

The inhibitive effect of some new 4-aryldiazono-2-pyrazolin-5-one derivatives on the corrosion of aluminium in hydrochloric acid solution

T H Rakha*, F I M Taha & I I Zaglol

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

The inhibitive action of new 4-aryldiazono-2-pyrazolin-5-one compounds on the dissolution of aluminium in 2M HCl has been investigated by weight loss, thermometric, hydrogen evolution and galvanostatic polarisation techniques. All the methods gave similar results. An increase in the concentration of compounds increases the inhibition efficiency leading to a decrease in the corrosion rate. The activation energy of the dissolution reaction increases as the inhibitor efficiency is increased. The values of free energy of adsorption ΔG_{ads}^0 have been calculated and discussed. These compounds act as general type inhibitor and adsorb on both anodic and cathodic sites. Electrocapillary curves support the tendency of inhibitors to adsorb on metallic surfaces.

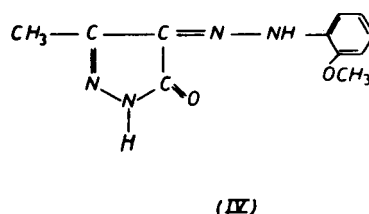
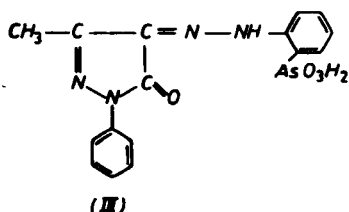
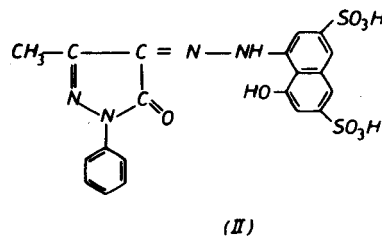
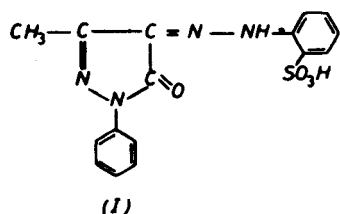
The use of some organic corrosion inhibitors in pickling baths is very beneficial, as corrosion represents a tremendous waste of natural resources. The inhibitory effects of hydrazones, hydrazides, oximes, carbonyl, β -diketo compounds and azopyrazoles have been extensively studied¹⁻⁸. The present work is undertaken to investigate the role played by some new 4-aryldiazonopyrazolone derivatives in retarding the dissolution of aluminium in 2M HCl, employing weight loss, thermometric, hydrogen evolution and galvanostatic polarisation methods.

Experimental Procedure

4-Aryldiazono-2-pyrazolin-5-one compounds were synthesized by coupling 3-methyl-1-phenyl-

2-pyrazolin-5-one or 3-methyl-2-pyrazolin-5-one with the diazotized sulphanilic, 3,6-disulphonic acid-8-hydroxy-1-naphthylamine, *o*-arsanilic acid or *o*-anisidine^{9,10}. The compounds synthesized and used in the present work are 3-methyl-1-phenyl-4-[*o*-(sulphonic acid) phenylhydrazono]-2-pyrazolin-5-one (I), 3-methyl-1-phenyl-4-[3,6-(disulphonic acid)-8-(hydroxy)-naphthylhydrazono]-2-pyrazolin-5-one (II), 3-methyl-1-phenyl-4-[*o*-(arsonic acid)-phenylhydrazono]-2-pyrazolin-5-one (III) and 3-methyl-4-(*o*-anisylhydrazono)-2-pyrazolin-5-one (IV). The purity of the compounds was checked by thin layer chromatography and their structures were identified by IR, NMR and elemental analyses⁹.

All other chemicals used were of AR grade.



*Author to whom correspondence should be addressed.

The composition of aluminium specimens used was: Al=99.535, Si=0.15, Fe=0.19, Mn=0.005, Mg=0.1 and Cu=0.02%. Aluminium specimens of size $10 \times 100 \times 2$ mm were used in thermometric method while specimens of size $20 \times 20 \times 2$ mm were used for weight loss and hydrogen evolution measurements. A cylindrical rod with a surface area of 0.72 cm^2 was used as an electrode in galvanostatic polarisation measurements¹¹. These specimens were abraded mechanically with different grades of emery paper, grinded with 4/0 polishing paper, degreased in an alkaline carbonate-phosphate mixture and cleaned as usual⁵. The electrocapillary measurements were made by using Metrhom polarecord E506 connected to E505 stand. A three electrode cell with SCE as reference and platinum wire as auxiliary electrode was employed through the measurements. All experiments were carried out at $25 \pm 1^\circ\text{C}$. The extent of corrosion inhibition by a certain concentration of a particular inhibitor is evaluated as follows:

From weight loss measurements

$$\% \text{ Inhibition} = \frac{W_{\text{free}} - W_{\text{inh}}}{W_{\text{free}}} 100 \quad \dots (1)$$

where W_{free} and W_{inh} are the losses in weight of the specimens in absence and in the presence of the inhibitor.

From thermometric measurements

$$\% \text{ Reduction in } RN = \frac{(RN)_{\text{free}} - (RN)_{\text{inh}}}{(RN)_{\text{free}}} 100 \quad \dots (2)$$

where the reaction number (RN) is defined as:

$$RN = \frac{T_m - T_i}{t} \text{ } ^\circ\text{C min}^{-1}$$

T_i = initial temperature, T_m = maximum temperature and t = the time in minutes from the start of the experiment to the attainment of maximum temperature.

The degree of surface coverage θ is defined by

$$\theta = 1 - \frac{(RN)_{\text{inh}}}{(RN)_{\text{free}}} \quad \dots (3)$$

From hydrogen evolution measurements

The percentage reduction in reaction rate (RR) is defined as:

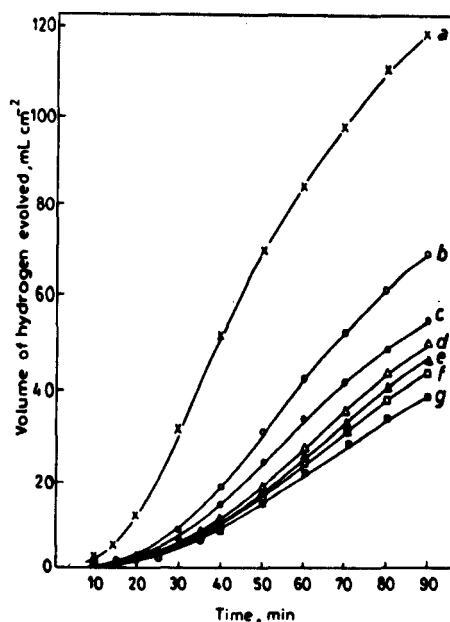


Fig. 1—Volume of hydrogen evolved-time curves in absence and presence of varying concentrations of compound IV in 2M HCl. (a) Free acid, (b) $1 \times 10^{-6}M$, (c) $5 \times 10^{-6}M$, (d) $1 \times 10^{-5}M$, (e) $5 \times 10^{-5}M$, (f) $1 \times 10^{-4}M$ and (g) $5 \times 10^{-4}M$.

$$\% \text{ Reduction in } RR = \frac{R_{\text{free}} - R_{\text{inh}}}{R_{\text{free}}} 100 \quad \dots (4)$$

where R_{free} and R_{inh} are the rates of aluminium dissolution in absence and in the presence of the inhibitor.

From galvanostatic polarisation measurements

$$\% \text{ Inhibition} = \frac{I_{\text{free}} - I_{\text{inh}}}{I_{\text{free}}} 100 \quad \dots (5)$$

where I_{free} and I_{inh} are the corrosion currents in absence and in the presence of the inhibitor.

Results and Discussion

Volume changes in evolved hydrogen from aluminium dissolution in 2M HCl was followed in absence and in the presence of 4-arylhydrazonopyrazolone derivatives. Fig. 1 shows the volume of hydrogen evolved as a function of time for different concentrations of compound IV. Similar data were obtained for the other compounds. The first part of the curve showing a slow RR is due to the dissolution of the oxide film originally present on the metal surface. When the oxide film is completely dissolved in acid, a sharp rise in RR occurs and the curve becomes linear with time. Curves for the systems containing the inhibitor fall below that for the free acid and their displacement increases with increase in concentration. The slope

Table 1—Effect of inhibitor concentration on the percentage reduction in reaction rate, reaction number and inhibition in acid solutions

Inhibitor concentration mol L ⁻¹	% Reduction in <i>RR</i>		% Reduction in <i>RN</i>				% Inhibition													
							Weight loss				Anodic polarisation				Cathodic polarisation					
	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
1 × 10 ⁻⁶	10.0	22.7	28.2	49.8	9.4	11.6	16.2	25.0	4.7	8.4	10.7	22.4	23.7	29.2	31.4	39.6	29.2	39.7	43.4	52.6
5 × 10 ⁻⁶	18.3	34.4	35.9	59.6	17.7	26.6	28.1	32.4	8.7	10.3	20.5	33.9	28.6	36.9	39.0	44.9	35.2	49.9	52.7	60.8
1 × 10 ⁻⁵	28.1	38.1	40.7	67.5	25.2	34.2	36.3	40.7	11.5	14.9	23.8	41.2	37.6	51.0	54.1	60.7	44.5	60.2	63.9	71.6
5 × 10 ⁻⁵	36.2	41.9	49.0	69.6	39.8	45.9	47.6	62.5	21.4	24.2	35.3	44.8	50.0	57.4	59.5	72.2	55.6	65.3	67.7	80.9
1 × 10 ⁻⁴	44.1	48.1	50.9	70.9	45.2	53.6	54.6	68.4	26.8	29.0	42.7	53.3	52.3	62.0	63.4	77.2	58.9	69.8	71.1	85.4
5 × 10 ⁻⁴	50.8	51.8	63.8	73.6	51.4	61.5	64.8	73.4	40.0	47.0	56.2	67.1	56.5	67.6	71.2	80.1	61.0	73.1	76.9	87.1

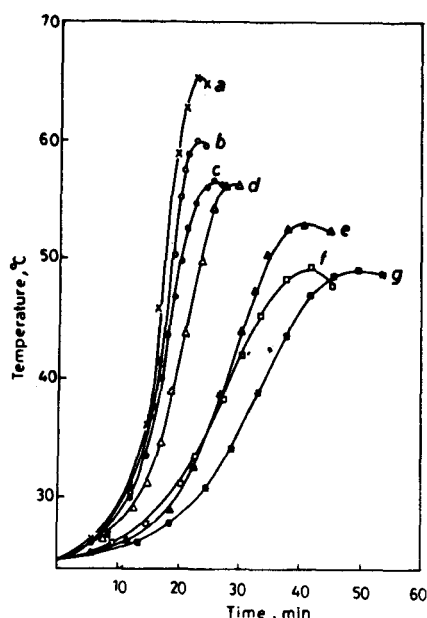


Fig. 2—Temperature-time curves in absence and presence of varying concentrations of compound IV in 2M HCl. (a) Free acid, (b) 1 × 10⁻⁶M, (c) 5 × 10⁻⁶M, (d) 1 × 10⁻⁵M, (e) 5 × 10⁻⁵M, (f) 1 × 10⁻⁴M and (g) 5 × 10⁻⁴M.

of the curves at a specific time gives the reaction rate in mL cm⁻² min⁻¹. The percentage reduction in *RR* after 60 min for all the inhibitors investigated are depicted in Table 1. Temperature-time curves of aluminium in 2M HCl were followed in absence and in the presence of the inhibitors studied. When the concentration of the added inhibitor increases, the thermometric curves are influenced as shown in Fig. 2. These curves are characterized by an initial slow rise in the temperature due to the oxide film originally present on the metal surface^{12,13} followed by a sharp rise and finally a decrease after attaining a maximum value. Strong adsorption is noted for nearly all the compounds used. The percentage reduction in *RN* are listed in Table 1. Moreover, the corrosion of aluminium in 2M HCl solutions containing different amounts of the additive compounds was studied

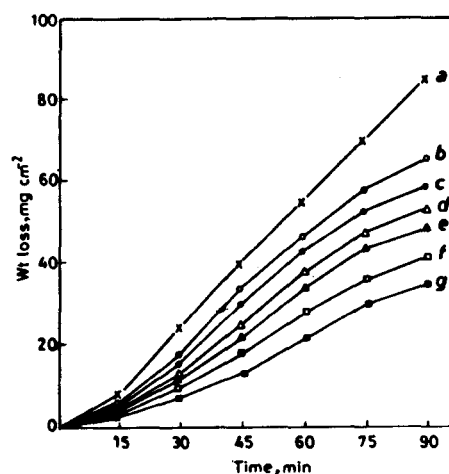


Fig. 3—Weight loss-time curves in absence and presence of varying concentrations of compound IV in 2M HCl. (a) Free acid, (b) 1 × 10⁻⁶M, (c) 5 × 10⁻⁶M, (d) 1 × 10⁻⁵M, (e) 5 × 10⁻⁵M, (f) 1 × 10⁻⁴M and (g) 5 × 10⁻⁴M.

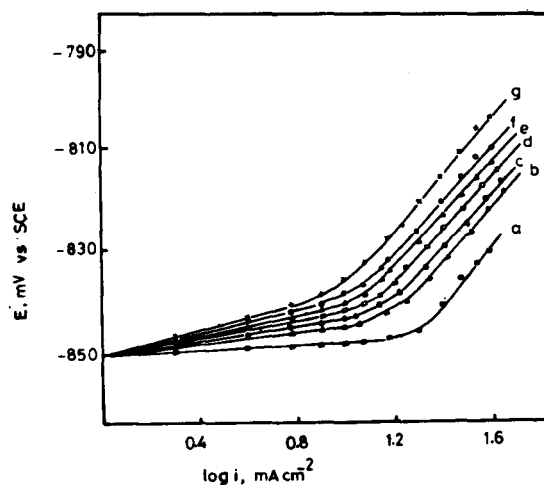


Fig. 4—Effect of concentration of compound II on the current-potential relations of the anodic aluminium dissolution reaction in 2M HCl at 25°C. (a) Free acid, (b) 1 × 10⁻⁶M, (c) 5 × 10⁻⁶M, (d) 1 × 10⁻⁵M, (e) 5 × 10⁻⁵M, (f) 1 × 10⁻⁴M and (g) 5 × 10⁻⁴M.

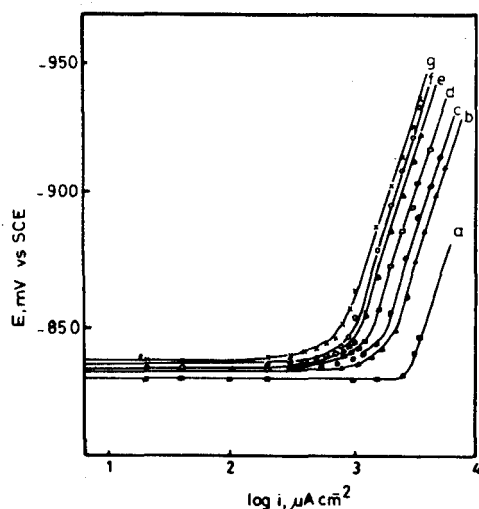


Fig. 5—Effect of the concentration of compound II on the current-potential relations of the cathodic polarisation of aluminium in 2M HCl at 25°C. (a) Free acid, (b) $1 \times 10^{-6}M$, (c) $5 \times 10^{-6}M$, (d) $1 \times 10^{-5}M$, (e) $5 \times 10^{-5}M$, (f) $1 \times 10^{-4}M$ and (g) $5 \times 10^{-4}M$.

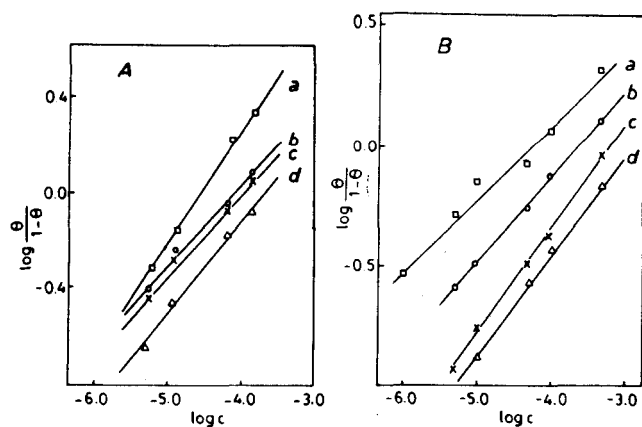


Fig. 6—Dependence of $\log \theta / 1 - \theta$ on logarithm of concentration of inhibitors. (A) Thermometric and (B) Weight loss. (a) IV, (b) III, (c) II and (d) I.

by using the weight loss method. Representative results are shown in Fig. 3 for compound IV. It is apparent that the weight loss of aluminium depends on the type and the concentration of the inhibitor. The percentage inhibition of the compounds after 60 min are included in Table 1.

The results of anodic and cathodic polarisation of aluminium in absence and in the presence of different concentrations of compound II are plotted in Figs 4 and 5. These results show as the inhibitor concentration increases, the Tafel lines are shifted to more positive and negative potentials for anodic and cathodic processes, respectively, relative to the free acid curve. This means that the compounds influence both anodic and cathodic processes. Examination of Tables 1 and 2 leads to the conclusion that the order of increasing the in-

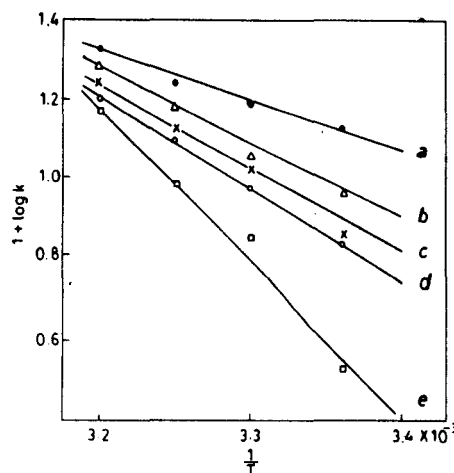


Fig. 7—Log $k - 1/T$ curves for aluminium dissolution in absence and presence of inhibitors at concentration of $10^{-4}M$. (a) Free acid, (b) I, (c) II, (d) III and (e) IV.

hibition efficiency is found to be: $I < II < III < IV$ from the four independent techniques.

The degree of surface coverage θ was calculated from both thermometric (Fig. 6A) and weight loss (Fig. 6B) methods. A correlation between $\log \theta / (1 - \theta)$ and $\log c$ of adsorbate is given by the Langmuir's adsorption isotherm Eq. (6).

$$\log c = \log \frac{\theta}{1 - \theta} - \log A \quad \dots (6)$$

$$\log A = -1.74 - \frac{\Delta G_{\text{ads}}^0}{2.303 RT} \quad \dots (7)$$

The experimental results (Figs 6A, B) are in good agreement with Eq. (6) with a slope deviated from unity. This deviation may be explained on the basis of the interaction of adsorbed species by mutual repulsion or attraction on the aluminium surface¹⁴⁻¹⁶.

The effect of temperature on the rate of dissolution of aluminium in 2M HCl was studied by the hydrogen evolution method in the range 25-45°C. For all arylhydrazonopyrazolone compounds, the logarithm of corrosion rate k is a linear function of $1/T$ (Fig. 7). The activation energy values E (Table 2) increase with increasing the inhibition efficiency of the compounds. Inhibitor IV which gives maximum inhibition efficiency yields the highest activation energy and the opposite is true for compound I. Also, an increase in the concentration of inhibitors increases the activation energy. The values of free energy of adsorption, ΔG_{ads}^0 , were calculated with the help of Eq. (7) at 25°C (Table 2). The results show that compound IV which gives maximum efficiency, exhibits the highest negative ΔG_{ads}^0 indicating that it is strongly adsorbed on the aluminium surface thus acting

Table 2—Inhibition efficiency, the activation energy and the free energy of adsorption of inhibitors at concentration of $10^{-4}M$

Inhibitor	% Reduction in RR	% Reduction in RN	% Inhibition			$E_a, KJ mol^{-1}$	$-\Delta G_{ads}^0, KJ mol^{-1}$	
			Weight loss	Anodic polarisation	Cathodic polarisation		Thermometric	Weight loss
I	44.1	45.2	26.8	52.3	58.9	36.36	32.26	30.26
II	48.1	53.6	29.0	62.0	69.8	41.15	33.09	30.54
III	50.9	54.6	42.7	63.4	71.1	45.93	33.19	32.03
IV	70.9	68.4	53.3	77.2	85.4	74.64	34.65	33.08

as a metal protecting agent. In general, the negative values of ΔG_{ads}^0 indicate the spontaneous adsorption of inhibitors on the metal oxide surface^{16,17}.

Variation in the structure of additive compounds, takes place through arylhydrazone side chain, 2-pyrazolin-5-one moiety being the same. Thus, variation in inhibition efficiency would mostly originate from this part of the molecule. Compound II is more effective than I probably due to its larger molecular size that may facilitate better surface coverage. Compound III is more effective than II despite its smaller molecular size. This is most probably, because it has the less electron withdrawing group namely, *o*-AsO₃H₂. The 1-phenyl group attached to the heterocyclic nitrogen atom in compounds I, II and III reduces the basicity of the nitrogen atom due to the conjugation of its unshared electron pair with the π -orbitals of the aromatic nucleus¹⁸, therefore, the inhibition efficiency of compounds I-III comes before IV. The high electron releasing ability of the *o*-methoxy group brought the compound IV on the top of the series¹⁸. Moreover, the preserved basicity of the heterocyclic nitrogen atom due to the absence of 1-phenyl group facilitates the adsorption of this compound on the aluminium oxide surface.

The extent of adsorption on metallic surfaces was elucidated from electrocapillary curves determined in the presence and absence of inhibitors. Curves for the adsorption of various inhibitors from 2M HCl at a concentration of $10^{-4}M$ (Fig. 8) revealed that the order of decrease in this ability is concordant with the order of decrease in the inhibitor efficiency indicated by weight loss, thermometric, hydrogen evolution and galvanostatic polarisation measurements.

Conclusion

The inhibition of aluminium corrosion in 2M HCl by 4-arylhydrazonopyrazolone derivatives is directly related to the spontaneous and strong ad-

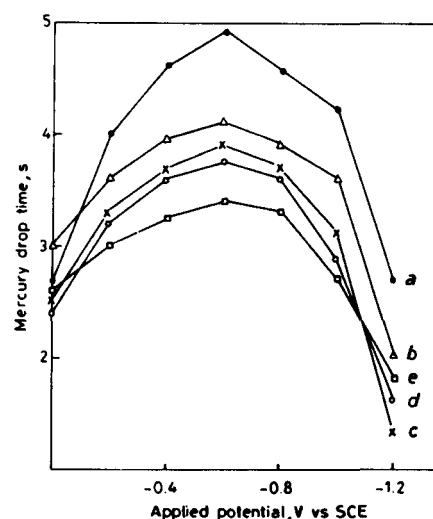


Fig. 8—The relation between the applied potential and mercury drop time in absence and presence of inhibitors in 2M HCl. (a) Free acid, (b) I, (c) II, (d) III and (e) IV.

sorption of these compounds on aluminium surface as elucidated from the E , negative ΔG_{ads}^0 values and the electrocapillary curves. There is a good correlation between the inhibition efficiencies calculated from the four experimental methods as indicated by the percentage reduction in RR, RN and inhibition in 2MHCl solutions.

References

- Hassan S M, Elawady Y A, Ahmed A I & Baghlaf A O, *Corros Sci*, 19 (1979) 951.
- Moussa M N H, Taha F I, Gouda M M A & Singab G M, *Corros Sci*, 16 (1976) 379.
- Ahmed A I, El-Asklany A H & Fouda A S, *J Indian Chem Soc*, 32 (1985) 367.
- Fouda A S, El-Asklany A H, Madkour L H & Ibrahim K M, *Acta Chim Hung*, 124 (1987) 377.
- Fouda A S, Moussa M N H, Taha F I & Elneanea A I, *Corros Sci*, 26 (1986) 719.
- Issa I M, Moussa M N H & Ghandour M A A, *Corros Sci*, 13 (1973) 791.
- Hassan S M, Moussa M N H, Taha F I & Fouda A S, *Corros Sci*, 21 (1981) 439.
- Fouda A S, Abu-El Nader H M, Moussa M N H & Shehatta I S, *Bull Chem Jpn*, 61 (1988) 4411.

- 9 Rakha T H, Stoicescu D & Baiulescu G E, *Anal Lett*, 16 (1983) 601.
- 10 Harhash A H, Amer F A & Metwally M A, *Mansoura Sci Bull*, 4 (1977) 223.
- 11 Mohamed A K, Rakha T H & Moussa M N H, *Bull Soc Chim Fr*, 127 (1990) 375.
- 12 Abu-El-Nader H M, Mostafa M R & Abu-El-Reash G M, *Bull Soc Chim Fr*, 3 (1988) 462.
- 13 Taha F I M, Shallaby A M, Ibrahim K M & Abdel Mak-soud S A, *Bull Soc Chim Fr*, 5 (1989) 591.
- 14 Abdul Azim A A, Shalaby L A & Abbs H, *Corros Sci*, 14 (1974) 21.
- 15 Fouda A S, Mostafa H A, Moussa M N & Darwish Y M, *Bull Soc Chim Fr*, 2 (1987) 261.
- 16 Mohamed A K, Bekheit M M & Fouda A S, *Bull Soc Chim Fr*, 128 (1991) 331.
- 17 Fouda A S & El-Asmy A A, *Monatsh Chem*, 118 (1987) 709.
- 18 Sykes P, *A guidebook to mechanism in organic Chemistry*, 6th ed (Longman Scientific and Technical, London), 1986, 23 & 71.