# N-Alkylation of some Secondary Styryl Enamides

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The preparation of some secondary styryl enamides of both the Z-and E-configuration, and their exclusively N-alkylation through their anions is described. Partial configurational inversion is observed under certain conditions during the alkylation of the diastereoisomeric N-(2-phenyl-1-methylethenyl)-ethanamides. Two further examples of the photoequilibration of a secondary enamide, and the preparation and N-benzylation of N-(2,2-diphenylethenyl)toluene-p-sulphonamide are also described.

In connection with experiments on the chemical reduction of the enamide (1)[1] we required samples of the analogues (2b) and (3b) of known configuration. We investigated their preparation by the N-benzylation of the corresponding NH-compounds (2a) and (3a). Our results led us to investigate more generally the N-alkylation of secondary styryl enamides and we now give a full account of this work. Alkylations of enamides at carbon, nitrogen, and oxygen have all been reported.[2] Phase-transfer alkylation usually gives the N-alkylated product, although under certain conditions co-formation of the O-alkylated product has been observed.[3] Treatment of bastidin-4 with iodomethane in dimethylformamide (DMF) at room temperature leads to N-methylation of the enamide function.[4] Most alkylations of the anions derived from enamides also lead to N-alkylation,[2,3,5] although the alkylation of the anion of an enamide where the acyl group was derived from an α-oxo-acid has recently been reported[6] to give the O-alkylated product.

The enamides (2a) and (3a) were prepared by the Beckmann rearrangement of (E)-[(E)-3-methyl-4-phenylbut-3-en-2-one
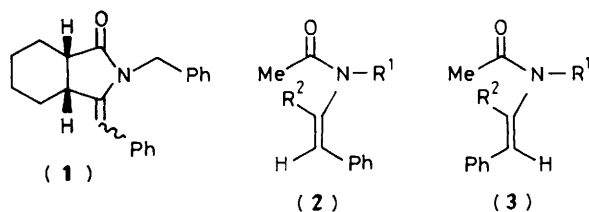
a; R¹ = H , R² = Me
b; R¹ = CH₂Ph , R² = Me
c; R¹ = R² = Me
d; R¹ = R² = H
e; R¹ = CH₂Ph , R² = H
f; R¹ = Me , R² = H

oxime]. The E-configuration at the carbon–carbon double bond was confirmed by a value of 8.4 Hz for $^3J_{C,H}$ the coupling constant for coupling between the methyl carbon and the vinylic proton, which lies in the range expected for a trans-relationship.[7] Two products of m.p. ca. 83 and ca. 93 °C, had previously been reported[8] from this rearrangement, and identified as (2a) and (3a); mixtures of the two, sometimes accompanied by the hydrolysis product, 1-phenylpropan-2-one, were formed when the reaction was carried out using phosphorus pentachloride in either ether or dioxane, followed by decomposition with aqueous sodium carbonate, and were separated, inefficiently, by fractional crystallisation or by preparative t.l.c. We found that running the rearrangement in ether using a modified direct isolation technique[9] (see

Experimental section) gave reproducible and acceptable yields of a mixture of (2a) and (3a), uncontaminated by the ketone, containing ca. 70% of the high m.p. isomer, which could be isolated by fractional crystallisation. Isolation of the pure, low m.p. isomer by chromatography was tedious even using the product mixture obtained by running the rearrangement on a smaller scale in dioxane, which contained a slightly higher proportion, ca. 40%, of that isomer. A mixture of (2a) and (3a) containing ca. 50% of each could be obtained by u.v. irradiation of a solution of the more readily available high m.p. isomer in benzene. The photoequilibration of enamides has been previously reported.[10] The assignment of configuration to the low and high m.p. isomers has been problematical. Originally, on the basis of the u.v. spectroscopic data the low m.p. isomer was assigned[8d] the Z-configuration. However, since in both isomers the phenyl group is twisted out of the plane of the olefinic system by the vicinal methyl or acetamido groups, the use of u.v. data is unreliable, and more recently the assignment has been reversed[8f] on the basis of the relative chemical shifts of the vinyl protons in the ^1H n.m.r. spectra. We have confirmed that the low m.p. isomer has the E-configuration (3a) by comparing the carbon–hydrogen spin-spin coupling constants $^3J_{C,H}$ of the vinylic methyl groups obtained from the ^{13}C n.m.r. spectra [(3a), 7.5 Hz; (2a), 5.0 Hz] and assuming, as is generally found to be the case,[7] that $^3J_{C,H}$ (trans) > $^3J_{C,H}$ (cis).

Benzylation of the Z-enamide (2a) by preparing the anion in DMF using sodium hydride followed by heating with benzyl chloride gave a mixture of two products in a 1:1 ratio, which could be separated by preparative t.l.c. Despite the presence of three potential sites of alkylation in the anion the close similarity of the ^1H and ^{13}C n.m.r. and the mass spectra of the products, and the values for the chemical shifts of the benzylic carbon atoms and protons showed that both products were the result of N-benzylation. The configurations at the carbon–carbon double bonds were again established on the basis of the relative magnitudes of $^3J_{C,H}$ for the vinylic methyl groups. Working on a small scale the (2b):(3b) ratio was reproducibly observed to be 1:1 though a larger proportion of the Z-isomer (2b) was inexplicably observed in a single larger scale preparation. The addition of sodium iodide to the alkylating system led to a greater proportion of the Z-isomer. Analogous trends with predominantly retention of configuration, were observed using the lower boiling solvent tetrahydrofuran (THF) and benzyl chloride, with or without the addition of sodium iodide. Benzylation of the E-enamide (3a) led to mixtures of the same N-benzylated products containing mostly the E-isomer (3b) with a larger degree of configurational retention being observed using benzyl chloride in DMF than with benzyl chloride and sodium iodide in THF. These results are summarised in Table 1. For the larger scale preparation of (2b) and (3b) it was convenient to benzylate mixtures of the secondary enamides (2a) and (3a) from the Beckmann rearrangement and then separate the products

Table 1. N-Alkylation of enamides (through their anions)

Entry no.	Compd.	Configuration	Solvent	Temp. (°C)¶	Alkylating agent	Z:E ratio in products
1	(2a)	Z	DMF	153	PhCH₂Cl	1:1*
2	(2a)	Z	DMF	153	PhCH₂Cl–NaI	11.5:1
3	(2a)	Z	THF	65	PhCH₂Cl	9:1
4	(2a)	Z	THF	65	PhCH₂Cl–NaI	49:1
5	(3a)	E	DMF	153	PhCH₂Cl	1:11.5
6	(3a)	E	THF	153	PhCH₂Cl–NaI	1:3
7	(2a)	Z	Et₂O	A	MeI	Z†
8	(2a)	Z	DMF	40	MeI	Z†
9	(2a)	Z	DMF	153	Me₂SO₄	2.3:1
10	(2a)	Z	Et₂O	35	Me₂SO₄	7.3:1
11	(3a)	E	DMF	153	Me₂SO₄	5.7:1
12	(3a)	E	Et₂O	A	MeI	E‡
13	(2a) (3a)§	E + Z	Et₂O	A	MeI	1:1
14	(3d)	E	DMF	153	PhCH₂Cl	E‡
15	(3d)	E	THF	65	PhCH₂Cl–NaI	E‡
16	(2d)	Z	DMF	153	PhCH₂Cl	Z†
17	(3d)	E	DMF	153	Me₂SO₄	E‡
18	(4a)	Z	DMF	153	PhCH₂Cl	Z†
19	(4a)	Z	DMF	153	PhCH₂Cl–NaI	Z†
20	(5a)	E	DMF	153	PhCH₂Cl	E‡

* In a large scale run the observed ratio was 3.5:1. † None of E-isomer detected. ‡ None of Z-isomer detected. § A 1:1 mixture of (2a) and (3a). ¶ 'A' refers to ambient temperature.

chromatographically. These results prompted us to examine the N-methylation of (2a) and (3a). Treatment of the anion from the Z-enamide (2a) prepared using sodium hydride in ether with iodomethane at 0 °C led after 24 h at ambient temperature to a single product which from its ¹H and ¹³C n.m.r. spectra was an N-methylated enamide. This was subsequently shown to be the Z-isomer (2c) on the basis of the values of the chemical shift of the vinylic proton and $^3J_{C,H}$ for the vinylic methyl group. The same result was obtained using DMF as the solvent at 40 °C. However, when the reaction was conducted in DMF at 153 °C using dimethyl sulphate as the methylating agent a mixture of the two N-methylated products (2c) and (3c) was formed, in moderate yield, with a Z:E ratio of 2.3:1. The use of ether at 35 °C in conjunction with dimethyl sulphate led to the conversion of (2a) into a mixture in which the ratio of the Z:E isomers had increased to 7.3:1. The identity of the second isomer with the E-configuration (3c) was confirmed by the value of $^3J_{C,H}$ and the chemical shift of the vinylic proton. Methylation of the E-enamide (3a) using iodomethane in ether at ambient temperature gave exclusively the E-product (3c). Methylation of (3a) using dimethyl sulphate in DMF at 153 °C gave a mixture of the two enamides (2c) and (3c) in which the Z:E ratio was 5.7:1. Methylation of a 1:1 mixture of (2a) and (3a) using iodomethane in ether at ambient temperature gave, as expected on the basis of the previous results, a 1:1 mixture of (2c) and (3c), separable by m.p.l.c. These results are summarised in Table 1. When the anion from (2a) was heated under reflux for 1.5 h in DMF and then quenched with water the crude product was shown by comparison with reference samples (n.m.r., t.l.c.) to consist of the Z-isomer (2a) (70%) and the E-isomer (3a) (30%). The enamide (2a) was unchanged after 10 days in deuteriotrichloromethane solution at ambient temperatures.

We next investigated the N-alkylation of the enamides (2d) and (3d) where there is less substitution at the carbon–carbon double bond and configurational assignments are more easily and unambiguously made using the values of the vinylic proton–proton coupling constants. The E-enamide (3d) is readily available by the Beckmann rearrangement of (E)-[(E)-4-phenyl-

but-3-en-2-one oxime].[11] It has been reported[8b,d] that the Z-enamide (2d) is also formed to the extent of 10% during this rearrangement and can be separated, as an oil, by preparative t.l.c., but we have never encountered (2d) as a result of this rearrangement. A 1:1 mixture of (2d) and (3d), the thermal equilibrium mixture is formed by the pyrolysis of 4-benzyl-2-oxazoline-5-one,[12] and a mixture of (2d) and (3d) with other products has been isolated as a result of the photochemical Beckmann rearrangement of (E)-[(E)-4-phenylbut-3-en-2-one oxime] and used to isolate the pure Z-enamide (2d) as a solid.[13] We again found it more convenient to obtain a mixture of (2d) and (3d), which contained ca. 80% of the Z-form (2d), by a photoequilibrium starting from the readily available E-form (3d),[11] and to isolate the Z-enamide by chromatography.

Benzylation of the E-enamide (3d), through the anion, in refluxing DMF, using benzyl chloride, gave only the E-form of the product (3e), as a solid; the ¹H n.m.r. spectrum confirmed that N-benzylation had occurred, but was complicated by the presence of two rotamers. T.l.c. confirmed the presence of a single configuration at the carbon–carbon double bond. Benzylation of the anion from (3d) in THF using benzyl chloride in the presence of sodium iodide likewise gave only (3e). Methylation of (3d), through the anion, using dimethyl sulphate in refluxing DMF gave a dark reaction product; comparison of the ¹H n.m.r. spectrum of this with the published spectra[14] of (2f) and (3f) showed it to contain only (3f). Since (3f) has been prepared by three different methods[15] from N-methylethanamide this identification also confirmed that methylation of the anion had occurred at nitrogen. Benzylation of the Z-enamide (2d), through the anion, in DMF using benzyl chloride, gave the Z-form of the product (2e), which proved to be difficult to obtain in a pure state. These results are summarised in Table 1. When the anion from (3d) was heated under reflux for 1.5 h in DMF and then quenched with water, only (3d) was recovered.

We finally investigated the benzylation of a third pair of diastereoisomeric enamides (4a) and (5a). A mixture of the two was obtained by the ethanoylation of the magnesio-imine formed by the reaction of ethylmagnesium bromide and cyanobenzene.[16] Only one of the diastereoisomers had been

(4)

(5)

a; R = H

b, R = CH₂Ph

(6)   (7)
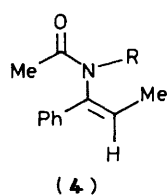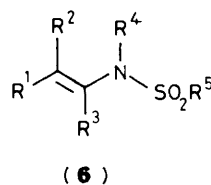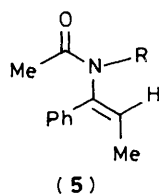
a ; R¹= R²= Ph , R³= R⁴= H , R⁵= p-C₆H₄Me

b ; R¹= R²= Ph , R³= H , R⁴= CH₂Ph , R⁵= p - C₆H₄Me

c ; R¹= R²= R³= Ph , R⁴= H , R⁵= Me

d ; R¹= R²= Ph , R³= R⁴= H , R⁵= p - C₆H₄Br
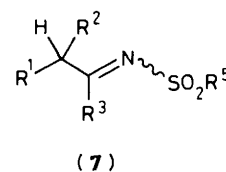
isolated previously,[16] although the formation of both the Z- and E-forms has since been noted in a similar reaction.[17] [1]H N.m.r. spectroscopy on our crude, solid product showed the presence of roughly equal amounts of the two diasteroisomers; direct crystallisation gave the previously reported[16] material, m.p. 126 °C, and preparative t.l.c. or column chromatography then permitted the isolation of the other isomer, m.p. 80—81 °C. No configuration had previously been assigned to the higher m.p. isomer[16] but on the basis of measurements on nuclear Overhauser enhancements (n.O.e.) we now tentatively assign to that isomer the Z-configuration (4a). For example in the E-isomer (5a) an n.O.e. from the vinylic methyl group to both the vinylic proton (7%) and the phenyl group (0.6%) was observed, whereas in the Z-isomer (4a) irradiation at the frequency of the methyl group only caused an n.O.e. at the vinylic proton (3%). Similarly, only in the case of (5a) was an n.O.e. observed from the NH proton to the vinylic proton. Benzylation of (4a), through the anion, using benzyl chloride in refluxing DMF, with or without the addition of sodium iodide, gave a single product to which, on the basis of its spectroscopic properties, we assign structure (4b). Benzylation of (5a), through the anion, using benzyl chloride in refluxing DMF gave a single product which was clearly distinguishable from (4b) by its [1]H n.m.r. spectrum and R_F value on analytical t.l.c., but which had a virtually identical mass spectrum, and to which we assign the structure (5b). These results are summarised in Table 1.

Our results show that in all cases alkylation of a secondary styryl enamide through its anion occurs at nitrogen. In the case of the enamides (2a) and (3a) some inversion of the carbon–carbon double bond configuration can occur, leading to diastereoisomeric mixtures of N-alkylated products. Similar behaviour has been reported for the related dehydroamino acid derivative (3; R¹ = H, R² = CO₂Et; PhCH₂O in place of Me).[18] In our studies the proportions of the diastereoisomers formed depended markedly on the alkylating agent used (and, for a particular alkyl group, on the nature of the leaving group), on the solvent and on the reaction temperature, but our limited results allow no generalisations to be made. We do, however, describe satisfactory procedures for the preparation of our target molecules (2b) and (3b).

We have also examined one case of the alkylation of an enesulphonamide (6a). In general, compounds of the type (6; R⁴ = H) are unstable with respect to the tautomeric form (7)[19] and two of the few examples to be isolated (6c) and (6d)[19,20] both have R¹ = R² = Ph. We chose to prepare the related compound (6a). N-2,2-Diphenyl-2-hydroxyethyl toluene-p-sulphonamide was prepared by the toluene-p-sulphonylation of 1,1-diphenyl-2-aminoethanol;[21] dehydration with phosphoric oxide, a route analogous to that used to prepare (6d),[20] gave a compound which was shown by its ^{1}H and [13]C n.m.r. spectra to be the required compound (6a). The presence of an NH signal as a doublet at δ 6.3 (exchangeable) and of a signal due to a vinyl proton as a doublet at 120.3 p.p.m. ruled out the tautomeric structure (7a) and also N-(p-tolylsulphonyl)-2,2-diphenylaziridine which might have been formed in the dehydration step; these alternative structures would have been

expected to have ^{13}C chemical shifts in the 180[19c] and 45 p.p.m.[22] regions respectively.

Benzylation of (6a) through its anion with benzyl chloride in refluxing DMF gave the N-benzylated product (6b), which was shown (^{1}H and [13]C n.m.r., i.r. and mass spectroscopy, t.l.c., m.p.) to be identical with an authentic sample prepared by the dehydration of the product from the reaction of 2,2-diphenyloxirane with N-benzyltoluene-p-sulphonamide.

Experimental

(Z)- and (E)-N-(1-Methyl-2-phenylethenyl)ethanamide (2a) and (3a).—Phosphorus pentachloride (21.5 g, 103 mmol) was added to (E)-[(E)-3-methyl-4-phenylbut-3-en-2-one oxime][23] (17.9 g, 0.20 mol) in dry ether (200 ml) at 0 °C, and the mixture was shaken for 30 min. The mixture was then poured slowly into a vigorously stirred mixture of crushed ice (100 g) and 40% aqueous potassium carbonate (100 ml), the pH being maintained at 7 (test paper) by the addition of solid potassium carbonate. The ether was then removed by a current of nitrogen, and the resultant solid was collected by filtration, and washed twice with light petroleum (b.p. 60—80 °C). Analytical t.l.c. (7:3 light petroleum–ethyl acetate) showed the presence of the E-(R_F 0.40) and Z-(R_F 0.52) isomers of N-(1-methyl-2-phenylethenyl)-ethanamide; [1]H n.m.r. spectroscopy showed the E:Z ratio at

Table 2. [1]H N.m.r. chemical shifts (δ) in $CDCl_3$ at 220 Hz,[a] isolated yields and microanalytical figures for enamides (2a—c) and (3a—c)

Enamides	MeCH=	COMe	PhCH=	NH	NMe	NCH$_2$Ph	Config'n	Isolated yield (%)	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	Molecular formula
(2a)[b]	1.90	2.20	5.73	7.45			Z	40%							
(3a)[b]	2.06[c]	2.07[c]	7.0	7.75			E	1							
(2b)	1.74	2.0	6.2			4.0[d] 5.3[d]	Z	35[e]	81.6	7.5	5.0	81.5	7.2	5.3	$C_{18}H_{19}NO$
(3b)	1.97	2.17	6.12			4.75[f]	E	24[g]	81.2	7.1	5.1	81.5	7.2	5.3	$C_{18}H_{19}NO$
(2c)	1.87	2.03	6.22		3.01		Z	70[h]	76.3	8.1	7.5	76.2	8.0	7.4	$C_{12}H_{15}NO$
(3c)	2.06	2.12	6.43		3.08		E	74[i]	75.9	7.8	7.2	76.2	8.0	7.4	$C_{12}H_{15}NO$

[a] All the compounds showed absorption in the region δ 7.1—7.4 (1 or 2 × Ph). [b] cf. Ref. 8f. [c] Interchangeable assignment. [d] AB system, J_{AB} 15 Hz. [e] 57% On a large scale run (Table 1 entry 1). [f] Singlet (2H). [g] 9% On a large scale (Table 1, entry 1). [h] Yield corresponding to entry 13, Table 1; 93% in each case for the experiments corresponding to entries 7 and 8 in Table 1. [i] Yield corresponding to entry 13, Table 1; 82% for the experiment corresponding to entry 12.

Table 3. [13]C N.m.r. chemical shifts (p.p.m.) and coupling constants ($^3J_{C,H}$) for the enamides (2a—c) and (3a—c) in $CDCl_3$ at 25.12 MHz

Enamide	MeCH=	COMe	NMe	NCH$_2$Ph	sp^2-Hybridised carbons	CO	$J_{C,H}$	Config'n
(2a)	21.8	23.6			116.5 126.5 128.1 128.5 133.7 135.8	169.1	5.0	Z
(3a)	17.7	24.3			116.5 125.9 128.1 128.7 133.2 137.0	169.4	7.5	E
(2b)	24.2	21.5	49.4		126.8 127.3 127.6 128.2 128.7 128.8 134.4 137.1 137.5[a]	169.4	4.8	Z
(3b)	17.7	21.9	49.4		127.3 127.8 128.3 128.5 128.9 131.4 135.4 137.7[a]	169.6	6.9	E
(2c)	21.6	20.5	31.8		126.0 127.1 127.3 128.3 134.1 137.1	168.9	4.6	Z
(3c)	16.7	21.5	32.7		127.2 128.2 128.4 129.0 135.1 139.3	169.5	6.4	E

[a] All ten signals not observed due to peak overlap.

Table 4. [1]H N.m.r. chemical shifts (δ) in $CDCl_3$ at 220 MHz,[a] isolated yields and anlytical data for the enamides (2d—e) and (3d—f)

Enamide	COMe	NH	NMe	NCH$_2$Ph	H$_A$	H$_B$	J_{AB}	Config'n	Isolated yield (%)	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	Molecular formula
(3d)[b]	2.13	8.66[c]			6.18[d]	7.55	13	E	40							
(2d)[b]	2.00	7.95[c]			5.7[f]	6.86	8	Z	60							
(3e)[g][h]	2.18 2.40			4.85 4.98	5.85 5.95	8.18 i	14.5 14.5	E	88	81.2	6.8	5.6	81.2	6.8	5.6	$C_{17}H_{17}NO$
(2e)	2.00			4.65	6.08	6.14	8.0	Z	51	m/z 251.1318			m/z 251.1310			$C_{17}H_{17}NO$
(3f)[g][j][h]	2.23 2.29		3.18		5.92 5.96	8.10 i	13 13	E	69							

[a] All the compounds showed absorption in the region δ 7.0—7.5 (1 or 2 × Ph). [b] cf. Ref. 13. [c] Doublet, J 9Hz. [d] Double doublet, J, 9 Hz J' 13 Hz. [e] broad signal. [f] Triplet, J = J' = 8 Hz. [g] Minor rotamer. [h] major rotamer. [i] Signal in the range δ 7.0—7.5. [j] cf. Ref. 14.

this stage to be 1:3. Crystallisation from hexane–benzene afforded (Z)-N-(1-methyl-2-phenylethenyl)ethanamide (2a), m.p. 95—96 °C (lit.,[8b] 92—93 °C) (6.5 g, 36%). The material from the mother liquor was chromatographed on a silica column using 7:3 light petroleum–ethyl acetate as the eluting solvent to yield a further (0.65 g, 3.6%) of the Z-enamide (2a) and an impure sample of the E-enamide. Preparative t.l.c. (1:1 light petroleum–ethyl acetate) then gave (E)-N-(1-methyl-2-phenylethenyl)ethanamide (2b), m.p. 81—82 °C (lit.,[8b] 83—84 °C) (0.3 g, 0.8%). The n.m.r. spectral data for these two enamides (2a) and (3a) is given in Tables 2 and 3.

Photoequilibration of the N-(1-Methyl-2-phenylethenyl)ethanamides.—(Z)-N-(1-Methyl-2-phenylethenyl)ethanamide (0.5 g, 2.8 mmol) in benzene (60 ml) was irradiated by a high-pressure Hanovia 100 W mercury, compact arc, u.v. lamp for 24 h under nitrogen. The solvent was then evaporated to leave an oil which showed R_F values on analytical t.l.c. (1:1 light petroleum–ethyl acetate) corresponding to both the E- and the Z-isomers. [1]H N.m.r. spectroscopy on the oil showed it to be a 1:1 mixture

of the two isomers by comparison with the spectra of the individual isomers.

(E)-N-(2-Phenylethenyl)ethanamide.—Treatment of 4-phenyl-but-3-en-2-one oxime[24] (8.00 g, 50 mmol) with phosphorus pentachloride (11.5 g, 54 mmol) in dry THF (100 ml) at 0—5 °C and work-up as for the Beckmann rearrangement described above gave a crude product which was extracted with ether (3 × 100 ml). The combined extracts were washed with water (100 ml), and dried, and the solvents evaporated. Column chromatography, using 2:3 ethyl acetate–light petroleum as the eluant gave a crystalline product, which on recrystallisation from light petroleum–benzene afforded (E)-N-(2-phenyl-ethenyl)ethanamide (3d), m.p. 113—114 °C (lit.,[8d] 114—115 °C).

(Z)-N-2-(Phenylethenyl)ethanamide.—(E)-N-(2-Phenylethen-yl)ethanamide (3d) (0.5 g) in benzene (60 ml) was irradiated under nitrogen for 24 h with a high pressure Hanovia 100 W mercury compact arc lamp. Removal of the solvent gave an oil. Material from three such irradiations (1.5 g) was shown by

Table 5. ^{1}H N.m.r. chemical shifts (δ) in $CDCl_3$ at 220 Hz,[a] isolated yields and mass spectroscopic and analytical data for the enamides (4a—b) and (5a—b)

Enamide	Me	COMe	CH=	NH	NCH$_2$Ph	Isolated yield (%)	Ten most intense peaks in mass spectrum m/z	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	Molecular formula
(4a) [b]	1.68[d]	2.03	5.88[e]	7.53		17	175 (M$^+$), 160, 133, 132 (base peak), 115, 105, 104, 77, 51, 43							
[c]	1.84[d]	1.77	6.04[e]	6.95			175 (M$^+$), 160, 133, 132 (base peak), 115, 105, 104, 77, 57, 43							
(5a)	1.70[d]	2.00	6.30[e]	6.88		2		m/z 175.0995			m/z 175.0997			C$_{11}$H$_{13}$NO
(4b)	1.16[d]	1.98	6.01[e]		3.59[f]	20	265 (M$^+$), 222, 174, 133, 115, 105, 104, 91, (base peak), 65, 43	81.4	7.3	5.3	81.5	7.2	5.2	C$_{18}$H$_{19}$NO
					5.39[f]			m/z 265.1462			m/z 265.1467			
(5b)	1.78[d]	2.23	5.45[e]	4.5[g]		24	265 (M$^+$), 222, 174, 133, 115, 105, 104, 91 (base peak), 65, 43	81.4	7.2	5.3	81.5	7.2	5.2	C$_{18}$H$_9$NO
								m/z 265.1472			m/z 265.1467			

[a] All the compounds showed absorption in the region δ 7.0—7.5 (1 or 2 × Ph). [b] Major rotamer. [c] Minor rotamer. [d] Doublet, J 7 Hz. [e] Quartet, J 7 Hz. [f] AB system, J, 15 Hz. [g] Singlet.

analytical t.l.c. (3:2 ethyl acetate–light petroleum) to consist of two components having R_F values of 0.54 and 0.29. ^{1}H N.m.r. spectroscopy on the material showed the two components to be present in the ratio 4:1. The components were separated by column chromatography using 7:3 light petroleum–ethyl acetate as the eluant. The major component, R_F 0.54, was (Z)-N-(2-phenylethenyl)ethanamide (2d) (0.9 g, 60%), m.p. 62—63 °C (lit.,[13a] 63—64 °C) and the minor component, R_F 0.29, the E-isomer (0.3 g), m.p. 113—114 °C.

Z *and* E-N-(1-*Phenylprop*-1-*enyl)ethanamide* (4a) *and* (5a).—The crude solid product (17.1 g, 67%) from the ethanoylation of the magnesioimine from cyanobenzene (14.9 g, 145 mmol) and ethylmagnesium bromide (170 mmol)[16] was shown by analytical t.l.c. (65:35 light petroleum–ethyl acetate) to contain two components with R_F values of 0.16 and 0.23. Crystallisation from light petroleum–ethyl acetate gave (Z)-N-(1-phenylprop-1-enyl)ethanamide (4a) (4.4 g 17.4%), R_F 0.16, m.p. 124—125 °C (lit.,[16] 126—126.5 °C). Column chromatography (6:4 light petroleum–ethyl acetate as eluant) gave further quantities of the Z-enamide and an oily fraction which on crystallisation from light petroleum–ethyl acetate afforded (E)-N-(1-*phenylprop*-1-*enyl)ethanamide* (5a), m.p. 80—81 °C, R_F 0.23. ^{1}H N.m.r. spectroscopic data and mass spectral data for (5a) is given in Table 5.

General Procedure for the Alkylation of Secondary Styryl Enamides.—Until work-up, operations were conducted under an atmosphere of nitrogen. Sodium hydride (50% dispersion in oil; 1 equiv.) was added to a well-stirred solution of the enamide (1 equiv.) in a dry solvent. The reaction mixture was then cooled to 0 °C and the alkylating agent (1.05 equiv.; 8.0 equiv. for MeI) was added all at once. After 24 h at the reaction temperature the mixture, at ambient temperature, was poured into water and extracted with ether (or dichloromethane if DMF was the solvent). The extracts were washed with water, and dried, and the solvents evaporated. Details of enamides used, alkylating agents, solvents, and reaction temperatures are given in Table 1. The crude products were analysed by t.l.c. and ^{1}H n.m.r. spectroscopy, and the components were separated and purified by column chromatography, preparative t.l.c., m.p.l.c. or bulb-tube distillation. The N-alkylated enamides, which with one exception [(5b), m.p. 80 °C, from benzene] were oils, together with the associated spectroscopic and analytical data, and the yields in which they could be isolated, are listed in Tables 2—5.

N-(2,2-*Diphenylethenyl)toluene*-p-*sulphonamide* (6a).—N-(2,2-Diphenyl-2-hydroxyethyl)toluene-p-sulphonamide[21,25] (3.2 g, 8.7 mmol) and phosphoric oxide (20.0 g, 140 mmol) were heated in refluxing benzene (150 ml) for 1 h. The mixture was then cooled and filtered and the solvent evaporated. Crystallisation from methanol gave N-(2,2-diphenylethenyl)toluene-p-sulphonamide (2.0 g, 66%), m.p. 169—170 °C, δ 2.43 (3 H, s, MeC_6H_4), 6.3 (1 H, d, NH), 6.78 (1 H, d, OH, singlet after exchange with D_2O) and 6.88—7.7 (14 H, c, ArH), δ_C 21.5 (Me), 120.3 (C=CH), 126.6, 126.8, 127.0, 128.1, 128.3, 129.3, 129.6 and 129.8 (aromatic CH) and 126.1, 136.4, 136.9, 139.4 and 143.9 p.p.m. (quaternary carbons) (Found: C, 72.1; H, 5.4; N, 4.0; S, 9.2. $C_{21}H_{19}NO_2S$ requires C, 72.2; H, 5.5; N, 4.0; S, 9.2%).

N-*Benzyl*-N-(2,2-*diphenyl*-2-*hydroxyethyl)toluene*-p-*sulphonamide*.—Reaction of 2,2-diphenyloxirane[26] (1.0 g, 5 mmol) with N-benzyltoluene-p-sulphonamide[27] (1.33 g, 5 mmol) in the presence of Triton B (0.1 ml) for 2 h at 100 °C gave a viscous liquid which was taken up in hot toluene. Overnight at 0 °C the solution deposited a solid which was collected and crystallised from aqueous ethanol to give N-*benzyl*-N-(2,2-*diphenyl*-2-*hydroxyethyl)toluene*-p-*sulphonamide* (1.2 g, 51%), m.p. 124—126 °C, δ 2.4 (3 H, s, MeC_6H_4), 3.90 and 4.08 (each 2 H, s, 2 × CH$_2$) 3.97 (1 H, br s, OH), 6.67—7.42 (17 H, c, ArH) and 7.67 (2 H, d, J 7.5 Hz, H$_B$ and H$_B'$ of AA'BB' system in C_6H_4) (Found: C, 73.3; H, 5.7; N, 3.1; S, 6.9 $C_{28}H_{27}NO_3S$ requires C, 73.5; H, 5.9; N, 3.0; S, 7.0%).

N-*Benzyl*-N-(2,2-*diphenylethenyl)toluene*-p-*sulphonamide* (6b).—(i) N-Benzyl-N-(2,2-diphenyl-2-hydroxyethyl)toluene-p-sulphonamide (1.0 g, 2 mmol) and phosphoric oxide (4.77 g, 33 mmol) were heated for 1 h in refluxing benzene (100 ml). The mixture was then cooled and filtered, and the solvent evaporated. Crystallisation from light petroleum gave N-*benzyl*-N-(2,2-*diphenylethenyl)toluene*-p-*sulphonamide* (0.5 g, 52%), m.p. 117—118 °C, δ 2.4 (3 H, s, MeC_6H_4), 4.17 (2 H, s, NCH$_2$Ph), 6.48 (1 H, s, C=CHN), 6.64—7.25 (15 H, c, 3 × Ph) and 7.32 and 7.72 (each 2 H, d, J 7.5 Hz, C_6H_4); δ_C 21.5 (MeC_6H_4), 51.7 (NCH$_2$Ph) and 122.7—143.6 (sp^2 hybridised carbons) p.p.m. (Found: C, 76.4, H, 5.7; N, 3.4; S, 7.2. $C_{28}H_{25}NO_2S$ requires C, 76.5; H, 5.7; N, 3.2; S, 7.3%).

(ii) Benzylation of N-(2,2-diphenylethenyl)toluene-p-sulphonamide (6a) (0.25 g) in DMF at 153 °C for 24 h following the general alkylation procedure (see above) gave N-benzyl-N-(2,2-

diphenylethenyl)toluene-*p*-sulphonamide (0.27 g, 87%) identical (m.p., t.l.c., ^{1}H n.m.r. spectrum) with the material from (i).

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