Intramolecular Cyclisations of Nitrile Imines bearing a Thioether Function

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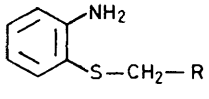
N-Aryl nitrile imines bearing a thioether function in the *ortho*-position were generated *in situ* on treating the corresponding hydrazonyl chlorides with triethylamine in boiling benzene. In all cases, the major products were 4,1,2-benzothiadiazines arising from intramolecular participation of the sulphur and subsequent evolution of transient cyclic ylides. Minor products due to an intramolecular 1,3-dipolar cycloaddition were sometimes obtained.

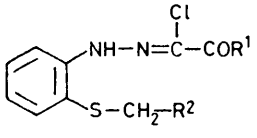
THE importance of the nitrile imines in the synthesis of five-membered heterocycles has been long recognized. In recent years, the investigation of properly substituted *N*-aryl nitrile imines has evidenced intramolecular reaction paths which appear to be of great interest from the mechanistic and synthetic points of view. In fact, *N*-aryl nitrile imines having in the *ortho*-position a suitably long chain with C=C, C≡C, or C≡N bonds can undergo intramolecular 1,3-dipolar cycloadditions to yield fused-ring 2-pyrazolines, pyrazoles, and 1,2,4-triazoles, respectively.[1-4] On the other hand, in cases where the *ortho*-substituent possesses αβ-unsaturation, ring-closure can occur through an intramolecular attack of the π-bond to the electron-deficient carbon of the nitrile imine.[5,6] In the course of a study on the behaviour of nitrile imines bearing a nitrile group as a potential dipolarophile, we have shown that the reaction of the hydrazonyl chloride (2f) with triethylamine gives (5c) as the major product.[3] Since this result has revealed an unprecedented participation of the thioether function in the intramolecular capture of nitrile imines, further work has been done with the aim of testing the generality of such a pattern of reaction and its validity as a new synthetic route to 4,1,2-benzothiadiazines. The present paper is concerned with the base-promoted behaviour of the structurally related hydrazonyl chlorides (2a—e), which possess various kinds of substitution at the sulphur atom.

RESULTS AND DISCUSSION

Compounds (2a—e) were prepared by diazotisation of anilines (1a—d) and subsequent coupling with the

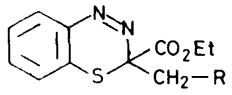


(1a): R = CH=CH$_2$
(1b): R = C(Me)=CH$_2$
(1c): R = Ph
(1d): R = CN

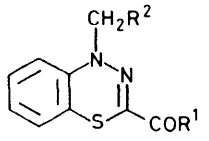


(2a): R^1 = OEt; R^2 = CH=CH$_2$
(2b): R^1 = OEt; R^2 = C(Me)=CH$_2$
(2c): R^1 = OEt; R^2 = Ph
(2d): R^1 = Me; R^2 = CN
(2e): R^1 = Ph; R^2 = CN
(2f): R^1 = OEt; R^2 = CN

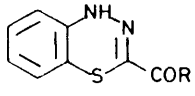
appropriate chloro-compound of formula R^{1}COCHCl-COMe. The reaction yield (see Table 1) was rather low in some cases because of the great lability of the intermediate diazonium salts, which readily cyclise to 1,2,3-benzothiadiazole.[7] Treatment of (2a—e) with an excess



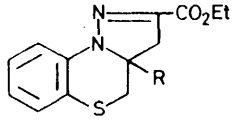
(3a): R = CH=CH$_2$
(3b): R = C(Me)=CH$_2$
(3c): R = Ph



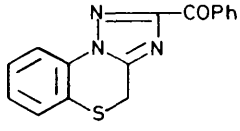
(4a): R^1 = Me; R^2 = CN
(4b): R^1 = Ph; R^2 = CN
(4c): R^1 = OEt; R^2 = Ph
(4d): R^1 = OEt; R^2 = CN



(5a): R = Me
(5b): R = Ph
(5c): R = OEt



(6a): R = H
(6b): R = Me



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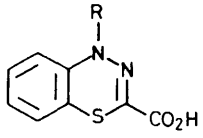
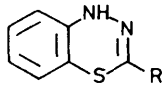


(8a): R = CH$_2$Ph
(8b): R = H



(9a): R = CH$_2$CH=CH$_2$
(9b): R = CH$_2$C(Me)=CH$_2$
(9c): R = CH$_2$Ph
(9d): R = CH=CHMe

of triethylamine in boiling benzene resulted in the product mixtures as described in Table 2.† The identity

† To minimise the formation of tarry material, the reaction of (2a—e) was carried out using a lower concentration than that previously reported for (2f).[3] The reaction of the latter substrate was then repeated under the new conditions.

of the products follows from their analytical and spectral data, the latter being collected in Table 3.

A diagnostic feature in the mass spectra of 3*H*-4,1,2-benzothiadiazines (3a—c) is the ($M^+ - 28$) peak due to the loss of nitrogen from the molecular ion, which is in line with a typical property of cyclic azo-compounds.[8] The presence of an azo-group is also indicated by the shape of the aromatic multiplet in the n.m.r. spectra: in fact, the proton in the 8-position resonates at lower field than the other protons of the condensed aryl ring; significantly, it is not so for 1*H*-4,1,2-benzothiadiazines (4a—c) and (5a—c). As it may be seen on examining the data in Table 3, the u.v. spectra provide an additional criterion for differentiating between the various kinds of products. Further support to some of the above formulations was achieved by ^{13}C n.m.r. spectroscopy; thus, the singlet at δ 71.0 in the case of (3b) is in accord with an sp^3-hybridised carbon attached to heteroatoms, while the most significant signal in the spectrum of (4a) is the triplet at δ 41.8 due to the CH_2CN grouping.

TABLE 1

Preparation of hydrazonyl chlorides (2) [a]

Compound	Yield (%)	M.p. (°C) [recrystallization solvent]	Eluant
(2a)	54	63—64 [n-Pentane]	n-Hexane–diethyl ether (2 : 1)
(2b)	59	*b*	Benzene–ethyl acetate (9 : 1)
(2c)	30	65—66 [n-Pentane]	n-Hexane–diethyl ether (3 : 1)
(2d)	45	107—108 [Di-isopropyl ether]	Di-isopropyl ether–diethyl ether (4 : 1)
(2e)	37	122—123 [Ethanol]	Di-isopropyl ether

[a] All compounds listed gave correct i.r. and n.m.r. spectra, which are not reported for the sake of brevity. [b] Undistilled oil, purity >95% (n.m.r.).

TABLE 2

Treatment of hydrazonyl chlorides (2) with triethylamine

Compound	Time/h	Products [a]	Yield (%)	Eluant
(2a)	26	(3a)	70	n-Hexane–diethyl ether (2 : 1)
		(6a)	7	
(2b)	30	(3b)	63	n-Hexane–diethyl ether (2 : 1)
		(6b)	6	
(2c)	24	(4c)	36	n-Hexane–diethyl ether (3 : 1)
		(3c)	33	
		(5c)	15	
(2d)	5	(5a)	42	Di-isopropyl ether
		(4a)	19	
(2e)	4	(5b)	22	Di-isopropyl ether
		(4b)	19	
		(7)	12	
(2f) [b]	5	(5c)	43	Di-isopropyl ether
		(4d)	15	

[a] In order of elution. [b] See text.

Chemical evidence in agreement with the structures (3a—c), (4c), and (5c) was obtained on treating these esters with sodium hydroxide in ethanol. The reaction

TABLE 3

Physical and spectral data of heterocyclic compounds (3), (4), (5), (6), and (7) [a]

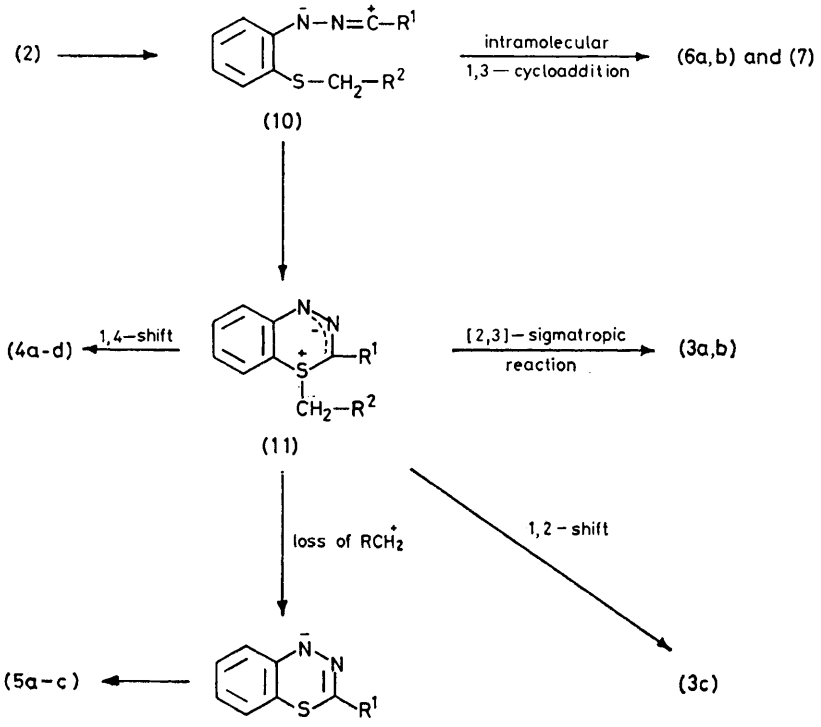
Compound	M.p. or b.p. (°C) [recrystallisation solvent]	$\nu_{max.}$ (Nujol)/cm^{-1}	$\lambda_{max.}$(ε) (Ethanol)/nm	δ($CDCl_3$)
(3a)	B.p. 145—150/0.1 mmHg [b]	1 730	437 (18 000), 421 (16 300), 298 (5 800), 291 (5 600)	1.13 (3 H, t), 3.00 and 3.17 (2 H, AB part of ABX system, J_{AB} 14 Hz, $J_{AX} = J_{BX}$ = 6 Hz), 4.16 (2 H, q), 5.0—5.4 (2 H, m), 5.7—6.3 (1 H, m), 7.2—7.5 (3 H, m), 7.9—8.1 (1 H, m)
(3b) [c]	B.p. 145—150/0.1 mmHg [b]	1 730	437 (19 800), 421 (18 100), 298 (6 100), 291 (5 800)	1.13 (3 H, t), 1.86 (3 H, s), 2.98 and 3.18 (2 H, AB system, *J* 14 Hz), 4.14 (2 H, q), 4.8—5.0 (2 H, m), 7.2—7.5 (3 H, m), 7.9—8.1 (1 H, m)
(3c)	B.p. 155—160/0.1 mmHg [b]	1 720	438 (15 400), 422 (13 900), 298 (5 700), 291 (5 500)	1.07 (3 H, t), 3.48 and 3.70 (2 H, AB system, *J* 14 Hz), 4.10 (2 H, q), 7.2—7.5 (8 H, m), 7.9—8.1 (1 H, m),
(4a) [d]	132 [e] (Di-isopropyl ether)	1 690	417 (1 600), 274 (15 600)	2.48 (3 H, s), 4.61 (2 H, s), 6.7—7.4 (4 H, m)
(4b)	151 [e] (Ethanol)	1 640	429 (1 300), 274 (15 000)	4.60 (2 H, s), 6.8—7.7 (7 H, m), 8.0—8.2 (2 H, m)
(4c)	87 [e] (Di-isopropyl ether)	1 700	423 (1 700), 266 (15 500)	1.36 (3 H, t), 4.47 (2 H, q), 5.03 (2 H, s), 6.5—7.1 (4 H, m), 7.25—7.6 (5 H, m)
(4d) [f]	101 [e] (Di-isopropyl ether)	1 715	393 (850), 265 (11 700)	1.36 (3 H, t), 4.33 (2 H, q), 4.61 (2 H, s), 6.7—7.3 (4 H, m)
(5a)	125 [g] (Di-isopropyl ether)	3 370 1 680	445 (1 900), 271 (15 400)	2.40 (3 H, t), 6.4—6.6 (1 H, m), 6.8—7.2 (3 H, m), 7.6 (1 H, br s)
(5b)	134 [g] (Di-isopropyl ether)	3 370 1 650	469 (2 550), 277 (18 500)	6.4—6.6 (1 H, m), 6.8—7.6 (6 H, m), 7.7 (1 H, br s), 7.9—8.1 (2 H, m)
(5c)	*h*	*h*	419 (1 050), 265 (14 800)	*h*
(6a)	104 [i] (n-Hexane)	1 720		1.37 (3 H, t), 2.8—3.6 (4 H, overlapping m), 4.2—4.7 (3 H, overlapping m), 6.7—7.3 (3 H, m), 7.5—7.7 (1 H, m)
(6b)	98 [i] (n-Hexane)	1 715		1.36 (3 H, t), 1.49 (3 H, s), 3.16 (2 H, s), 2.88 and 3.25 (2 H, AB system, *J* 13 Hz), 4.32 (2 H, q), 6.7—7.3 (3 H, m), 7.5—7.7 (1 H, m)
(7)	130 [i] (Ethanol)	1 650	317 (4 900), 261 (16 800), 235 (18 100)	4.27 (2 H, s), 7.2—7.7 (6 H, m), 7.9—8.1 (1 H, m), 8.3—8.5 (2 H, m)

[a] Correct molecular peaks were found in the mass spectra. [b] Orange oil. [c] ^{13}C N.m.r.($CDCl_3$): δ 13.8(q), 23.7(q), 42.4(t), 62.5(t), 71.0(s), 117.0(t), 118.8(s), 126.6(d), 127.2(d), 130.3(d), 131.3(d), 139.2(s), 141.7(s), 168.2(s). [d] ^{13}C N.m.r.($CDCl_3$): δ 25.1(q), 41.8(t), 112.3(d), 114.6(s), 118.3(s), 126.3—128.5, 137.8(s), 142.8(s), 191.5(s). [e] Orange crystals. [f] ^{13}C N.m.r.($CDCl_3$): δ 14.1(q), 41.9(t), 62.9(t), 112.3(d), 114.7(s), 118.7(s), 126.3—128.8, 138.1(s), 161.0(s). [g] Deep red crystals. [h] See ref. 3. [i] Pale yellow crystals.

gave the carboxylic acids (8a) and (8b) in the case of (4c) and (5c), while resulting in compounds (9a—c) in the case of (3a—c); the latter products are clearly formed through a sequence involving hydrolysis, decarboxylation, and prototropic shift.* It is worthwhile to note that, on the basis of the available evidence, the formulae (4a—c) appear to be unquestionable in spite of the absence of i.r. absorption due to the CN group.

We have reported in a previous paper [3] that the reaction of (2f) with triethylamine gave, together with a major quantity of (5c), a minor product which was formulated as 2-ethoxycarbonyl-4*H*-[1,2,4]triazolo-[5,1-*c*][1,4]benzothiazine on the basis of the elemental analysis and the i.r. and ^{1}H n.m.r. spectra. In the light of the results later obtained on studying the hydrazonyl chlorides (2a—e), this structural assignment has been reconsidered and more information has been acquired on recording u.v., mass, and ^{13}C n.m.r. spectra. All spectral properties (see Table 3) parallel very closely those of compounds (4a—c). Consequently, the minor product deriving from (2f) has to be re-formulated as 1-cyanomethyl-3-ethoxycarbonyl-1*H*-4,1,2-benzothiadiazine (4d).

The behaviour of the hydrazonyl chlorides (2) can be rationalised by means of the mechanistic picture given in the Scheme. It involves the preliminary formation of the nitrile imines (10) followed by intramolecular attack of the thioether function to the electron-deficient carbon of the 1,3-dipole, thus generating the unusual sulphur ylides (11).† The latter intermediates evolve to stable compounds by moving the R^2CH_2 moiety according to one (or more) of the following competitive processes: (*i*) 1,2-shift from sulphur to carbon, (*ii*) 1,4-shift from sulphur to nitrogen, and (*iii*) loss of a cationic fragment (the fate of which has not been established). The intimate mechanism of the former process, however, is not the same in all cases: in fact, while the migration of the benzyl group is a true 1,2-shift, the formation of (3a,b) is better interpreted as a [2,3]-sigmatropic change involving a five-membered cyclic transition state.‡ While the pathways (*i*) and (*iii*) have precedent in rearrangements of sulphur ylides,[10] pathway (*ii*) has to be related to the particular structure of (11), which possess a diaza-allyl anion moiety. It is to be noted that the tricyclic compounds (6a,b) and (7) arise from the same nitrile imine intermediates *via* an intramolecular 1,3-dipolar cycloaddition to the multiple bond of the R^2 substituent, similar to that previously observed for other functionalised nitrile imines.[1-4] However, the behaviour of (10a,b) is markedly different from that of the corres-



SCHEME

* Compound (9a) isomerises readily under basic conditions so that it was actually obtained along with (9d) in the reaction of (4a) with sodium hydroxide.

† An alternative possibility is that the benzothiadiazine skeleton is formed without the intermediacy of nitrile imines, but directly from the starting hydrazonyl chlorides through a nucleophilic displacement of the halogen by the neighbouring thioether group. This hypothesis must be discarded because control experiments showed that compounds (2) do not react in the absence of triethylamine.

‡ According to a general feature of the pericyclic reactions,[9] this rearrangement should encounter a rather moderate enthalpy barrier, which may justify the lack of other modes of evolution for the *S*-allyl-substituted ylides.

ponding *N*-(2-allyloxyphenyl) nitrile imines, which underwent exclusively intramolecular cycloaddition to the olefinic bond;[4] such a pathway, in the case of (10a,b), is overwhelmed by the concurrent sulphur participation.

In conclusion, the results described here reveal a great ability of the thioether group to capture, at least intramolecularly, the nitrile imine function. Considering that divalent sulphur is known to react easily with carbenes,[10] these results are of interest with respect to the question of the carbenic nature of nitrile imines. That the latter substrates could, in principle, behave as azocarbenes was envisaged a long time ago,[11] but little evidence of this has hitherto been available in the chemical literature.[6,12] Theoretical calculations [13] suggest that, in the presence of nucleophilic species, the linear nitrile imine function could be forced to assume a bent carbene-like form which permits a more favourable orbital interaction; this may be the case for the intramolecular reaction presented here.

EXPERIMENTAL

M.p.s were taken on a Büchi apparatus and are uncorrected. ^{1}H and ^{13}C N.m.r. spectra were obtained on Varian HA-100 and XL-100 instruments, respectively; all chemical shifts are given in p.p.m. from internal $SiMe_4$. I.r. and u.v. spectra were recorded on Perkin-Elmer 377 and Cary 219 spectrophotometers, respectively.

Satisfactory elemental analyses were obtained for all new compounds with the exception of (2b) (see Table 4). Compounds (1a),[14] (1b),[15] (1c),[16] and (1d) [3] were prepared according to literature methods. Treatment of these amines with hydrogen chloride in ethereal solution provided the corresponding hydrochlorides, which were used to synthesise (2a—e).

TABLE 4

Elemental analyses

	Required (%)			Found (%)		
Compound	C	H	N	C	H	N
(2a)	52.3	5.1	9.4	52.5	5.3	9.5
(2c)	58.5	4.9	8.0	58.6	4.8	7.8
(2d)	49.4	3.8	15.7	49.7	3.9	15.6
(2e)	58.3	3.7	12.7	58.3	3.8	12.5
(3a)	59.5	5.4	10.7	59.4	5.5	10.7
(3b)	60.8	5.9	10.1	60.6	6.0	9.9
(3c)	65.4	5.2	9.0	65.3	5.4	8.7
(4a)	57.1	3.9	18.2	56.9	3.9	18.0
(4b)	65.5	3.8	14.3	65.6	4.1	14.3
(4c)	65.4	5.2	9.0	65.4	5.4	8.7
(5a)	56.2	4.2	14.6	56.3	4.1	14.6
(5b)	66.1	4.0	11.0	66.3	3.8	11.1
(6a)	59.5	5.4	10.7	59.3	5.5	10.5
(6b)	60.8	5.9	10.1	61.0	5.8	9.9
(7)	65.5	3.8	14.3	65.5	3.9	14.1
(8a)	49.5	3.1	14.4	49.3	3.3	14.5
(8b)	63.4	4.3	9.9	63.6	4.2	9.8
(9a)	63.1	5.3	14.7	63.2	5.4	14.5
(9b)	64.7	5.9	13.7	64.5	6.0	13.6
(9c)	70.0	5.0	11.7	70.2	5.0	11.5
(9d)	63.1	5.3	14.7	63.0	5.3	14.6

Preparation of Hydrazonyl Chlorides (2a, b, d, e).—A solution of sodium nitrite (18 mmol) in water (20 ml) was added to a suspension of the hydrochloride of amine (1) (15 mmol) in 1N hydrochloric acid (30 ml) with stirring and cooling at −5 °C. The mixture was adjusted to pH 4 by sodium acetate and the chloro-compound (15 mmol) in methanol (15 ml) was added with vigorous stirring. After 2 h stirring at room temperature, the mixture was extracted with ether, and the organic layer was dried over sodium sulphate and evaporated. The residue was chromatographed on a silica gel column to give the desired hydrazonyl chloride (2) (see Table 1).

Preparation of Hydrazonyl Chloride (2c).—A mixture containing the hydrochloride of amine (1c) (8 mmol), 1N hydrochloric acid (16 ml), methanol (20 ml), and ethyl 2-chloroacetoacetate (16 mmol) was cooled at −5 °C. Sodium nitrite (10 mmol) in water (15 ml) was added with vigorous stirring and cooling. The mixture was adjusted to pH 4 with sodium acetate and stirred at room temperature for 3 h. The aqueous layer was decanted off and the remaining paste was dissolved in ether. The ethereal solution was washed with water, dried over sodium sulphate, and evaporated, and the residue was chromatographed on a silica gel column to give (2c) (see Table 1).

Treatment of Hydrazonyl Chlorides (2) *with Triethylamine.*—A solution of (2) (5 mmol) and triethylamine (20 mmol) in dry benzene (500 ml) was refluxed for the time given in Table 2. The mixture was washed several times with water, dried over sodium sulphate, and evaporated. The residue was chromatographed on a silica gel column to afford the products indicated in Table 2. Physical and spectral properties are collected in Table 3.

Treatment of (3a) *with Sodium Hydroxide.*—Compound (3a) (0.21 g) was dissolved in 0.1N ethanolic sodium hydroxide (80 ml) and left at room temperature for 4 h. The solution was neutralized with aqueous hydrochloric acid, the solvent was partly removed under reduced pressure, and the residue was taken up with water and ether. The organic layer was dried over sodium sulphate and evaporated. The residue was chromatographed on a silica gel column with hexane–diethyl ether (1 : 1) as eluant. First fractions gave (9a) (55 mg), b.p. 110—115 °C/0.1 mmHg; $\nu_{max.}$(film) 3 280 cm^{-1}; $\delta(CDCl_3)$ 3.0—3.3 (2 H, m), 5.0—5.3 (2 H, m), 5.5—6.1 (1 H, m), 6.5—6.7 (1 H, m), 6.8—7.2 (3 H, m), and 7.5 (1 H, broad s); $\lambda_{max.}$(ethanol) 310 (ε 2 300) and 243 nm (17 000).

Further fractions gave (9d) (50 mg), m.p. 80 °C (from di-isopropyl ether); $\nu_{max.}$(Nujol) 3 280 cm^{-1}; $\delta(CDCl_3)$ 2.87 (3 H, d, *J* 5 Hz), 6.2—6.5 (2 H, m), 6.5—6.8 (1 H, m), 6.9—7.3 (3 H, m), and 7.5 (1 H, br s); $\lambda_{max.}$(ethanol) 318 (2 600) and 257 (20 200) nm.

Treatment of (3b) *with Sodium Hydroxide.*—Compound (3b) (0.26 g) was treated with sodium hydroxide according to the above procedure (5 h). The product was (9b) (0.15 g), b.p. 110—115 °C/0.1 mmHg; $\nu_{max.}$(film) 3 280 cm^{-1}; $\delta(CDCl_3)$ 1.78 (3 H, s), 3.18 (2 H, s), 4.97 (2 H, s), 6.5—6.8 (1 H, m), 6.9—7.3 (3 H, m), and 7.4 (1 H, br s); $\lambda_{max.}$(ethanol) 305 (ε 4 100) and 241 nm (23 100).

Treatment of (3c) *with Sodium Hydroxide.*—Compound (3c) (45 mg) was treated with sodium hydroxide as described for (3a) (1 h) to give (9c) (23 mg), m.p. 96 °C (from di-isopropyl ether); $\nu_{max.}$(Nujol) 3 280 cm^{-1}; $\delta(CDCl_3)$ 3.70 (2 H, s), 6.5—6.7 (1 H, m), and 6.8—7.4 (9 H, overlapping signals); $\lambda_{max.}$(ethanol) 309 (ε 2 900) and 242 nm (21 400).

Treatment of (4c) *and* (5c) *with Sodium Hydroxide.*—A solution of (4c) (0.13 g) in 0.1N ethanolic sodium hydroxide (40 ml) was left at room temperature for 3 h. After partial removal of the solvent under reduced pressure, the mixture was acidified with aqueous hydrochloric acid and extracted with chloroform. The organic layer was dried over sodium sulphate and evaporated. The residue was treated with di-

isopropyl ether and filtered to afford the acid (8a) (65 mg) as red crystals, m.p. 118—120 °C (decomp.); $\nu_{max.}$(Nujol) 3 000—2 500 and 1 670 cm^{-1}; $\delta(CDCl_3)$ 4.94 (2 H, s), 5.6 (1 H, br s), 6.4—6.7 (1 H, m), 6.8—7.1 (3 H, m), and 7.2—7.5 (5 H m).

Under the same conditions, compound (5c) gave acid (8b) (55%) as red crystals, m.p. 201—203 °C (decomp.); $\nu_{max.}$ (Nujol) 3 250, 3 000—2 500, and 1 680 cm^{-1}; $\delta(C_3D_6O)$ 4.7 (1 H, broad s), 7.3—8.1 (4 H, m), and 13.3 (1 H, br s).

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