 300		631	16 700
p-Chloroaniline	**D-8**	592	14 800	571	13 200	**DS-8**	591	15 800
		628	14 800	611	13 400		632	15 300
p-Toluidine	**D-9**	604	14 900	583	14 200	**DS-9**	604	16 200
		636	15 200	620	14 400		643	16 300
o-Toluidine	**D-10**	598	14 400	581	14 800	**DS-10**	602	16 500
		630	14 700	617	15 100		635	16 800

TABLE 4
Technical Properties of the Acid Dyes Derived from 1-Amino-2,4-dichloroanthraquinone (**DS1–DS8**) and 1-Amino-2,4-dibromoanthraquinone (**DS9–D10**)

Dye no.	*Dyed fabric*	*Water*[a]			*Washing*[a]			*Perspiration*[a]						*Rubbing*		*Lightfastness*	
								Alkaline			*Acid*			*Dry*	*Wet*	*1/3*	*1/1*
		1	2	3	*1*	2	3	*1*	2	3	*1*	2	3				
DS-1	Nylon	4–5	2–3	3	4–5	4–5	4–5	4–5	3	3	4–5	2	2–3	5	4–5	6	6–7
	Wool	4–5	4	4–5	4–5	4–5	4–5	4–5	2–3	4	4–5	3–4	4	4–5	4	5	5–6
DS-2	Nylon	4–5	2–3	3–4	4–5	4	4	4–5	2–3	2–3	4–5	2–3	3–4	5	4–5	6–7	7
	Wool	4–5	3–4	4–5	4–5	3–4	4	4–5	2–3	3–4	4–5	3	4	5	4–5	5	5–6
DS-3	Nylon	4–5	2–3	3–4	4–5	4	4	4–5	2–3	3	4–5	2–3	3–4	5	4–5	6	7
	Wool	5	3–4	4–5	4–5	4	4	4–5	3	4–5	5	3	3–4	4–5	4	5	5–6
DS-4	Nylon	4–5	3	3–4	4–5	4–5	4–5	4–5	3	3	4–5	3–4	4	5	4–5	6–7	7
	Wool	4–5	3–4	4–5	4–5	4	4–5	4–5	3	4	4–5	3–4	4	4–5	4	5	5–6
DS-5	Nylon	4–5	2–3	3	4–5	4	4–5	4–5	2–3	3	4–5	2–3	3	5	4–5	6–7	7
	Wool	4–5	4	4–5	4–5	4–5	4–5	4–5	3–4	3	4–5	3–4	4	4–5	4	5	5–6
DS-6	Nylon	4–5	2	3	4–5	4	4	4–5	2	2–3	4–5	2–3	3	5	4–5	6–7	7
	Wool	4	4	4	4	4–5	4	4	3	3	4	3–4	3–4	4–5	4	5	5–6
DS-7	Nylon	4–5	2–3	3	4–5	4–5	4–5	4–5	2–3	2–3	4–5	2–3	3–4	5	4–5	6–7	7
	Wool	4–5	4	4–5	4–5	4	4	4–5	3	3–4	4–5	3–4	4	4–5	4	5	5–6
DS-8	Nylon	4–5	3	4	4–5	4	4	4–5	3	3–4	4–5	3	4	5	4–5	6	7
	Wool	4–5	3–4	4–5	4–5	4	4–5	4–5	3	4	4–5	3–4	4	4–5	4	5	5–6
DS-9	Nylon	4–5	2–3	3–4	4–5	4–5	4	4–5	2–3	3	4–5	2–3	3–4	5	4–5	6–7	7
	Wool	5	3–4	4–5	4–5	3–4	4	4–5	2–3	3–4	5	3	4–5	5	4–5	5	5–6
DS-10	Nylon	4–5	2–3	3–4	4–5	4–5	4–5	4–5	2–3	3	4–5	3	4	4–5	4–5	6–7	7
	Wool	5	3–4	4–5	4–5	4	4	4–5	3	3–4	5	3	4	5	4–5	5	5–6

All the fastness tests were carried out according to Ref. 11.

[a] 1, Change of shade of dyed fabric; 2, 3, staining of adjacent material. When the dyed fabric is nylon the adjacent material is nylon (2) or wool (3). When the dyed fabric is wool the adjacent material is wool (2) or cotton (3).

polyamide fibres of **DS-2** dye being brighter in hue. In general however, replacement of the bromine atom in the 2-position by chlorine has no significant effect on the application and spectrophotometric properties of the dyestuffs and fastness properties are the same (see Table 4). 1-Amino-2,4-dichloroanthraquinone (**I**), a facile synthesis of which is reported in this present work, is thus a useful alternative to 1-amino-2,4-dibromoanthraquinone in the synthesis of blue acid dyes.

3 EXPERIMENTAL

3.1 Preparation of 1-amino-2,4-dichloroanthraquinone (I)

Method 1

1-Aminoanthraquinone (11·2 g, 0·05 mol) in 300 cm^3 of anhydrous tetrachloroethylene and thionyl chloride (6·5 g) were warmed to 70°C and maintained at this temperature for 2 h. After cooling the reaction mixture to 50°C and addition of iodine (0·1 g), the mixture was chlorinated with gaseous chlorine at 50–80°C. After 5 h chlorination was complete, as determined by TLC on Silufol UV_{254} plates using as eluent either ethyl acetate/toluene (1:2, v/v) ($R_f = 0{\cdot}88$ for 1-amino-2,4-dichloroanthraquinone, $R_f = 0{\cdot}69$ for 1-aminoanthraquinone) or chlorobenzene ($R_f = 0{\cdot}27$ for 1-amino-2,4-dichloroanthraquinone, $R_f = 0{\cdot}10$ for 1-aminoanthraquinone).

After removing tetrachloroethylene in steam, the reaction product was filtered and dried at 80°C. Yield 14·3 g, m.p. 207–208°C.

$C_{14}H_7NO_2Cl_2$ requires: Cl, 24·3; N, 5·0%.
Found: Cl, 24·2; N, 5·1%.

Method 2

1-Aminoanthraquinone (11·2 g; 0·05 mol) and iron (0·1 g) powder were mixed with 300 cm^3 of anhydrous tetrachloroethylene and the mixture warmed to 80°C. Gaseous chlorine was passed very slowly through the mixture, during which process the temperature rose to 110–115°C. After 4 h TLC (as above) showed all the 1-aminoanthraquinone to have reacted. After removing tetrachloroethylene with steam and drying the residue at 80°C, 14·5 g of 1-amino-2,4-dichloroanthraquinone, m.p. 207–208·5°C, was obtained.

Found: Cl, 24·5; N, 5·0%

3.2 Condensation of 1-amino-2,4-dichloroanthraquinone with *p*-toluidine (D-2)

A mixture of 4·5 g (0·055 mol) of anhydrous sodium acetate and 100 g of *p*-toluidine was heated to 140°C. After cooling the mixture to 120°C, 14·6 g

(0·055 mol) of 1-amino-2,4-dichloroanthraquinone were added and the mixture heated at 190°C for 5 h until all the 1-amino-2,4-dichloroanthraquinone had reacted. After cooling the reaction mixture to 70°C, 100 cm^3 of methanol was added and the liquor left to stand overnight. The product was filtered, washed three times with 100 cm^3 of methanol, then with water acidified with hydrochloric acid to pH 4 and then finally with water. After drying at 80°C, 14·5 g of crude product was obtained, m.p. 223–226°C. Yield 79·8%. This was recrystallized from DMF to give the pure dye, m.p. 226–228°C.

The synthesis of the other dyes (**D1**, **D3–D10**) was carried out in a similar way.

3.3 Example of sulfonation dye DS-2

A mixture of 7·25 g (0·02 mol) of dye **D-2** and 50 g of 5% oleum was stirred at 20°C for 3 h until sulfonation was complete, viz., a test sample was totally soluble in hot water. The mixture was poured into 200 g of ice-water and the dye was filtered and washed with cold water until acid-free to Congo Red paper. It was diluted with water, neutralized to pH 7 with 30% sodium hydroxide, diluted to 1300 cm^3 with water at 75–80°C and finally salted out by addition of 65 g of sodium chloride. After cooling to room temperature the dye was filtered and dried at 80°C.

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