

Kinetics and mechanism of thermal gas-phase elimination of α -substituted carboxylic acids: role of relative basicity of α -substituents and acidity of incipient proton

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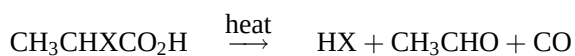
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ABSTRACT: 2-Phenoxypropanoic acid together with five of its aryl derivatives, its phenylthio and its *N*-phenylamino analogues were pyrolyzed at 494–566 K. The reactions were homogeneous, polar and free from catalytic and radical pathways, and obeyed a first-order rate equation. The limits of the Arrhenius $\log A$ (s^{-1}) and E ($kJ\ mol^{-1}$) values obtained for these reactions averaged 11.98 ± 1.71 and 158.1 ± 17.4 , respectively. Analysis of the pyrolysates showed the elimination products to be carbon monoxide, acetaldehyde and the corresponding phenol, thiophenol or aniline compounds. The pyrolysis of 2-phenoxy- and 2-(*N*-phenylamino)-1-propanol was also investigated over the temperature range 638–792 K. The kinetic results and products analysis lend support to a reaction pathway involving a five-membered cyclic polar transition state. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: α -substituted carboxylic acids; thermal gas-phase elimination; pyrolysis; cyclic polar transition state

INTRODUCTION

The overall reaction scheme for the α -substituted carboxylic acids under discussion follows the pathway



where X is either a halogen, a hydroxy or alkoxy group, an aryloxy moiety or its amino or thio analogues. Hydroxy, alkoxy and phenylacetic acids and acids in which the methyl hydrogens have been replaced by alkyl groups were also examined.

An extensive study by Chuchani and co-workers led to the elucidation of the mechanism of the thermal gas-phase elimination of the halo and hydroxy acids and their alkyl esters.^{1–4} The transition state of the reaction was believed to be concerted, polar, five-membered and to involve the acid group proton rather than the aliphatic methyl hydrogen atom (Scheme 1, **I**). Alternatively, the cyclic nature of the transition state was depicted by curved arrows (Scheme 1, **II**). To represent the transition state as an intimate ion pair, the limit dipolar structure (Scheme 1, **III**) was invoked, and on the basis of which participation of the carbonyl moiety in bond formation and bond fission would be considered feasible.

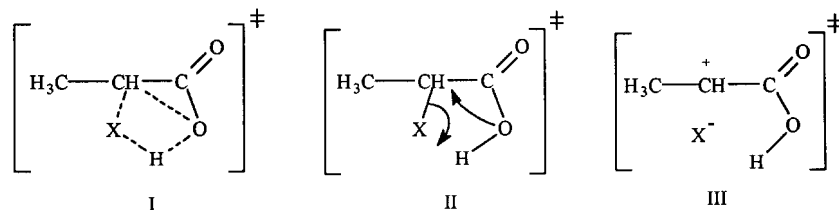
The proposed transition state (Scheme 1) helps to explain the composition of the products of reaction: HX in addition to CH_3CHO and CO obtained from the fragmentation of an α -lactone intermediate (Scheme 2).

The evidence given in support of the proposed mechanism is based on the relative acidity of the incipient hydrogen, the basicity of X and the electronic and steric effects of α -alkyl groups which influence the stability of the carbocation centre of the intimate ion pair. Further, the qualitative correlation of reactivity with structure is consistent. However, the relative rate factors reported for these systems are by comparison rather small (1 – 10^2).

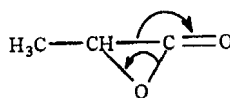
The mechanism of pyrolysis of pyruvic and benzoylformic acids, the methyl esters and related hydroxyketones has been shown to involve both four and five-membered transition states.^{5–7} In this paper, we report on the thermal gas-phase elimination of α -substituted propanoic acid and β -substituted 1-propanol, the substituent in both systems being an aryl moiety. Relative rate factors of 10^2 – 10^7 have been observed, indicative of the major contribution to reactivity by the mesomerically electron-accommodating phenoxy group and its thio and amino analogues.

Recent theoretical calculations from a protracted study by Andres and co-workers^{8–12} have confirmed the experimental results of Chuchani and co-workers, and have provided further insight into the nature of the molecular transition structures along the reaction coordinate which placed the mechanism of these unimolecular thermal gas-phase elimination processes on a firm theoretical and experimental basis. For an accurate

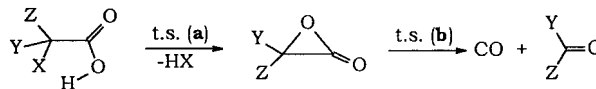
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Scheme 1. Cyclic five-membered transition state and implicit intimate ion pair



Scheme 2



Scheme 3

computation of the kinetic parameters, detailed characterization using *ab initio* analytical gradients at the MP2/6-31G** level of theory, optimization routines and population analysis were found to be necessary. A comparative study of the global PES and stationary points on the basis of molecular geometries and intrinsic reaction coordinates, electronic and transition structures and theoretical rate coefficients calculated in terms of transition-state theory suggested an irreversible two-step reaction pathway which reconciles very well theory with experiment and the rate constants obtained in the two studies. The level of quantum mechanical calculations made it possible to discriminate against a single-step (concerted) mechanism and in favour of a transition structure involving a distorted five-membered ring structure leading to the elimination of HX ahead of cyclization to give an α -lactone intermediate with pre-organization and H-bonding being invoked.

The rate-limiting step was considered to involve the transition structure [Scheme 3, t.s. (a)] in which fragmentation and α -lactone formation are assisted by the oxygen atom of the carbonyl moiety from the carboxyl group. The reactive global PES identified and characterized a second transition structure [t.s. (b)] associated with the decomposition of the α -lactone intermediate to give carbon monoxide and the aldehyde as the other products of reaction. Accordingly, the molecular transition structures along the reaction coordinate follow Scheme 3. This mechanism is consistent with the results of the present study.

RESULTS AND DISCUSSION

For each substrate, first-order rate coefficients were obtained at regular temperature intervals over the range 51 ± 10 K. The results are given in Table 1. Each rate constant is an average of at least three independent measurements in agreement to within $\pm 2\%$. The reactions for which the kinetic data were obtained have been

ascertained to be homogeneous, unimolecular, non-catalytic and non-radical processes.^{1,13} Arrhenius plots of the data were strictly linear over $\geq 95\%$ reaction, with correlation coefficients in the 0.99 ± 0.005 range.¹³⁻¹⁵ An example of these plots is given in Fig. 1. The log A (s^{-1}) and E_a ($kJ\ mol^{-1}$) values and the first-order rate constants of the ten compounds under investigation are given in Table 2. The compounds investigated were 2-phenoxypropanoic acid (1), 2-(*p*-nitrophenoxy)propanoic acid (2), 2-(*p*-chlorophenoxy)propanoic acid (3), 2-(*m*-chlorophenoxy)propanoic acid (4), 2-(*p*-methylphenoxy)propanoic acid (5), 2-(*p*-methoxyphenoxy)propanoic acid (6), 2-(*N*-phenylamino)propanoic acid (7), 2-thiophenoxypropanoic acid (8), 2-(*N*-phenylamino)-1-propanol (9) and 2-phenoxy-1-propanol (10).

The products of pyrolysis were analysed using on-line GC-MS and FT-IR pyroprobe techniques. The constituents of all pyrolysates were ascertained to be an arene (PhOH, PhSH or PhNH₂) fragment, together with CH₃CHO and CO. Mass spectrometric analysis was particularly helpful in the identification of the aromatic fragments and confirmation of their presence as constituents of the pyrolysates.

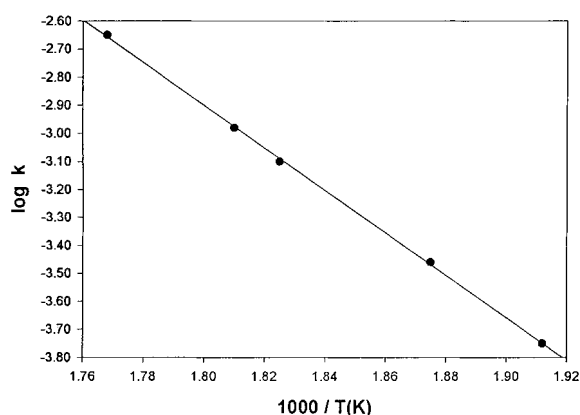
The present and published¹⁻⁴ rate constants and relative rates thereof have been reassessed for 600 K. This is to provide uniformity and thus allow meaningful comparisons and structure-reactivity correlations to be drawn. Based on these results and with reference to the energetically more favourable molecular transition pathway in the reactive global PES of the quantum mechanical analysis of the elimination process, the following mechanistic interpretations and general conclusions could be offered.

1. The reaction pathway is considered to involve the cyclic five-membered transition state associated with elimination of HX and formation of an α -lactone intermediate, and the present analysis of relative reactivities is based on this pathway. The participation of the oxygen atom of the carbonyl

Table 1. Rate coefficients [$10^4 k$ (s^{-1})] for pyrolysis of substrates **1–10**

Compound	<i>T</i> (K)	$10^4 k$ (s^{-1})	Compound	<i>T</i> (K)	$10^4 k$ (s^{-1})
1	514.6	1.04	6	512.2	0.77
	522.4	1.74		526.1	1.94
	534.2	3.73		537.2	4.02
	546.3	8.05		549.2	8.21
	551.0	10.5		554.8	11.4
	561.8	20.7		557.9	13.8
2	564.5	22.3		563.0	18.3
	514.5	0.76	7	494.1	3.20
	523.4	1.43		505.0	7.47
	531.2	2.77		510.2	10.5
	538.1	4.57		518.7	19.9
	549.4	10.4		522.9	27.4
	557.7	17.5		526.3	33.8
	559.0	19.8		534.7	65.9
	564.0	27.8	8	517.0	1.04
3	518.1	1.13		535.0	3.14
	520.2	1.31		546.8	6.38
	524.6	1.80		551.1	7.87
	531.7	3.10		562.5	14.7
	540.9	5.91		568.7	20.3
	549.8	11.0		578.0	33.5
	555.5	15.5	9	740.0	1.05
	558.7	18.8		750.0	1.79
	566.2	31.3		774.2	5.99
4	511.3	0.70		784.0	9.80
	518.3	1.15		792.0	14.1
	536.2	4.16	10	638.0	0.93
	550.1	10.2		658.5	3.05
	554.2	13.0		667.7	5.30
	556.9	15.7		674.7	7.81
5	560.4	18.9		684.9	14.4
	515.0	1.48			
	524.0	2.69			
	543.1	7.91			
	550.1	12.2			
	557.2	17.4			
	565.8	29.9			

moiety of the carboxylic acid group in the cyclization process leading to the formation of the α -lactone intermediate together with H-bonding

**Figure 1.** Arrhenius plot for 2-phenoxypropanoic acid (**1**)

between the acid proton and X offer bond-formation processes that are expected to compensate for energy requirements and to moderate charge development associated with bond fission.

- The effect of the α -substituent (X) is related to what has been described as the basicity of X. This refers to the capacity of the substituent (X) to accommodate the negative charge being developed in the transition state. The correlation of relative reactivity with group (X) is shown below for α -substituted propanoic acid:

X :	Cl	Br	OH	OPh	HNPh	SPh
				(1)	(7)	(8)
$10^4 k (s^{-1})$:	1.81	5.17	2.11	155	3150	97.4
k_{rel} :	1	2.86	1.17	85.6	1740	53.8

By comparison, the aryl substituents ($-\text{NHPh}$,

Table 2. Arrhenius parameters and rates [$10^4 k$ (s^{-1})] at 600 K for substrates **1–10**

Compound	Log A (s^{-1})	E_a (kJ mol $^{-1}$)	$10^4 k_{600}$ (s^{-1})
1	11.32 $\pm$ 0.17	150.8 $\pm$ 1.8	155
2	13.70 $\pm$ 0.15	175.5 $\pm$ 1.5	260
3	13.02 $\pm$ 0.12	168.2 $\pm$ 1.2	233
4	12.25 $\pm$ 0.13	160.6 $\pm$ 1.3	187
5	10.44 $\pm$ 0.00	140.7 $\pm$ 0.02	157
6	11.15 $\pm$ 0.09	149.7 $\pm$ 0.91	132
7	13.48 $\pm$ 0.00	160.6 $\pm$ 0.02	31.5×10^2
8	10.26 $\pm$ 0.05	141.0 $\pm$ 0.57	97.4
9	13.27 $\pm$ 0.13	244.4 $\pm$ 1.5	95.5×10^{-6}
10	13.19 $\pm$ 0.00	210.4 $\pm$ 0.03	7.47×10^{-3}

—OPh, —SPh) show substantially larger relative rates as a result of their pronounced resonance effects. The trend among the aryl groups reflects the relative acid strength of the incipient phenol, thiophene and aniline fragments following protonation by the carboxylic acid hydrogen, as well as the relative stability and proton affinity of the conjugate base of each of the departing aromatic fragments.

- The influence of the aryl substituents on the negative charge being developed in the transition state of the reaction is further revealed by the electronic effects of groups suitably substituted at the *meta* and *para* aromatic ring positions of the phenoxy moiety.

Group :	H	4-NO ₂	4-Cl	3-Cl	4-CH ₃	4-OCH ₃
	(1)	(2)	(3)	(4)	(5)	(6)
$10^4 k(s^{-1})$:	155	260	233	187	157	132
k_{rel} :	1	1.68	1.50	1.21	1.01	0.85

The change in relative rate, although moderate, is nevertheless systematic and consistent with expected electron-withdrawing and electron-donating effects of substituents at the *meta* and *para* positions. Cyclization associated with the formation of the lactone intermediate and H-bonding between X and the acid proton might have combined to reduce the negative charge being developed on the oxygen of the phenoxy moiety and thus moderate the effects of substituents. Structural modification of relative contribution to molecular reactivity of a bond-breaking process, albeit in a cyclic six-membered transition state, has been shown to influence the magnitude of the effects of substituents on the acidity of an incipient proton and its contribution to bond formation.¹⁴

- A dramatic change in reactivity is observed when the acidity of the incipient hydrogen is reduced by replacing the carboxylic acid proton with an alcohol hydroxyl hydrogen. A relative rate factor of 2×10^3 is obtained when the rates of pyrolysis of 2-phenoxypropanoic acid (**1**) and 2-phenoxy-1-pro-

panol (**10**) are compared. The rate factor is much greater (3.3×10^7) when the comparison involves the more basic 2-(*N*-phenylamino) moiety of the acid (**7**) and that of the corresponding alcohol (**9**). It should be noted that a maximum factor of only 100 has been reported involving the rates of 2-bromopropanoic acid and its methyl ester.^{1–4}

EXPERIMENTAL

Kinetic measurements

The reactor, kinetic procedure and instrumentation used for the measurement of specific first-order rate constants at given reaction temperatures of 5–10 °C intervals have been described.^{7,13} Dilute (ppm) standard solutions of the substrates in a suitable solvent (acetonitrile) were prepared, and a suitable internal standard (chlorobenzene) was added to each solution. Care was taken to ensure that both the solvent and the internal standard are not pyrolysable under the conditions of the reaction. Further, the standard solutions used in the kinetic runs always comprised a mixture where the substrate gave a threshold peak which is one third higher than that of the internal standard in the analytical high-performance liquid chromatographic (HPLC) trace. Preparation of a standard solution allows several kinetic runs to be performed on the same reaction mixture.

A sample (0.2 ml) of the standard solution was placed in the reaction tube (9 ml) and the contents were sealed under vacuum; a pressure of ~ 0.3 mbar was maintained during this process. The tube was mounted in the pyrolyser heated to a selected temperature and for a given length of time to allow about 10–20% threshold pyrolysis. Pyrolysis was then followed at regular intervals until $>95\%$ reaction was obtained. The contents of the reaction tube were analysed using HPLC. The configuration and model of both the pyrolysis and HPLC units have been detailed in a previous paper.⁷ The experimental and analytical techniques for evaluation of rates have been described in detail.¹³ Rates were reproduced in presence and absence of a radical scavenger (cyclohexene); homogeneity and any possible adverse surface effects were also tested following earlier procedures.¹³ An increase of the reactor surface area of up to about ninefold produced no detectable change in the rate of reaction; the increase in surface area was achieved using reaction tubes packed with glass helices. It is noteworthy that the present values of the Arrhenius log A (s^{-1}) and E_a kJ mol $^{-1}$ are well within the ranges expected for unimolecular polar thermal elimination reactions, and are distinctly different from the values of 16 s^{-1} and 315 kJ mol $^{-1}$ expected for radical elimination reactions.¹⁶

The rate coefficients were calculated using the

expression $kt = \ln(a_0/a)$ for first-order reactions.^{13,15} The Arrhenius parameters were obtained from a plot of $\log k$ vs $1/T$ (K), an example of which is shown in Fig. 1. The elimination rate constant at T (K) is given by

$$\log k = \log A(\text{s}^{-1}) - E_a(\text{kJ mol}^{-1})/4.574T(\text{K})$$

Product analysis. The on-line GC-MS pyroprobe and the flow techniques for the identification of the constituents of the products of pyrolysis have been described in previous reports.^{7,15} The products analysed were for pyrolyses conducted at temperatures commensurate with those of the kinetic measurements. No secondary decomposition was observed for any of the compounds under study up to 98% pyrolysis.

Syntheses. *2-Aryloxypropanoic acids (1–6).* Typically, ethyl 2-phenoxypropionate was prepared by refluxing equimolar amounts of phenol, ethyl 2-chloropropionate and potassium carbonate in dry acetone (200 ml) for 10 h followed by normal work-up and subsequent distillation to produce ethyl 2-phenoxypropionate in 82% yield (b.p. 119°C at 5 mmHg; lit.¹⁷ b.p. 125°C at 6 mmHg for ester). Of this ester, 8 g were then hydrolysed using 10% aqueous sodium hydroxide solution (100 ml) and refluxing the mixture for 3–4 h until the disappearance of the upper ester layer was deemed complete. The contents of the flask were then cooled and acidified by the dropwise addition of dilute hydrochloric acid. The white crystalline flaky solid which separated out was filtered and dried to yield 2-phenoxypropanoic acid (**1**). The 2-aryloxypropanoic acids (**2–6**) were prepared from the appropriately substituted phenols following the procedure described above for 2-phenoxypropanoic acid (**1**).

2-(N-Phenylamino)propanoic acid (7). Ethyl 2-(N-phenylamino)propionate required in this synthesis was prepared by refluxing a mixture of ethyl 2-chloropropionate (0.1 mol), aniline (0.1 mol) and sodium hydroxide (0.2 mol) at 125°C for 12 h, followed by normal work-up and subsequent distillation to produce ethyl 2-(N-phenylamino)propionate in 45% yield. A mixture of ethyl 2-(N-phenylamino)propionate (8 g) and 10% aqueous sodium hydroxide solution (100 ml) was refluxed for 3–4 h until the disappearance of the upper ester layer was complete. The contents of the flask were then cooled and acidified with the dropwise addition of dilute hydrochloric acid. The white crystalline solid which separated out was then filtered, dried and recrystallized from light petroleum to obtain 2-(N-phenylamino)propionic acid in 70% yield.

2-Thiophenoxypropanoic acid (8). The same general procedure as described for the aryloxy acids (**1–6**) but using thiophenol produced thiophenoxy acid in 80% yield.

2-(N-Phenylamino)-1-propanol (9). A solution of ethyl 2-(N-phenylamino)propionate (0.02 mol) in 50% aqueous ethanol (50 ml) was added dropwise to a solution of sodium borohydride (0.09 mol) in 50% aqueous ethanol (500 ml). The resulting mixture was then refluxed for 4.5 h. After normal work-up, the resulting liquid was distilled to produce 2-(N-phenylamino)-1-propanol in 70% yield.

2-Phenoxy-1-propanol (10). A solution of 2-phenoxypropanoic acid (0.01 mol) in dry diethyl ether (10 ml) was added dropwise to a stirred slurry of lithium aluminium hydride (0.01 mol) in dry diethyl ether (100 ml) at a rate sufficient to maintain reflux (3–4 h). The mixture was then cooled to room temperature. The excess hydride was decomposed by dropwise addition of water, and the resulting white suspension was filtered. The filtrate was dried over Na_2SO_4 and concentrated *in vacuo*, then distilled to produce 2-phenoxy-1-propanol in 75% yield.

Characterization. The solids were recrystallized from diethyl ether–light petroleum and the liquids were purified by distillation under reduced pressure. The melting points (uncorrected) were recorded from a Gallenkamp Sanyo apparatus, and both melting and boiling points were compared with literature values.^{17–25} In addition, characterization included IR (on neat liquid samples or KBr discs), ^1H NMR (DMSO or CDCl_3 as solvents), and mass spectrometric analyses. FT-IR spectra were recorded on a Perkin-Elmer 2000, NMR spectra on a Bruker AC80 and mass spectra on a Finnigan Mat INCOSXL spectrometer. Typical data were as follows. 2-Phenoxypropanoic acid (**1**): m.p. 114–116°C, lit.^{17,18} 116°C; IR (KBr), ν_{max} 1718 cm^{-1} ; NMR, δ (DMSO) 1.49 (d, 3H, CH_3), 4.18 (q, 1H, CH), 6.80–7.01 (m, 3H, ArH), 7.18–7.37 (m, 2H, ArH). 2-Phenoxy-1-propanol (**10**): b.p. 124°C/20 mmHg, lit.^{17,19} 124°C/20 mmHg; IR (neat), ν_{max} 3608 cm^{-1} ; NMR, δ (DMSO) 1.23 (d, 3H, CH_3), 2.46 (br s, 1H, OH, exchanges with D_2O), 3.69 (br s, 2H, CH_2), 4.45 (m, 1H, CH), 6.84–7.01 (m, 3H, ArH), 7.16–7.36 (m, 2H, ArH); MS, $M^+ = 152.1$. 2-(*p*-Nitrophenoxy)propanoic acid (**2**): m.p. 137–138°C, lit.²⁰ 139–140°C. 2-(*p*-Chlorophenoxy)propanoic acid (**3**): m.p. 115–116°C, lit.²⁰ 115–116°C. 2-(*m*-Chlorophenoxy)propanoic acid (**4**): m.p. 113–115°C, lit.²¹ 113–114°C. 2-(*p*-Methylphenoxy)propanoic acid (**5**): m.p. 100–101°C, lit.²¹ 101–102°C. 2-(*p*-Methoxylphenoxy)propanoic acid (**6**): m.p. 99–101°C, lit.²² 93–94°C. 2-(N-Phenylamino)propanoic acid (**7**): m.p. 165°C, lit.²³ 165°C. 2-Thiophenoxypropanoic acid (**8**): b.p. 160°C/6 mmHg, lit.²⁴ 168–170°C/9 mmHg. 2-(N-Phenylamino)-1-propanol (**9**): b.p. 115°C/3.8 mmHg, lit.²⁵ 122°C/4 mmHg.

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REFERENCES

1. Chuchani G, Rotinov A. *Int. J. Chem. Kinet.* 1989; **21**: 367.
2. Chuchani G, Dominguez RM, Rotinov A. *Int. J. Chem. Kinet.* 1991; **23**: 779.
3. Chuchani G, Martin I, Rotinov A, Dominguez RM. *J. Phys. Org. Chem.* 1993; **6**: 54.
4. Chuchani G, Martin I, Rotinov A. *Int. J. Chem. Kinet.* 1995; **27**: 849.
5. Taylor R. *Int. J. Chem. Kinet.* 1987; **19**: 709.
6. Taylor R. *Int. J. Chem. Kinet.* 1991; **23**: 247.
7. Al-Awadi NA, El-Dusouqui OME. *Int. J. Chem. Kinet.* 1997; **29**: 295.
8. Safont VS, Moliner V, Andres J, Domingo LR. *J. Phys. Chem. A* 1997; **101**: 1859.
9. Domingo LR, Andres J, Moliner V, Safont VS. *J. Am. Chem. Soc.* 1997; **119**: 6415.
10. Domingo LR, Picher MT, Andres J, Safont VS, Chuchani G. *Chem. Phys. Lett.* 1997; **274**: 422.
11. Domingo LR, Picher MT, Safont VS, Andres J, Chuchani G. *J. Phys. Chem. A* 1999; **103**: 3935.
12. Rotinov A, Chuchani G, Andres J, Domingo LR, Safont VS. *Chem. Phys.* 1999; **246**: 1.
13. Al-Awadi NA, Elnagdi MH, Mathew T. *Int. J. Chem. Kinet.* 1995; **27**: 517.
14. Al-Awadi NA, Elnagdi MH, Kaul K, Ilingovan S, El-Dusouqui OME. *Tetrahedron* 1998; **54**: 4633; *J. Phys. Org. Chem.* 1999; **12**: 654.
15. Al-Awadi NA, Al-Bashir RF, El-Dusouqui OME. *J. Chem. Soc., Perkin Trans.* 1989; **2**: 579.
16. Holbrook KA, In *The Chemistry of Acid Derivatives: Supplement B*, Patai S (ed). Wiley:Chichester, 1992; Chapt. 15.
17. Lide DR. (ed). *CRC Handbook of Chemistry and Physics*. 1991/1992.
18. Buckingham J Macdonald F (eds), *Dictionary of Organic Compounds* (6th edn). 1995.
19. Collet A, Jacques J. *J. Chem. Soc., Chem. Commun.* 1976; 708.
20. Johnson DA, Richardson EJ, US Patent 3278524 1966; *Chem. Abstr.* 1967; **66**: 18709K.
21. Synerholm ME, Zimmerman PW. *Contrib. Boyce Thompson Inst.* 1945; **14**: 91; *Chem. Abstr.* 1946; **40**: 1474(3).
22. Birch HF, Flynn DG, Robertson A, Curd FH. *J. Chem. Soc.* 1936; 1834.
23. Szulc Z, Mlochowski J, Palus J. *J. Prakt. Chem.* 1988; **330**: 1023, and references cited therein.
24. Ramberg L, Hedlund I. *Ark. Kemi Mineral. Geol.* 1937; **12A**; *Chem. Abstr.* 1937; **31**: 4292(7).
25. Huy-Giao D, Lattes A. *C.R. Acad. Sci., Ser. C* 1967; **264**: 1864.