A new synthesis of aryl isothiocyanates: carbon disulfide as a dipolarophile. The reaction of (4,5,6,7-tetrahydro-2*H*-1,2,3-benzotriazolium-1-yl)arylaminide 1,3-dipoles with carbon disulfide: synthesis, kinetics, mechanism. Azolium 1,3-dipoles

Richard N. Butler * and Leonie M. Wallace

Chemistry Department, National University of Ireland, Galway (NUIG), Galway, Ireland

A new synthesis of aryl isothiocyanates in which the aryl nitrogen moiety ultimately comes from an arylhydrazine is described. Treatment of (4,5,6,7-tetrahydro-2*H*-1,2,3-benzotriazolium-1-yl)arylaminide 1,3-dipoles (derived from cyclohexane-1,2-dione bis(arylhydrazones)) with carbon disulfide in acetone at ambient temperatures gives high yields of aryl isothiocyanates and 2-aryl-4,5,6,7-tetrahydro-2*H*-1,2,3-benzotriazole as a leaving group. The kinetics and mechanism of the reaction were investigated. The mechanism involves a polar cycloaddition of the triazolium-aminide to the CS₂ generating a partially ring-closed intermediate which fragments to the aryl isothiocyanate. Carbon disulfide is not a kinetic superdipolarophile with (1,2,3-benzotriazolium-1-yl)aminide 1,3-dipoles.

Aryl isothiocyanates are normally synthesized from thermal decomposition of monoarylthioureas or more commonly from the reactions of primary aryl amines with carbon disulfide, thiophosgene or reagents derived from thiophosgene.[1,2] The necessary dehydrosulfurisation of the thiocarbamic acid intermediates has been achieved with reagents such as hydrogen peroxide[3] or dicyclohexylcarbodiimide in pyridine.[4] Treatment of aryl isocyanides with dibenzoyl disulfide has provided another route to aryl isothiocyanates.[5] New routes are of continuing interest and recently a new synthesis *via* arylimino-1,2,3-dithiazoles has been reported.[6] Herein we describe a new, unexpected route to aryl isothiocyanates using carbon disulfide where the aryl-nitrogen group comes ultimately from an aryl hydrazine and no unattractive secondary reagents are involved.

Results and discussion

The triazolium-1-ylarylaminides **2** (Scheme 1) are readily obtained[7,8] by oxidation of the bis(arylhydrazone)s **1** which are themselves available from condensation of 1,2-diketones with arylhydrazines. While common 1,2-diaryldiketones, such as benzil, could be used we found that cyclohexane-1,2-dione derivatives gave particularly easy reactions and hence we used the substrates **2**. On simple stirring of compounds **2** with carbon disulfide in acetone at ambient temperatures surprisingly the aryl isothiocyanates **4** were obtained in high yields (Table 1), along with the 2-aryl-4,5,6,7-tetrahydro-2*H*-1,2,3-benzotriazoles **5** and sulfur. The yields of aryl isothiocyanates began to decline with the incorporation of electron


a Ar = Ph
b Ar = *p*-MeC₆H₄
c Ar = *m*-MeC₆H₄
d Ar = *o*-MeC₆H₄
e Ar = *p*-MeOC₆H₄
f Ar = *p*-ClC₆H₄
g Ar = *p*-CNC₆H₄
h Ar = *p*-NO₂C₆H₄

Scheme 1

J. Chem. Soc., Perkin Trans. 1, 2000, 4335–4338 **4335**
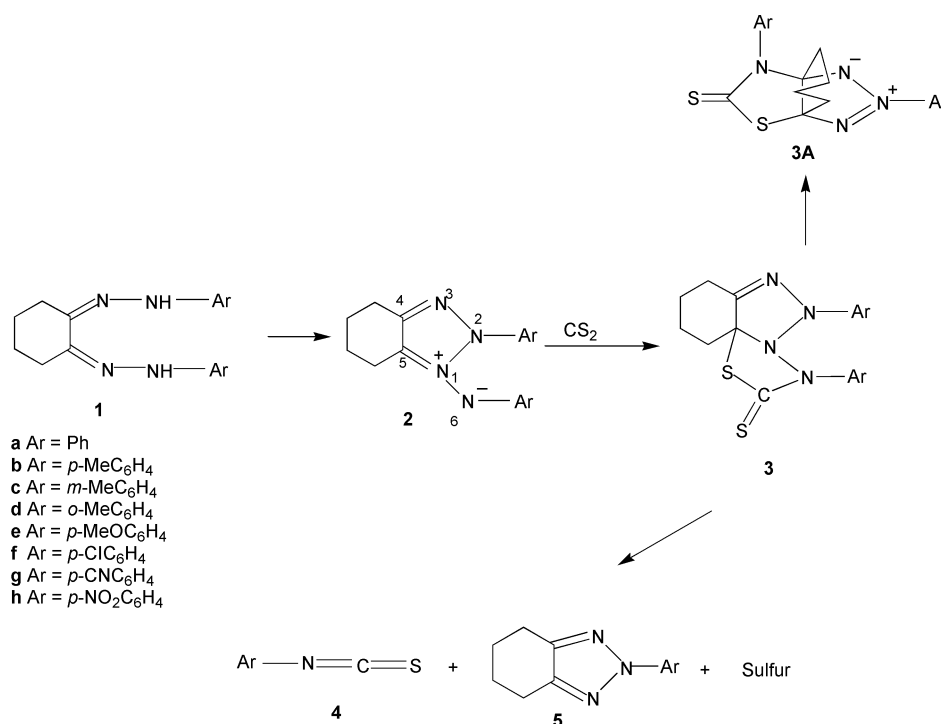
Table 1 Products from the reaction of **2** with CS_2

No.	Products Compound	Mp/°C	Yield (%)	$\delta_C{}^e$ (ppm)	ν^e/cm^{-1}	Compound	Mp/°C	Yield (%)
1	**4a**	Oil	89	135.0	2083	**5a**	92–94	90
2	**4b**	25–27[a]	93	134.4	2054	**5b**	120–121	90
3	**4c**	Oil	80	134.7	2106	**5c**	56–58	84
4	**4d**	Oil	94	134.9	2089	**5d**	Oil	84
5	**4e**	Oil	80	133.8	2108	**5e**	75–77	96
6	**4f**	40–42[b]	65	136.7	2034	**5f**	120–121	61
7	**4g**	119–120[c]	25	139.7	2137	**5g**	175–177	71
8	**4h**	109–110[d]	17	140.3	2104	**5h**	208–210	75

[a] Lit.,[19] mp 25–26 °C. [b] Lit.,[19] mp 42–44 °C. [c] Lit.,[19] mp 119–123 °C. [d] Lit.,[19] mp 110–112 °C. [e] For –N=C=S unit.

withdrawing groups in the aryl ring and with *p*-CN and *p*-NO$_2$ substituents the yields were particularly low (Table 1, entries 7 and 8). From our previous studies[7,8] of the behaviour of the 1,3-dipoles of type **2** we might expect a pathway involving a cycloaddition to give the initial cycloadduct **3**. Normally this would rapidly rearrange *in situ* to the more stable structure **3A** and we have isolated structures analogous to this for other cumene-type dipolarophiles. In principle structures **3** and **3A** could fragment to the products **4**, **5** and sulfur but because of the stability of structures related to **3A** where the moiety S=C–N–Ar was present we would expect products **3A** to be stable and readily detected. Structures such as **3A** were not encountered in the present reactions. They are easily detectable because of the quaternary bridgehead carbon-13 signals. In a number of cases the reactions were pursued at temperatures down to −60 °C but no intermediates were detected and the products were rapidly formed in similar high yields even at −60 °C.

(1)

6 $\xrightarrow[- CS_2]{CS_2}$ **7**
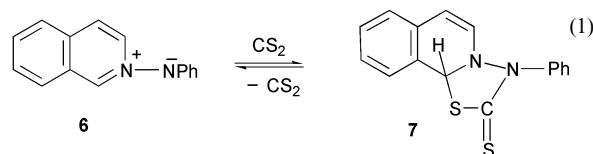
The reaction of CS_2 with the isoquinolinium-2-ylaminide **6** [reaction (1)] is well known,[9–11] and the contrast in its behaviour with the 1,3-dipoles **6** and the triazolium-aminide 1,3-dipoles **2** is significant and illustrates how different may be the reactions of azolium and azinium 1,3-dipoles. The cycloadducts **7** are stable compounds which have been extensively used[9–11] as storage repositories for the dipoles **6**. These can be readily thermally released from the cycloadducts **7** which do not fragment to aryl isothiocyanates.[9–11]

Cycloadducts from azolium-*N*-aminide 1,3-dipoles are usually unstable and the chemistry of azolium-*N*-aminide 1,3-dipoles is dominated by secondary reactions, usually rearrangements, after the initial cycloaddition.[7] The marked difference in the behaviour of the dipoles **2** and **6** with carbon disulfide and the fact that no cycloadduct or rearranged cycloadduct was isolated from the reaction with the dipoles **2** made a mechanistic study of this unexpected reaction fully warranted.

Kinetics and mechanism

(a) Solvent effects and activation parameters. We have previously reported[12–14] detailed kinetic studies of reactions of 1,3-dipoles of general type **2** [also with Ar groups replacing (CH$_2$)$_4$] with alkene and alkyne dipolarophiles. The reactions were found to be stereospecific concerted 1,3-dipolar cycloadditions involving transition state mixing of the dipole HOMO with the dipolarophile LUMO. The kinetics of the present reaction with CS_2 were measured using UV spectra by following the disappearance of the dipoles **2** at 400 nm (**2h**, 460 nm) under

Table 2 Second-order rate constants for the reaction of **2** with CS_2 (at λ 400 nm)

No.	Substrate	Solvent (T/°C)	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}	
1	**2a**	EtOAc (27)	3.9	$\Delta E^{\ddagger} = 32$ kJ mol^{-1}
2	**2a**	EtOAc (37)[a]	8.8	$\Delta H^{\ddagger} = 30$ kJ mol^{-1}
3	**2a**	EtOAc (51)	11.1	$\Delta S^{\ddagger} = -192$ J K^{-1} mol^{-1}
4	**2a**	EtOAc (60)	15.9	
5	**2a**	MePh (37)[a]	2.5	
6	**2a**	MeOPh (37)[a]	8.0	
7	**2a**	MeAc (37)[a]	25.1	
8	**2a**	MeCN (37)[a]	63.1	
9	**2b** (*p*-Me)	MeAc (37)	10.6	
10	**2f** (*p*-Cl)	MeAc (37)	17.5	
11	**2h** (*p*-NO$_2$)[b]	MeAc (37)	10.1	
12	**2e** (*p*-MeO)	MeAc (37)	0.85	

[a] Data for Fig. 1, Line A, E_T(30) values from ref. 16. [b] Wavelength for kinetic measurements 460 nm.

pseudo-first-order conditions with excess carbon disulfide. Plots of the k_1 values thus obtained against concentration of CS_2 gave second-order rate constants k_2 for the reactions (Table 2). Arrhenius data measured in the range 27 to 60 °C gave $\Delta E^{\ddagger}$ 32 kJ mol^{-1}, $\Delta H^{\ddagger}$ 30 kJ mol^{-1} and $\Delta S^{\ddagger}$ −192 J K^{-1} mol^{-1}. The low activation energy reflects an extreme ease of reaction which is also a synthetic feature of the process. The negative entropy value is compatible with either a concerted or a two-step cycloaddition.[15a] The influence of solvent polarity on the rates proved significant (Fig. 1). Concerted cycloadditions are striking for their insensitivity to solvent polarity.[15b] Fig. 1 shows the absence of any influence of solvent polarity ($E_{T(30)}$ values[16]) on the rates of the cycloaddition of the dipoles such as **2** with acrylonitrile (line B).[12] The reaction of the 1,3-dipoles **2** with CS_2 herein was significantly affected by solvent polarity (line A) (Table 2) and the process appears to be different to that operating with alkene and alkyne dipolarophiles. The progressive increase in rate from toluene to acetonitrile by over a factor of 30 suggests a more polar transition state in the reaction by comparison with the rates for acrylonitrile. However for a reaction involving a dipolar or diradical intermediate such as **9**, *i.e.* a two-step cycloaddition, the influence of solvent polarity on the rates might be expected[15b] to be at least an order of magnitude higher than that observed. Hence while a highly polar transition state is indicated a key question is whether the S(8)–C(5) bond is well developed in the transition state and whether a cycloaddition to the adduct **3** actually takes place.

(b) Substituent effects. Substituents in the *N*-aryl rings of dipoles of type **2** show a rare inverted V shaped Hammett plot in cycloadditions with alkyne and alkene dipolarophiles,[12,13] and both electron withdrawing and donating groups inhibit the rates. This arises because of a special structural effect in the
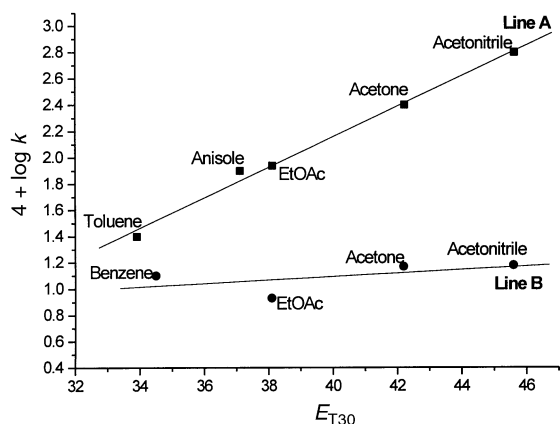
Fig. 1 Solvent effects for the reaction of **2a** with CS$_2$ (line A) and for a similar 1,3-dipole with acrylonitrile (line B, from reference 12).

1,3-dipoles **2** where the exocyclic 1-*N*-aryl moiety is twisted with the phenyl ring orthogonal to the plane of the triazole ring due to steric effects from the groups at C-5 and N-2. Hence in the ground state the structures **2** are not classical 1,3-dipoles because both ends of the dipole are not conjugated.[13] A rotation of the 1-*N*-aryl group to make it co-planar with the triazole ring is required before the molecules can enter a normal 1,3-dipolar cycloaddition.[13] In the ground state the positive terminus of the 1,3-dipole resides in the triazolium ring and this is stabilized by electron donating substituents in the 2-*N*-aryl group while the negative terminus of the dipole resides on the exocyclic N(6) atom and this is stabilized by electron withdrawing substituents in the aryl group. In the twisted ground state of the molecule electron-donating and electron-withdrawing groups can separately stablise each end of the dipole thereby both increasing the activation barrier and giving a rare phenomenon where electron donating and withdrawing substituents slow the reaction rate. We have previously discussed these effects in detail.[12,13] The influence of *N*-aryl substituents on the rates can therefore indicate whether or not both ends of the 1,3-dipole are involved in the reaction.

The influences of a number of substituents in the aryl group on the reaction with CS$_2$ are shown in Table 2. The results were similar to those for the dipolarophiles dimethyl acetylenedicarboxylate[13] and acrylonitirile[12] and both electron withdrawing and donating groups inhibited the reaction. Inhibition of the rates by electron-donating substituents is significant. It rules out a simple nucleophilic addition to give **9** and indicates that the C(5)–S(8) bond is significantly developed in the transition state. The similarity in the substituent effects to those of alkyne and alkene dipolarophiles where rearranged cycloadducts have been isolated points to the involvement of both termini of the dipole but the solvent polarity data in Fig. 1 show that the reactions are significantly different. We suggest a polar transition state **10** (path B, Scheme 2) where the N–C bond is fully formed while the S–C bond is only partially formed as the fragmentation to the products sets in. Destabilisation of the species **10** by the influence of electron withdrawing groups at the positive triazolium terminus could cause a more rapid and less controlled fragmentation leading to decomposition and lesser yields of aryl isothiocyanates. It seems unlikely that the adduct **3** is fully formed. If it were, a rearrangement to **3A** or a reversal to dipole and CS$_2$, as occurs for compound **7**, would be the most likely outcome.

(c) CS$_2$ *versus* alkyne dipolarophiles. The rate constant for the reaction of the dipole **2a** with dimethyl acetylenedicarboxylate (DMAD) in acetone at 37 °C is 42×10^{-3} dm^3 mol^{-1} s^{-1} while that for CS$_2$ is 25.1×10^{-3} dm^3 mol^{-1} s^{-1} (Table 2). Hence, unlike thio-ketones[17] and thio-esters[18] carbon disulfide is not a superdipolarophile with these 1,3-dipoles. Removing a CO$_2$Me
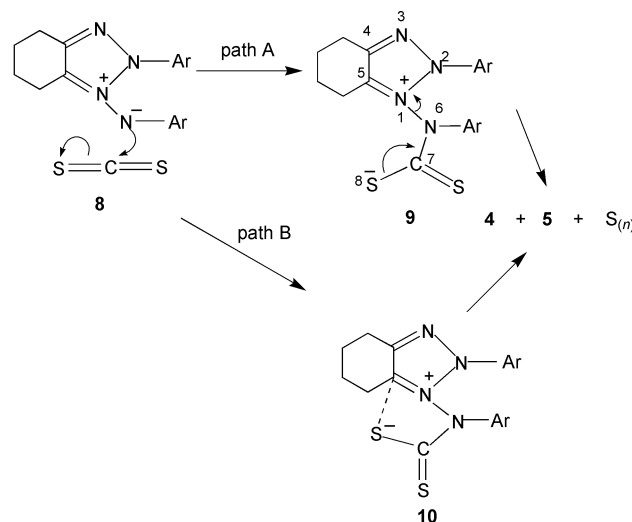
Scheme 2

group from DMAD reduces the rate and for methyl propiolate we measured a rate constant of 5.4×10^{-3} dm^3 mol^{-1} s^{-1}. Hence this reactive alkyne is about five times slower than CS$_2$ and would be a good candidate to trap any possible intermediates which might build up in the reaction with CS$_2$. Synthetic reactions were carried out with the dipole **2a** in a competitive situation with 15 molar excesses of CS$_2$ and methyl propiolate (Scheme 3) in dry acetone at ambient temperature. No inter-
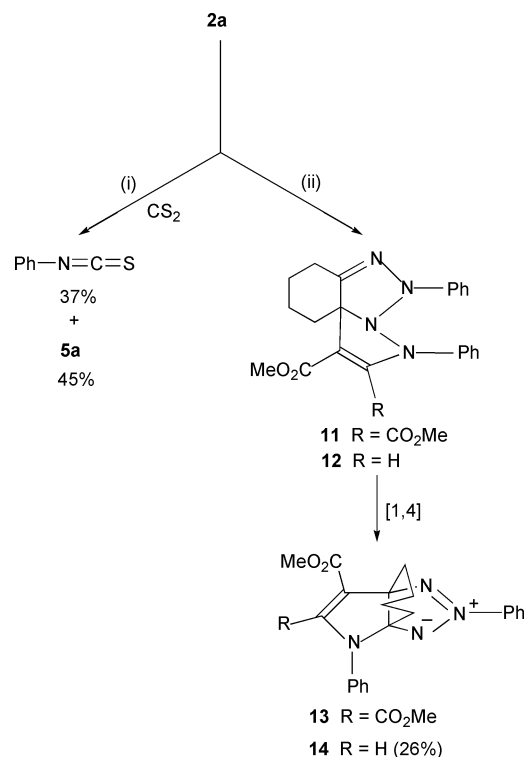
Scheme 3 *Reagents*: (i) CS$_2$ (15 mol); (ii) H–C≡C–CO$_2$Me (15 mol).

mediates were trapped by the methyl propiolate. Instead competitive reactions gave rise to a product mixture of compounds **14**, **5a** and phenyl isothiocyanate as well as some gums and sulfur (Scheme 3). This was not unexpected as it is unlikely that the species **10** could be trapped although an intermediate such as **9** should have been trapped and given rise to different products. Compound **13** is the product from the reaction of **2a** with DMAD and is formed *via* a cycloaddition–rearrangement sequence which we have described previously.[7,13] Compound **14**, an analogue, can be readily identified from its proton

and carbon-13 NMR spectra. We will comment on the regiochemistry of the reaction in a future work on regiochemistry with unsymmetrical alkynes and alkenes.

Experimental

Mps were measured on an Electrothermal apparatus. IR spectra were measured with a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. NMR spectra were measured on a JEOL LAMBDA 400 MHz instrument with tetramethylsilane as internal reference and deuteriochloroform as solvent; J values are given in Hz. Microanalyses were measured on a Perkin-Elmer model CHN analyser. The substrates **2** were prepared as previously described.[7,8] The following are typical examples for the preparation of compounds **4** and **5**.

(a) A solution of compound **2a** (0.29 g, 1 mmol) in dry acetone (3 ml) was treated with a 15 molar excess of carbon disulfide (0.9 ml, 15 mmol). The solution was stirred at ambient temperature for 30 min. The solvent was evaporated under reduced pressure. The residue in dichloromethane (3 ml) was placed on a silica gel-60 column (230–400 mesh ASTM). The products were eluted using a gradient mixture (1:0 to 1:1 v/v) of petroleum-spirit (bp 40–60 °C): CH_2Cl_2. The first product off the column in petroleum-spirit was phenyl isothiocyanate **4a** an oil (0.13 g, 89%); v_{max} (mull) 2083 cm^{-1} (N=C=S); δ_H(CDCl$_3$) 7.21–7.46 (5H, m, H$_{arom}$); δ_C(CDCl$_3$) 131.1, 125.7, 129.4, 127.2 (C-1, C-2, C-3, C-4) and 135.0 (N=C=S); followed by 2-phenyl-4,5,6,7-tetrahydro-2H-1,2,3-benzotriazole **5a**, a beige solid (0.18 g, 90%), mp 92–94 °C (from acetone) (Found: C, 72.4; H, 6.5; N, 21.1. C$_{12}$H$_{13}$N$_3$ requires C, 72.3; H, 6.6; N, 21.1%); v_{max} (mull) 1593 cm^{-1} (C=N); δ_H(CDCl$_3$) 1.84 (4H, m, cyclohexyl methylenes (-CH$_2$-CH$_2$-)), 2.77 (4H, m, cyclohexyl methylenes (-CH$_2$-C=N-)), 7.21–7.43 (3H, m, H$_m$, H$_p$ of 2-N-Ph) and 7.97–8.00 (2H, d, H$_o$ of 2-N-Ph); δ_C(CDCl$_3$) 21.7, 22.9 (CH$_2$)$_4$, 145.4, 118.0, 129.0, 126.3 (C-1′, C-2′, C-3′, C-4′ resp. of 2-N-Ph) and 139.9 (C-4 and C-5).

(b) A solution of substrate **2e** (0.35 g, 1 mmol) in dry acetone (3 ml) was treated with a 15 molar excess of carbon disulfide (0.9 ml, 15 mmol). The solution was stirred at ambient temperature for 30 min. The solvent was evaporated under reduced pressure. The residue in dichloromethane (3 ml) was placed on a silica gel-60 column (230–400 mesh ASTM). The products were eluted using a gradient mixture of petroleum-spirit (bp 40–60 °C): CH_2Cl_2 as described. The first product off the column was p-methoxyphenyl isothiocyanate **4e**, an oil (0.13 g, 79%); v_{max} (mull) 2108 cm^{-1} (N=C=S); δ_H(CDCl$_3$) 3.77 (3H, s, OCH$_3$), 6.82 (2H, d, J 8.8, H$_m$) and 7.11 (2H, d, H$_o$); δ_C(CDCl$_3$) 55.5 (OCH$_3$), 123.4, 126.9, 114.8, 158.5 (C-1, C-2, C-3, C-4) and 133.8 (N=C=S); followed by 2-(p-methoxyphenyl)-4,5,6,7-tetrahydro-2H-1,2,3-benzotriazole **5e**, a pale yellow solid (0.22 g, 96%), mp 75–77 °C (from acetone) (Found: C, 67.9; H, 6.8; N, 18.5. C$_{12}$H$_{15}$N$_3$O requires C, 68.1; H, 6.6; N, 18.3%); v_{max} (mull) 1592 cm^{-1} (C=N); δ_H(CDCl$_3$) 1.84 (4H, m, cyclohexyl methylenes (-CH$_2$-CH$_2$-)), 2.76 (4H, m, cyclohexyl methylenes (-CH$_2$-C=N-)), 3.78 (3H, s, OCH$_3$), 6.93 (2H, d, J 9.0, H$_m$ of 2-N-p-C$_6$H$_4$OCH$_3$) and 7.88 (2H, d, H$_o$ of 2-N-p-C$_6$H$_4$OCH$_3$); δ_C(CDCl$_3$) 21.8, 23.0 (CH$_2$)$_4$, 55.4 (p-OCH$_3$), 144.9, 119.5, 114.1, 158.2 (C-1′, C-2′, C-3′, C-4′ resp. of 2-N-p-C$_6$H$_4$OCH$_3$) and 133.9 (C-4 and C-5).

(c) A solution of compound **2g** (0.17 g, 0.5 mmol) in dry acetone (3 ml) was treated with a 15 molar excess of carbon disulfide (0.45 ml, 7.5 mmol). The solution was stirred at ambient temperature for 30 min. The solvent was evaporated under reduced pressure. The residue in dichloromethane (3 ml) was placed on a silica gel-60 column (230–400 mesh ASTM). The products were eluted using a gradient mixture of petroleum-spirit (bp 40–60 °C): CH_2Cl_2 as described. The first product off the column was p-cyanophenyl isothiocyanate **4g**, white needles (0.02 g, 25%), mp 119–120 °C (from petroleum-spirit (bp 40–60 °C)) (Found: C, 60.0; H, 2.3; N, 17.2. C$_8$H$_4$N$_2$S

requires C, 60.0; H, 2.5; N, 17.5%); v_{max} (mull) 2226 (C≡N), 2137 cm^{-1} (N=C=S); δ_H(CDCl$_3$) 7.24 (2H, d, J 8.8, H$_o$) and 7.59 (2H, d, H$_m$); δ_C(CDCl$_3$) 117.9 (C≡N), 136.1, 126.4, 133.6, 110.6 (C-1, C-2, C-3, C-4) and 139.7 (N=C=S); followed by 2-(p-cyanophenyl)-4,5,6,7-tetrahydro-2H-1,2,3-benzotriazole **5g**, a cream solid (0.08 g, 71%), mp 175–177 °C (from acetone) (Found: C, 69.4; H, 5.6; N, 24.6. C$_{13}$H$_{12}$N$_4$ requires C, 69.6; H, 5.4; N, 25.0%); v_{max} (mull) 2224 (C≡N), 1602 cm^{-1} (C=N); δ_H(CDCl$_3$) 1.9 (4H, m, cyclohexyl methylenes (-CH$_2$-CH$_2$-)), 2.8 (4H, m, cyclohexyl methylenes (-CH$_2$-C=N-)), 7.71 (2H, d, J 8.8, H$_m$) and 8.08 (2H, d, H$_o$); δ_C(CDCl$_3$) 21.8, 22.7 (CH$_2$)$_4$, 142.5, 118.1, 133.3, 109.4 (C-1′, C-2′, C-3′, C-4′ resp. of 2-N-p-C$_6$H$_4$CN) and 147.2 (C-4 and C-5).

Kinetics

The rate constants were measured by following the disappearance of the dipole to infinity at the wavelengths shown (Table 2) using a Cary1/Cary3E UV-visible scanning spectrophotometer equipped with an internal timer and a constant temperature cell compartment. Temperatures were accurate to ±0.5 °C. The accuracy of reproduction on the rate constants was ±2.5%. Rates were measured under pseudo-first-order conditions with the dipolarophile present in a molar excess of at least 1000. The pseudo-first-order rate constants k_1 were obtained from straight-line plots of ln ($A_t − A_\infty$) vs. t; the slopes of which were $−k_1$. Second-order rate constants k_2 were obtained from plots of these k_1 values against the dipolarophile concentration. The rate constants quoted are the mean value of at least 3 runs. The solvents were purified according to standard procedures and the substrates were prepared as previously described[7,8] and recrystallised at least twice beforehand.

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