JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 49–54 (1997)

GAS-PHASE THERMOLYSIS OF *N*-SUBSTITUTED DIALLYL- AND ALLYLPROPARGYLAMINES

GONZALO MARTIN, JULIAN ASCANIO AND JESUS RODRIGUEZ
Centro de Quimica, IVIC, Apartado 21827, Caracas 1020A, Venezuela

Various diallyl- and allylpropargylamines were pyrolyzed in a stirred-flow reactor at temperatures in the range of 330–500 °C, pressures of 8–16 Torr and residence times of 0·4–2·4 s using toluene as carrier gas. The reaction products were propene, allene and aldimines. The allene to propene ratio changed considerably with the third substituent on the N atom. At conversions in the range 13–55%, the consumption of the amines showed first-order kinetics. The following Arrhenius parameters [A (s^{-1}) and E_a ($kJ\,mol^{-1}$)] were obtained from the rate coefficients: diallyl-*tert*-butylamine, $\log A = 10{\cdot}32 \pm 0{\cdot}12$, $E_a = 139 \pm 2$; diallylneopentylamine, $\log A = 12{\cdot}87 \pm 0{\cdot}26$, $E_a = 168 \pm 3$; allylpropargyl-*tert*-butylamine, $\log A = 10{\cdot}23 \pm 0{\cdot}18$, $E_a = 126 \pm 2$; allylpropargyltosylamine, $\log A = 13{\cdot}05 \pm 0.36$, $E_a = 197 \pm 5$; and allylpropargylphenylamine, $\log A = 12{\cdot}10 \pm 0{\cdot}35$, $E_a = 162 \pm 4$. Polar, six-center cyclic transition states are suggested for the elimination of propene and allene, via non-concerted bond breaking–bond forming mechanisms.

INTRODUCTION

In a previous paper,[1] it was reported that electron-withdrawing groups such as CH_2CN, CH_2SCH_3 and CH_3SO_2, as third substituents on the N atom of allylpropargylamine, decreased the overall reactivity of the latter towards the unimolecular retro-ene and retro-ine elimination of propene and allene, respectively. The allene to propene ratio decreased with these substituents in the order $CH_2CN > H > CH_2SCH_3 > CH_3SO_2$, implying an increase in reactivity towards the retro-ene reaction path. Polar, six-center cyclic transition states were inferred from the estimated ground-state atom charge distribution of the reactant molecules, since partially positive α-H atoms had to be transferred to partially negative terminal allyl or propargyl C atoms, respectively. The overall reactivity appeared to increase with increasing negative charge in the latter C atoms, while propene formation appeared to be favored by an increased positive charge on at least one of the α-H atoms of the propargyl moiety. The N atoms, on the other hand, bear net negative charges. The decrease in overall reactivity brought about by the above substituents may also be due to the destabilization of the transition state by their $-I$ effect on the negative N atom. In this work, groups with $+I$ effect were examined by studying the reaction kinetics of diallyl-*tert*-butylamine (DATB), allylpropargyl-*tert*-butylamine (APTB) and diallylneopentylamine (DANP), expecting an enhanced reactivity if they supply negative charge to the N atom in the transition state. Two more groups with a $-I$ effect were also studied: allylpropargylphenylamine (APPH) and allylpropargyltosylamine (APTO).

EXPERIMENTAL

DATB and DANP were synthesized from *tert*-butylamine, neopentylamine and allyl bromide, respectively (DATB, b.p. 56–58 °C/20 Torr, 57% yield; DANP, b.p. 72–73 °C/35 Torr, 48% yield). APTB was obtained by reaction of *tert*-butylamine with propargyl bromide, isolation of the *tert*-butylpropargylamine and reaction of the latter with allyl bromide (b.p. 58–60 °C/24 Torr, 65% yield). APTO was obtained by reaction of allylpropargylamine[2] with *p*-toluenesulfonyl chloride; its purification was carried out by sublimation of the crude solid product (m.p. 61–62 °C, 58% yield). APPH was synthesized by reaction of aniline with allyl bromide, isolation of the *N*-allylaniline and reaction of the latter with propargyl bromide (b.p. 104–106 °C/0·6 Torr, 60% yield). All the starting materials were obtained from Aldrich. The syntheses involved the addition of the alkenyl halide to the amine dissolved in dichloromethane, in the presence of excess trimethylamine, filtering off the trimethylamine hydrohalide and low-pressure distillation of the solvent and product in a vacuum line.

The synthesized amines, confirmed to be more than 99% pure, as well as the gas hydrocarbon products,

CCC 0894–3230/97/010047–06
© 1997 by John Wiley & Sons, Ltd.

Received 30 April 1996
Revised 26 August 1996

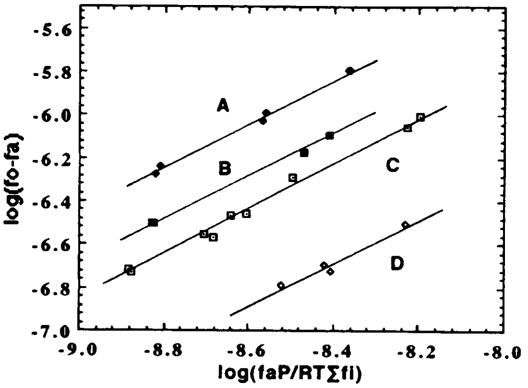

Figure 1. Reaction order plots: (A) APTB at 380 °C; (B) DANP at 400 °C; (C) DATB at 410 °C; (D) APPH at 390 °C; f_0, reactant inflow; f_a, reactant outflow; Σf_i, total outflow; P, total pressure; R, gas constant; T, absolute temperature

were analysed by GLC using the previously reported[1] columns and conditions. The structures of the reactants and products were confirmed by mass and ^{1}H NMR spectroscopy using Kratos RFA25 GLC–MS and Bruker AM300 instruments, respectively. The amines were thermolyzed at temperatures in the range 330–500 °C, pressures in the range 8–16 Torr and residence times of 0·4–2·4 s, using toluene as carrier gas, with toluene to reactant flow-rate ratios of $\geqslant$30. The titration of SO_2 and the test for the presence of imines were performed as reported.[1] The experimental technique, reaction order measurement and rate coefficient calculation have been described elsewhere.[3–5]

RESULTS

Figure 1 shows the reaction order plots, whose slopes yielded the following order values for the initial consumption of each reactant, at the indicated temperature, percentage reaction (%r) and variation of reactant inflow ($\Delta f_A{}^0$): DATB, 1·06 ± 0·03 (410 °C, 38%r, $\Delta f_A{}^0$ = 5·0-fold); DANP, 0·96 ± 0·06 (400 °C, 25%r, $\Delta f_A{}^0$ = 2·9-fold); APTB, 1·03 ± 0·07 (380 °C, 25%r, $\Delta f_A{}^0$ = 3·0-fold); and APPH, 1·0 ± 0·1 (389 °C, 37%r, $\Delta f_A{}^0$ = 2·0-fold). For APTO and for all these reactants an order of one was then assumed.

Table 1 gives the result of representative runs carried out for DATB and DANP and Table 2 gives those for APTB, APTO and APPH. A minimum of 20 runs were made with each reactant.

The Arrhenius parameters, derived from least-squares linear fits of the respective rate coefficients for total C_3 hydrocarbon formation, and for the allene- and propene-forming pathways, are given in Table 3, together with data from previous work.

DATB formed as reaction products propene and *tert*-butylprop-2-enaldimine. The latter was stable enough to be identified by GLC–MS of its toluene solution, m/z (%) 111 (7·3, M^+), 96 (100), 81 (10·7), 68 (4·6), 57 (83·5), 56 (43·4), 55 (19·3), 54 (16·5), 41 (58·6), 39 (30·7), and also by a positive imine test of the liquid product fraction with 2,4-dinitrophenylhydrazine.

DANP also formed propene and the corresponding neopentylprop-2-enaldimine. The latter polymerized during room temperature separation of the propene from the liquid fraction, but the GLC–MS analysis of the liquid fraction still showed a peak corresponding to the monomer, m/z (%) 125 (6·4, M^+), 110 (4·2), 82

Table 1. Stirred flow pyrolysis results for diallylamines

Compound	T (°C)	$k \times 10^4$ (s^{-1})[a]	Θ (s)[b]	%r (C_3H_6)[c]	P (Torr)	$f_A{}^0 \times 10^8$ [d]	$f_c/f_A{}^0$ [e]
Diallyl-*tert*-butylamine	380·7	1754	1·16	16·92	13·5	157·0	62
	389·6	2579	1·14	22·77	12·8	113·3	62
	399·9	3548	1·19	29·62	13·2	118·9	58
	410·4	5604	1·10	38·17	14·3	252·1	30
	410·5	5057	1·12	36·06	13·5	50·3	148
	409·5	5255	1·13	37·29	13·5	49·6	148
	419·2	7044	1·15	44·72	13·2	66·9	104
Diallylneopentylamine	359·7	1023	1·48	13·14	11·5	55·70	93
	371·8	1829	1·09	16·61	12·6	154·5	48
	379·8	2682	1·19	24·27	12·8	93·26	74
	389·6	4399	1·02	31·07	12·7	90·51	87
	400·8	7343	0·45	24·99	8·59	265·4	44
	409·0	10156	0·39	28·25	8·44	157·6	85

[a] k, rate coefficient from propene measurement.
[b] Θ, residence time.
[c] %r (C_3H_6), percentage reaction from propene measurement.
[d] $f_A{}^0$, reactant inflow, mol s^{-1}.
[e] $f_c/f_A{}^0$, toluene to reactant flow ratio.

Table 2. Stirred flow pyrolysis results for allylpropargylamines

Compound	T(°C)	$k_{C_3} \times 10^4$ (s^{-1})[a]	Θ (s)[b]	%r (C_3H_4)[c]	%r (C_3H_6)[d]	P (Torr)	$f_A{}^0 \times 10^8$[e]	$f_c/f_A{}^0$[f]
Allylpropargyl-*tert*-butylamine	331·0	1984	1·19	16·70	2·39	10·1	106·7	55
	341·9	3195	1·17	24·15	3·14	10·3	102·0	58
	350·4	4511	1·21	31·19	4·09	9·9	134·2	40
	359·6	6792	1·17	39·26	5·07	10·1	96·9	58
	370·7	9805	1·04	44·48	5·90	13·2	131·9	62
	380·1	14111	0·83	46·58	7·26	11·9	300·2	30
Allylpropargyltosylamine	460·1	1003	1·44	7·10	5·53	15·7	61·0	122
	470·7	1585	1·41	10·39	7·85	15·6	71·8	87
	480·1	2484	0·92	11·02	7·66	11·1	87·1	77
	490·3	3798	0·81	13·14	9·85	10·1	69·6	99
	499·9	5496	0·98	19·52	15·44	11·6	73·9	87
Allylpropargylphenylamine	379·8	1451	1·40	11·91	4·99	13·3	143·2	42
	389·2	2057	1·13	14·22	4·65	13·0	86·7	83
	400·6	3418	1·07	17·88	8·83	13·6	181·3	43
	408·8	4592	1·04	22·84	9·44	13·1	154·3	49
	419·0	7563	1·07	30·20	14·16	12·8	130·0	55

[a] k_{C_3}, rate coefficient for total C_3 production.
[b] Θ, residence time.
[c] %r (C_3H_4), percentage reaction from allene measurement.
[d] %r (C_3H_6), percentage reaction from propene measurement.
[e] $f_A{}^0$, reactant inflow in mol s^{-1}.
[f] $f_c/f_A{}^0$, toluene to reactant flow ratio.

Table 3. Kinetic parameters for allylpropargylamines and diallylamines

Reactant: R in $CH_2{=}CHCH_2N(R)CH_2C{\equiv}CH$	k[a]	E_a (kJ mol^{-1})	Log A	$-\Delta S$‡ (J mol^{-1} K^{-1})[b]	k_{r420}[c]	k_{r470}[c]	A/P[d]	Ref.
H	k_T	133 ± 4	10·07 ± 0·31	67	1	1	5·3 ± 0·3	1
H	k_A	133 ± 4	10·02 ± 0·29	68	1	1		
H	k_P	134 ± 5	9·36 ± 0·37	81	1	1		
CH_2SCH_3	k_T	168 ± 5	12·55 ± 0·38	20	0·68	1·05	2·5 ± 0·2	1
CH_2SCH_3	k_A	180 ± 5	13·32 ± 0·36	5	0·58	0·99		
CH_2SCH_3	k_P	180 ± 4	12·92 ± 0·34	13	1·2	2·1		
SO_2CH_3	k_T	184 ± 5	12·56 ± 0·34	22	0·04	0·08	1·3 ± 0·1	1
SO_2CH_3	k_A	182 ± 4	12·22 ± 0·31	26	0·03	0·05		
SO_2CH_3	k_P	182 ± 5	12·11 ± 0·32	28	0·13	0·22		
$SO_2C_6H_4$-*p*-CH_3	k_T	197 ± 5	13·05 ± 0·36	10	0·01	0·03	1·4 ± 0·2	This work
$SO_2C_6H_4$-*p*-CH_3	k_A	197 ± 7	12·82 ± 0·46	14	0·01	0·02		
$SO_2C_6H_4$-*p*-CH_3	k_P	197 ± 5	12·66 ± 0·37	17	0·03	0·07		
t-C_4H_9	k_T	126 ± 2	10·23 ± 0·18	63	4·9	4·5	7·6 ± 0·3	This work
t-C_4H_9	k_A	126 ± 1	10·13 ± 0·10	65	4·3	4·0		
t-C_4H_9	k_P	131 ± 3	9·72 ± 0·23	73	3·8	3·7		
C_6H_5	k_T	162 ± 4	12·10 ± 0·35	28	0·67	0·96	2·5 ± 0·2	This work
C_6H_5	k_A	139 ± 5	10·10 ± 0·42	68	0·42	0·45		
C_6H_5	k_P	149 ± 8	10·44 ± 0·65	59	0·80	0·95		
CH_2CN	k_T	146 ± 4	10·73 ± 0·30	55	0·46	0·56	6·7 ± 0·6	1
CH_2CN	k_A	145 ± 4	10·60 ± 0·34	57	0·48	0·54		
CH_2CN	k_P	145 ± 4	9·77 ± 0·34	73	0·38	0·43		
R in $(CH_2{=}CHCH_2)_2NR$								
H	k_P	155 ± 1	11·04 ± 0·13	49	1	1		9
$CH_2{=}CHCH_2$	k_P	160 ± 1	11·74 ± 0·07	35	1·4	1·5		10
t-C_4H_9	k_P	139 ± 2	10·32 + 0·12	62	3·2	2·5		This work
$(CH_3)_3CCH_2$	k_P	168 ± 3	12·87 ± 0·26	13	7·2	8·2		This work
CH_2CN	k_p	183 ± 3	13·00 ± 0·20	11	0·71	0·97		11

[a] k_T = total C_3 rate coefficient; k_A = allene rate coefficient; k_P = propene rate coefficient.
[b] ΔS‡, entropy of activation calculated at 400 °C.
[c] k_r, rate coefficient, relative to allylpropargylamine and diallylamine, per α-H atom, calculated at 420 and 470 °C.
[d] A/P, allene to propene ratio.

(13·8), 68 (93·7), 57(8·2), 55 (9·2), 41 (100), 39 (44·7). The imine test was positive when carried out in absence of toluene carrier.

APTB yielded as gaseous products allene and propene in a ratio of 7·6 ± 0·3 in favor of allene. The liquid product fraction gave a positive test with 2,4-dinitrophenylhydrazine, indicating the formation of imine products.

Within the extent of reaction examined (12–35%), APTO yielded a mixture of gaseous products composed of 39 ± 2% allene, 27 ± 1% propene, 34 ± 2% SO_2 and 3·6 ± 0·5% C_2 hydrocarbons. The ratio of allene to propene was thus 1·44 ± 0·15. The imine test made with the liquid fraction was always negative. Upon distillation of the toluene, this fraction left behind a nonvolatile residue. The mass spectrum of the latter was complex up to signals of m/z 250, after which the only large signals had m/z 340 and 404, suggesting the loss of SO_2 from the heavier fragment upon electron impact.

APPH formed as gaseous products only allene and propene in a ratio of 2·5 ± 0·4 in favor of allene. The aldimine test was unambiguosly positive when the reactor effluent was collected directly in 2,4-dinitrophenylhydrazine solution.

DISCUSSION

The experimental evidence as regards stoichiometry and activation parameters suggests that the amines studied thermolyze by the same mechanisms as those of other amines shown in Table 3, that is, retro-ene and retro-ine paths via six-center cyclic transition states. All the A factors for these reaction pathways are within the range $10^{11\cdot3\pm2}$ s^{-1}. The allylpropargylamines with A values towards the lower end of this range (R = H, t-C_4H_9, Ph, CH_2CN) have E_a values of about 140 ± 7 kJ mol^{-1} for the retro-ene path and of about 136 ± 7 kJ mol^{-1} for the retro-ine path. These amines appear to yield high (2·5–6·7) allene to propene ratios. Those with A values towards the upper end of the range (R = CH_2SCH_3, SO_2CH_3, tosyl) have values of E_a of about 186 ± 7 kJ mol^{-1}, implying looser and more energetic transition states by which the retro-ene path is favoured (allene to propene ratios *ca* 1·3–2·5).

The overall reactivity for the allylpropargylamines is found to decrease in the order $t\text{-}C_4H_9 > H > CH_2SCH_3 \approx C_6H_5 > CH_2CN > SO_2CH_3 > SO_2C_6H_4\text{-}p\text{-}CH_3$, where APTB is at least four times more reactive than allylpropargylamine whereas APTO is about 70 times less reactive than the latter. This reactivity sequence may be inferred from the rate coefficients, relative to allylpropargylamine, shown for 420 and 470 °C, and calculated by using the respective Arrhenius equation. A third substituent in the N atom exerting a $+I$ effect is seen to increase the overall reactivity, whereas a substituent with a $-I$ effect decreases it. In diallylamine, reactivity is also enhanced by a $+I$ effect, so DATB and DANP are about three and seven times more reactive than diallylamine, respectively.

Table 4 shows the optimized ground-state net charges in the atoms likely to form the structure of the six-center transition states of both allene and propene elimination. These were calculated by means of Zerner's ZINDO program, Biosym/MSI version, using the INDO method.[6–8] The latter appears to yield charge values for the N atom of these amines more in accord with the expectation of a less negative N atom if a $-I$ group is attached to it. This was not reflected in the previous[1] AM1 calculations.

The atom numbers are as shown in Figure 2 for APTB. As suggested,[1] the overall reactivity appears to increase with increasing negative charge on the C-2 and C-13 atoms. The formation of propene seems favored by increasing positive charge on H-6. On the other hand, the increased overall reactivity brought about by the *tert*-butyl and neopentyl substituents implies that in the transition state the N atom should become less negative than in the ground state. The drain of negative charge is compensated by the $+I$ effect of the latter substituents, thus stabilizing the transition state.The suggested transition states would resemble the molecular conformations shown in Figure 2 for APTB. In these, the terminal allyl and propargyl C atoms bear partial negative charges whereas the α-H atoms to be transferred have acidic character. The 1–5 H atom transfer probably takes place first, followed by the corresponding C—N bond fission step. Since the triple bond is more nucleophilic than the double bond, the

Table 4. Net atomic charges in atomic units

Reactant[a]	C-2	C-3	C-4	H-5	H-6	N-7	C-8	H-9	H-10	C-11	C-13	Ref.
APA	−0·148	−0·052	0·085	0·050	0·056	−0·408	0·057	0·039	0·048	−0·057	−0·143	1
APTB	−0·149	−0·047	0·089	0·048	0·054	−0·362	0·059	0·046	0·040	−0·052	−0·150	This work
APCNA	−0·142	−0·054	0·086	0·054	0·057	−0·344	0·056	0·046	0·053	−0·060	−0·138	1
APPH	−0·144	−0·049	0·090	0·050	0·059	−0·333	0·063	0·041	0·047	−0·052	−0·145	This work
APMSA	−0·128	−0·048	0·100	0·051	0·085	−0·306	0·070	0·037	0·065	−0·056	−0·140	1
APTO	−0·141	−0·055	0·098	0·067	0·086	−0·301	0·067	0·076	0·057	−0·064	−0·133	This work

[a] APA = allylpropargylamine; APCNA = allylpropargylcyanomethylamine; APMSA = allylpropargylmethanesulfonylamine.

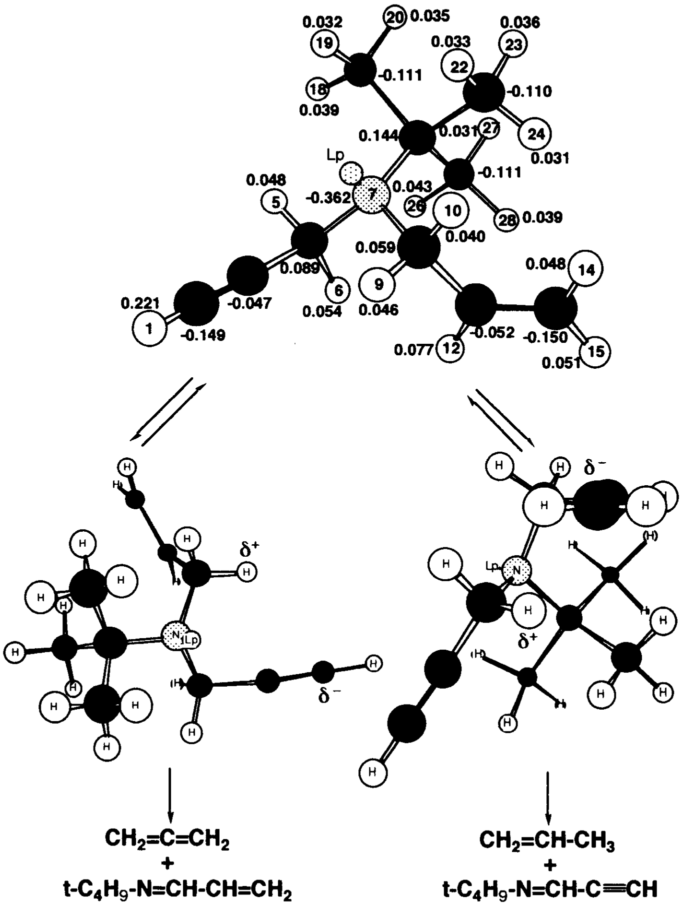

Figure 2. Atom charges in APTB and reaction stoichiometry

favored reaction path is always towards the retro-ine elimination. The substituents with a $+I$ effect should favor this process by supplying electron density to the N atom, whereas $-I$ groups have the opposite effect.

The above results can be viewed within the spectrum of six-center cyclic transition states for the E_i elimination mechanism, analysed in detail in the literature,[12-17] with regard to the atoms forming the ring and the effect of substituents attached to them. The present and previous results with diallyl- and allylpropargylamines (Table 3) indicate that these reactions are in the region of the said spectrum in which nucleophilic attack of the double or triple bond on the α-C—H bond is the important step in the reaction.

The formation of SO_2 in the thermolysis of APTO may be ascribed to decomposition of both *N*-tosylprop-2-enaldimine and *N*-tosylprop-2-inaldimine via free radical mechanisms. Radical fragment recombinations would likely generate the observed solid products. The thermolysis of APTO resembled that of allylpropargylmethanesulfonylamine,[1] for which an order one was measured.

REFERENCES

1. G. Martín, J. Ascanio and J. Rodriguez, *Int. J. Chem. Kinet.* **26**, 487–496 (1994).
2. D. A. Ben-Efraim, *Tetrahedron* **29**, 4111–4125 (1973).
3. G. Martín, H. Martinez and J. Ascanio, *Int. J. Chem. Kinet.* **22**, 1127–1136 (1990).
4. G. Martín, H. Martinez and J. Ascanio, *Int. J. Chem. Kinet.* **21**, 193–206 (1989).
5. M. F. R. Mulcahy and D. J. Williams, *Aust. J. Chem.* **14**, 534–544 (1961).
6. M. C. Zerner, G. H. Loew, R. F. Kirchener and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.* **102**, 589–599 (1980).
7. J. D. Head and M. C. Zerner, *Chem. Phys. Lett.* **131**, 359–366 (1986).
8. W. D. Edwards and M. C. Zerner, *Theor. Chim. Acta* **72**, 347–361 (1987).

9. K. W. Egger and P. Vitins, *Int. J. Chem. Kinet.* **6**, 371–382 (1974).
10. P. Vitins and K. W. Egger, *Helv. Chim. Acta* **57**, 17–23 (1974).
11. G. Martín, J. Ascanio and J. Rodriguez, *Int. J. Chem. Kinet.* **27**, 99–108 (1995).
12. R. August, I. McEwen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 1683–1689 (1987).
13. N. Al-Awadi and R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 177–182 (1988).
14. N. Al-Awadi and R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 1589–1592 (1986).
15. R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 809–811 (1983).
16. R. Taylor and M. P. Thorne, *J. Chem. Soc., Perkin Trans. 2* 799–802 (1976).
17. S. de Burgh Norfolk and R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 280–285 (1976).