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Ionization and esterification with diazo - diphenyl methan , of a series of 3-(7-substituted -1-naphthyl) propiotic and 3-(7-substituted -1- naphthyl) acrylic acid.

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Keyword
Esterification, Ionization, Hydrolysis, Substitu effect, Field effect.

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Abstract:

Alkaline hydrolysis rates coefficients for the series of methyl 3-(7-substituted-1-naphthyl) propynoate was calculated in 70%v/v dimethylsulphoxide-water at various temperatures (25,30,40, and 50° C). The pKa values of 3-(7-substituted-1-naphthyl) propynoic acid and (E)-3-(7-substituted-1-naphthyl) propenoic acid calculated in 80%w/w 2-methoxyethanol-water at room temperature (25.0° C). logk2 of esterification rate coefficients for 3-(7-substituted-1-naphthyl) propynioc acid and (E)-3(7-substituted-1-naphthyl) propenioc acid with DDM have been measured at 30.0° C. Reversed substituent dipolar effects were found in the ionization reaction. In the esterification reaction with DDM the result shows similar but reduced substituted effects. Rate retardations was found in the alkaline hydrolysis. It could be result from steric effect or reversal of substituent dipolar effect with a combination of steric effect.

Keywords: esterification, ionization, hydrolysis, Substituent effect, Field effect.

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دراسة تأثير الانتقال القطبي للمجاميع المعوضة في تفاعلات التأين والاسترة للاحماض الكاربوكسيلية 3- (7 – معوض – 1 – ثنائي) حامض البروباليك و3 – (7 – معوض -1 – نفثايل) حامض الأكريليك.

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الخلاصة:

قيست قيم ثابت التأين للأحماض الكاربوكسيلية 3 - (7 – معوض – 1 – ثنائي) حامض البروباليك و 3 – (7 – معوض - 1 – نفثايل) حامض الأكريليك عند درجة 25 ° م في المحلول المائي 2-ميثوكسي ايثانول (80% وزنا) عند درجة حرارة الغرفة 25 ° م . ومعامل سرع التفاعل للتحلل المائي لأسترات الاحماض المقابلة قيست عند درجات حرارية مختلفة) 25 , 30 , 40 , 50 ° م) في المحلول المائي ثنائي الميثايل سلفوكسايد(70%) DMSO حجما.

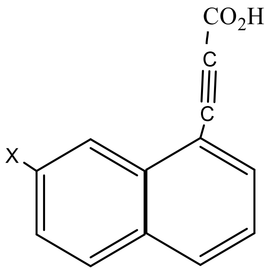
وقيست ايضا معامل سرع تفاعل استره الاحماض الكاربوكسيلية مع DDM عند 30 °م.

أظهرت نتائج تأين الاحماض الكاربوكسيلية التاثير المعاكس للانتقال القطبي للمجاميع المعوضة في هذه الاحماض الكاربوكسيلية . اما في تفاعلات استره الاحماض الكاربوكسيلية كانت النتائج ايضا التأثير المعاكس للمجاميع المعوضة ولكن أضعف من تاثيرها في الاحماض الكاربوكسيلية. وقد وجد في تفاعلات التحلل المائي لاسترات الاحماض المقابلة الاعاقة لسرعة التفاعل، وهذا يمكن ان يفسر سبب التأثير الفراغي والمعاكس للمجموعة المعوضة.

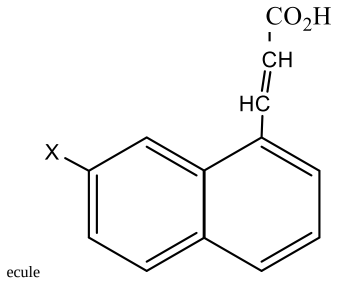
الكلمات المفتاحية: الاسترة، التأين، التحلل المائي، تأثير المجموعة المعوضة، تأثير المجال.

Introduction:

The objective of this study was to determine the reverse transmission of dipolar substituent effects. From previous work on transmission of dipolar substituent effect considered to be the fundamental of the prediction of molecular reactivity **[1-10]**. It is conceivable to explain clearly the polar effects of the transmission via path of direct field of electrostatic **[1,2,6,7,10]**. Studies **[1, 4, 11, 12]** explained the substituent dipolar effects reverse by using the right design circumstances which is currently in the molecular reliable model, such a model (3-substituted propiolic acid) has been suggested 1st time by Roberts and carbon **[13]**. This “J-shaped “molecule is an excellence design and perfect for dipolar substituent transmission effects study as shown in systems below:



(1)



(2)

Two novel systems 3- (7 - substituted -1- naphthyl) propynioc acids and (E)- 3- (7 – substituted -1- naphthyl) propenioc acids has been prepared for the present study. The pka values of the acids and their rates of esterification with DDM (diazodiphenylmethane) has been measured to assess their reactivity.

Results and Discussion:

The values of Pka in table 1 of the acids ,3-(7-substituted-1-naphthyl) propynioc and (E) - 3 -(7-substituted-1-naphthylpropenioc in 80%w/w 2-methoxyethanol-water are shown.

Table 1. The PKa Values of 3-(7-subsituted-1-naphthyl) propynioc acid and (E) – 3 -(7-substituted -1-naphthyl) propenioc acid 80%w/w at 25℃ in the 2-methoxyethanol- water.

Acid	**substituted**	**PKa**[a]	**ΔPKa**[b]
Propiolic	H	4.45 (Lit. [11], 4.42)	0.00
	Br	4.82	-0.37
	Cl	4.84	-0.39
Acrylic	H	6.69 (Lit. [11],6.71)	0.00
	Br	7.02	-0.33
	Cl	6.95	-0.26

a: PKa magnitude are regenerate in ±0.02 unit.

b: ΔPKa = PKa(H) – Pka (substituted).

The pka value of the unsubstitued of the substituted phenyl (4.30 and 6.68) respectively **[15]** more acidic than unsubstitued acid of this series of novel compounds. Thus, there is no solvation steric effect is combined with change from the phenyl to 1-naphthyl group in both system (1) and (2).

For the (7-bromo-, and 7-chloro-) substituents are electron – withdrawing groups, which would be predictable to be more acidic, it is found in the present study acid weakening about 0.3 to 0.4 pka units. Therefore, the transmission of polar substituent effect in this both model systems (1) and (2) are reversed dipolar substituent effects are observed.

Esterification With Diazodiphenylmethane (DDM) :-

The rate coefficients in the following table (2) of 3-(7-substituted-1-naphthyl) propiolic and (E)-3-(7-substituted-1-naphthyl) propenioc acids with diazodiphenylmethane in 2- methoxy ethanol at temperature 30.0 °C are shown. The rate-determining step of the reaction involves proton transfer from an acid to DDM [16].

Table 2._K2 (Rate coefficients) [a] for the esterification of acids with diazodiphenylmethane in 2-methoxyethanol at 30℃.

Acid	substituted	K_2 ($dm^3.mol^{-1}.min^{-1}$)	Log K_2
Propiolic	**H**	**16.5 (Lit. [11], 16.7)**	**1.217**
	Br	**10.2**	**1.009**
	Cl	**10.5**	**1.021**
Acrylic	**H**	**0.733 (Lit. [11],0.729)**	**-0.135**
	Br	**0.648**	**-0.188**
	Cl	**0.660**	**-0.181**

a : The mean of measurements is of at least two determinations, within ±3%.

The transmission of dipolar substituent effect is the same reversal of the 3-(7-substituted-1-naphtyl) propynioc and (E)-3-(7-substituted-1-naphthyl) propenioc acids.

The Δlog 0.208 for 3-(7-bromo-1-naphthyl) propynioc acids in the first model system shows the normal substituent effect was reversed polar effect.

Therefore, in good agreement with a quantitave reversal of the transmission of polar substituent effect [17].

Alkaline Hydrolysis:-

In the following **Table 3** the rate coefficients are shown for the alkaline hydrolysis of the corresponding ester of substituted propynioc acid.

Table 3 the rate coefficients are shown for the alkaline hydrolysis of the corresponding ester of substituted propynioc acid

Substituent	K_2 ($dm^3.mol^{-1}.min^{-1}$)			
	25.0 ℃	**30.0**℃	**40**℃	**50**℃
H	35.1	42.1(Lit. [11],43.8)	84.2	162.8(Lit. [11], 155.3)
Br	15.9	19.2	37.2	74.4
Cl	12.4	14.8	28.3	56.8

a: Rate coefficients are regenerate to within ±3%.

Steric effect can cause retardation of the rate. This retardation can cause reversal substituent effect or both of them (reversal substituents effect and steric effect) [18]

In Table (4) the activation parameters at 30.0° C are shown.

Table 4. Activation of parameters at 30℃, alkaline hydrolysis of the methyl 3 –(7 – substituted -1- naphthyl) propionates 70% (V/V) DMSO – water [a].

Substituent	ΔH ($Kcal.mol^{-1}$)	Δ S ($cal.mol^{-1}.K^{-1}$)
H	11.7	- 21
Br	12.3	- 12
Cl	12.2	- 13

a- Values of ΔS and ΔH are measured within $\mp 302\ cal.mol - 1$ and $\mp 2\ cal.mol^{-1}. K^{-1}$, respectively.

The ΔH and ΔS effect noted in covenant with this explanation. The ΔH values are increased. It was reliable with a reversed dipolar substituents effect of 7- substituted [18]. In the Δ S values no significant changes as would be expected in the steric effect absence.

Experimental: The preparation of (E) -3- (1-naphthyl) propenioc acid and 3-(1-naphthyl) propynioc acid used in this study has been described by Byron L. west [14]. These compounds were synthesized by the following procedure. The 1-hydroxymethyl naphthalene has been oxidized to an aldehydes .

The aldehydes gave propenioc acids by reaction of Perkin. The propynioc acids were synthesized by bromination and dehydrobromination of the propenioc acids.

7- Bromo-1-naphthaldehyde:-

This compound was prepared by adding 7-bromo-1-hydroxymethylnaphthalene (7.9 g, 33.3 mmol) in anhydrous methylene chloride (15ml) in many portion to the pyridinium chlorochromate (10.8 g, 0.1mol) in anhydrous methylene chloride (100 ml), was stirred for 3 hours. Dry diethyl ether was added and the clear liquid from the gum was decanted.

The precipitate product has been washed by (50 ml) of dry diethyl ether where upon it resultant with a black granular. By passing through a silica gel column was purified the crude solution. It was eluted with (15 ml) of dry diethyl ether. The yellowish solution was recrystallized from petroleum (b.p.60-80 °C) to give the aldehyde as colorless needles (6.2 g, 78.5%), m.p.83-84 °C,

Anal.calcd. for $C_{11}H_7OBr$:(C, 56.2; H, 3.0; 0, 6.8; Br, 34.0%)

Found: (C, 56.3; H, 2.9; 0, 6.9; Br, 33.9%).

7- chloro -1- naphthaldehyde :-

This compound was synthesized by the previous method as shown above. It gave the colorless needles (5.8 g, 73.4%), m.p. 93-94°C.Anal. Calcd. For $C_{11}H_7OCl$:

(C, 69.3; H, 3.7; 0, 8.4; Cl, 18.6%)

Found: (C, 69.1; H, 3.72; 0, 8.6; Cl, 18.5)

E-3-(1-naphthyl) propenioc acid:

The compound synthesized by using perkin reaction [14] to give the acid m.p. 207-208 ℃ (lit. [14], 207.5 ℃).

3-(1-Naphthyl) propynioc acid:-

This compound was synthesized by the following sequence. The ethyl (E)-3-(1-Naphthyl) propenoate was prepared from (E)-3-(1-Naphthyl) propenioc acid. The ethyl ester was brominated and the dehydrobromination by alcoholic potassium hydroxide gave 3-(1-Naphthyl) propynioc acid, m.p. 137-139℃ (lit. [14], 138-139℃)

E-3-(7-Bromo-1-naphthyl) propenioc, E-3-(7-chloro-1-naphthyl) propenioc, 3-(7-Bromo-1-naphthyl) propynioc and 3-(7-chloro-1-naphthyl) propynioc .

Acids was prepared with the previous method using the naphthyl aldehydes. The melting points, elemental analysis and the solvents of recrystallization for each acid as in table5. The spectra of infrared (IR) of the ester are shown in table6.

Table 5. Physical constants for the propynioc and propenioc acids.

substituent	m.p ℃	Lit.m.p. ℃	Formula	Found (%)			Requires (%)			Recrystallization solvent
				C	H	other	C	H	other	
3-(7-substitueted-1-naphthyl) propiolic acids.										
H	137-138	138-139^b	$C_{13}H_8O_2$	-	-	-	-	-	-	
Br	162-163	-	$C_{13}H_7BrO_2$	56.6	2.5	29.0(Br)	56.8	2.6	29.1(Br)	Chloroform-ethanol
Cl	154-155	-	$C_{13}H_7ClO_2$	67.8	3.0	15.3(Cl)	67.7	3.1	15.4(Cl)	Chloroform-ethanol
Methyl3-(7-substitueted-1-naphthyl) propiolates										
H	b.p.121 at 0.5mmhg	b.p.120 at 0.5mmhg^b	$C_{14}H_{10}O_2$	-	-	-	-	-	-	
Br	64-65	-	$C_{14}H_9BrO_2$	60.2	3.2	27.3 (Br)	58.2	3.1	27.6(Br)	Light petroleum ether(60-80℃)
Cl	71-72	-	$C_{14}H_9ClO_2$	68.4	3.6	14.5 (Cl)	68.7	3.7	14.5(Cl)	Light petroleum ether(60-80℃)
E-3-(7-substitueted-1-naphthyl) acrylic acids										
H	208	207.5^b	$C_{13}H_{10}O_2$	-	-	-	-	-	-	
Br	236	-	$C_{13}H_9BrO_2$	56.2	3.2	29.6 (Br)	56.3	3.3	28.8(Br)	Acetone-ethanol
Cl	228	-	$C_{13}H_9ClO_2$	66.8	3.7	15.2 (Cl)	67.1	3.9	15.2(Cl)	Acetone-ethanol

a-Ref.14, b-Ref.11.

Table 6. Infra-red (IR) spectroscopy properties of methyl 3 – (7- substituted – 1 –Naphthyl) propiolates[a].

Substituent	Ester carbonyl frequency, V_{max} (cm^{-1})	Triple bond frequency V_{max} (cm^{-1})
H	1725 (1731) [b]	2212
Br	1728	2226
Cl	1729	2224

a: Spectra obtained in nujol mull and measurements reproducible to ∓1cm^{-1}.

b: Shoulder.

Conclusions:

In the present study was found, the transmission of substituent dipolar effect shows best understood to explain the transmission of direct field effects, Ϭ- inductive and π–inductive effects .

For aromatic systems, π-inductive effect is more significant than the Ϭ-inductive effect.

We suggest to synthesized new model system which can show the border line condition of the separation of inductive effect and the direct field effect through the molecular cavity.

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