# The case of the missing acetylene. The mechanism of an intramolecular $S_N(V)$ reaction and a new route to 1-methylbenzo[*de*]quinolines

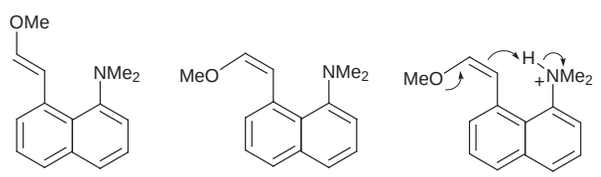
**David R. W. Hodgson, Anthony J. Kirby * and Neil Feeder**

*University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW*

***Received (in Cambridge) 21st December 1998, Accepted 15th February 1999***

1-Halogeno-2-(1-naphthyl)alkenes with a dimethylamino group in the *peri* position are smoothly converted to 1-methylbenzo[*de*]quinoline under mild conditions, in a process involving the loss of MeBr rather than HBr. The *Z*-bromide is 45 times more reactive than its *E*-isomer, and 7 times more reactive than the *Z*-chloride. These systems were designed to show efficient elimination of HBr, but acetylene is not a likely intermediate. There is good evidence to support *both* of two alternative addition–elimination mechanisms: a *6-endo-dig* route which would involve a "normal" addition–elimination process in an unusual setting; and a tandem 5-*exo-dig* Michael addition–carbene rearrangement. The evidence so far does not permit a final choice between the two.

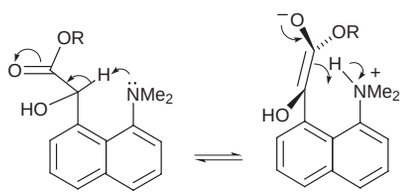
As part of our continuing investigation of the efficiency of proton transfer catalysis in chemistry and enzymology we recently prepared the enol ethers **1***E* and **1***Z*,[1] and showed that



**1***E* **1***Z* **2**

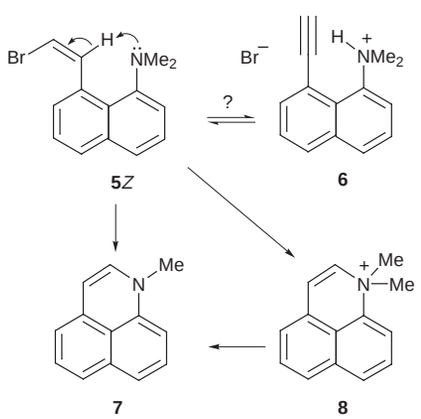
these compounds are hydrolysed extraordinarily rapidly, with half-lives of about 10 s at 39 °C. The mechanism involves intramolecular general acid catalysis by the neighbouring dimethylammonium group (**2**), which has an effective molarity (EM)[2] greater than $10^5$ M. This is the most efficient example known of this mode of catalysis, for which EMs in model systems are typically less than 10 M. The exceptional efficiency can be explained by the formation of a strong intramolecular hydrogen bond in the product, which also stabilises the transition state leading to it, but is absent in the starting material. This favourable combination of properties is not easily achieved in a simple system, which needs to be more or less rigid to support an intramolecular H-bond strong enough to persist in water; whereas an enzyme has the possibility of controlling the geometry of the relevant interactions as the reaction proceeds. Furthermore, since many enzyme reactions are reversible under physiological conditions, the only arrangement generally consistent with optimum catalytic efficiency is specific stabilisation of the transition state, which in the case of proton transfer catalysis means the formation of a transient strong hydrogen bond which is absent in both starting material and product.

Proton transfer to carbon offers the best chance of setting up this combination of properties in a simple system, since C–H protons are not normally good hydrogen bond donors, and our work with the enol ethers **1** suggested compound **3**, of interest as a close model for mandelate racemase. However, systems based on **3** showed no measurable deuterium exchange reaction in $D_2O$.[3] This might be because the intramolecular proton transfer, though fast, is faster still in the reverse direction (**4**), taking advantage of the hydrogen bond expected to persist between the enolate carbon and the $NH^+$ proton, and thus too fast to allow exchange with solvent $D_2O$.



**3** **4**

This reasoning led us to investigate the vinyl bromide **5**. The elimination reaction is expected to be irreversible, it involves optimum geometry for the proton transfer part of the reaction, and we expect no significant intramolecular hydrogen bonding in the starting material or in the product alkyne **6** (Scheme 1).



**5***Z* **6** **7** **8**

**Scheme 1**

However, we find in practice that though **5** is reactive, it is converted not to the acetylene, but to the product **7** of nucleophilic substitution at the $sp^2$ carbon centre. The $S_N(V)$ reaction is itself a topic of considerable current interest,[4,5] and we have investigated the reactions of **5** and some related compounds in an attempt to understand the mechanism of this unusual reaction.

## Kinetic methods and results

When the (*Z*)-vinyl bromide **5***Z* was dissolved in acetonitrile-$d_3$ the $^1H$ NMR spectrum of the solution showed that the starting material disappeared with a half-life of about 4 hours at 40 °C.

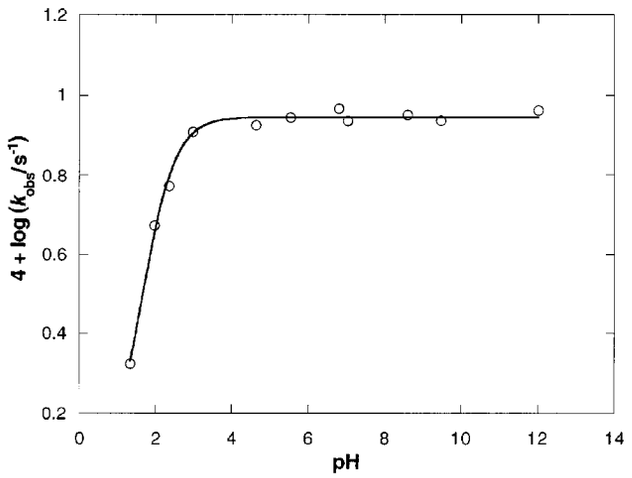



**Fig. 1** pH–Rate profile for the cyclisation of **5***Z*, in 50% acetonitrile–water at 60 °C. The reaction is exclusively that of the free base form of the substrate. The points are experimental (for details see the text), the line was calculated using a plateau rate constant of $9.45 \times 10^{-4}$ $s^{-1}$ and a value of 1.62 for the p$K_a$ of the $Me_2NH^+$ group.

**Table 1** Pseudo-first order rate constants for the disappearance of vinyl bromide **5***Z* in the presence of NaI, in acetonitrile[a]

| [NaI]/mol $dm^{-3}$ | *T*/K | $k_{obs}/10^{-4}$ $s^{-1}$ |
|---|---|---|
| 0.1 | 343.15 | 7.18 |
| 0.1 | 333.15 | 2.63 |
| 0.03 | 333.15 | 2.80 |
| 0.01 | 333.15 | 2.79 |
| 0.001 | 333.15 | 2.83 |
| 0.1 | 323.15 | 1.19 |
| 0.1 | 313.15 | 0.418 |

[a] Measurements at 380 nm. Good linear plots had correlation coefficients better than 0.999. Activation parameters at 0.1 M NaI: $\Delta H^{\ddagger} = 86.5 \pm 2.0$ kJ $mol^{-1}$; $\Delta S^{\ddagger} = -61 \pm 6$ J $K^{-1}$ $mol^{-1}$ (25 °C).

Signals of an initial product appeared then disappeared to reveal the spectrum of the final product. This was clearly not the expected alkyne **6**, but was identified as 1-methylbenzo[*de*]quinoline **7** by comparison of its $^1$H NMR spectrum with that of the known compound.[6] A volatile second product (singlet at $\delta$ 2.68) is presumed to be MeBr, and thus the intermediate the *N,N*-dimethylammonium compound **8**. The same final product was formed, more slowly, under the same conditions from the corresponding (*Z*)-vinyl chloride, and from the (*E*)-vinyl bromide **5***E*. Approximate rate ratios (acetonitrile-$d_3$, 40 °C) were 45 and 7, for the reactions of **5***Z*/**5***E* and **5***Z*Br/**5***Z*Cl, respectively.

Repeated UV scans of the reaction under these conditions showed progressive changes below 270 nm and between 300–340 nm, but no isosbestic point, consistent with the involvement of an intermediate. After this had been identified as the dimethylammonium compound **8** we ran the experiment again in acetonitrile containing 0.1 M sodium iodide. Under these conditions the demethylation step is fast, the intermediate does not accumulate and an isosbestic point is observed (Table 1).

In 50% (unbuffered) aqueous acetonitrile (the vinyl halides are not soluble in water) $^1$H NMR experiments showed that the demethylation step is much slower, and the *N,N*-dimethylammonium compound **8** the only product even at 60 °C. Thus the rates of disappearance of the vinyl halides could be studied as uncomplicated first order processes. The amine buffers used (for solubility reasons) at higher pH were found to demethylate the intermediate **8** at a significant rate: where this happened rate constants were calculated from the equation for consecutive first order reactions. The results of experiments at a series of pHs appear in Table 2, and rate constants are plotted as a function of pH in Fig. 1. Data collected to measure kinetic isotope effects on the reaction in the plateau region under the same conditions are summarised in Table 3.

**Table 2** Pseudo-first order rate constants for the disappearance of vinyl bromide **5***Z* in 50% acetonitrile–water at 60 °C

| Buffer | pH | $k_{obs1}/10^{-4}$ $s^{-1}$ | $k_{obs2}/10^{-6}$ $s^{-1}$ |
|---|---|---|---|
| 0.05 M HCl | 1.35 | 2.11 | — |
| 0.01 M HCl | 1.97 | 4.71 | — |
| 0.005 M HCl | 2.35 | 5.92 | — |
| 0.001 M HCl | 2.97 | 8.08 | — |
| 0.1 M Formate | 4.64 | 8.40 | — |
| 0.1 M Acetate | 5.54 | 8.78 | — |
| 0.1 M TRIS | 6.80 | 9.25 | 1.03 |
| 0.1 M TRIS/70 °C | 6.80 | 21.9 | |
| 0.1 M TRIS/60 °C | 6.80 | 9.16[a] | |
| 0.1 M TRIS/50 °C | 6.80 | 3.31 | |
| 0.1 M TRIS/40 °C | 6.80 | 1.19 | |
| 0.2 M TRIS | 7.03 | 8.63 | 2.05 |
| 0.3 M TRIS | | 9.00[a] | 3.11 |
| 0.1 M CHES | 8.59 | 8.91 | 3.90 |
| 0.1 M CAPS | 9.47 | 8.63 | 5.90 |
| 0.01 M KOH | | 9.15 | 9.05 |

[a] Measurements at 309.4 nm. All runs gave excellent first order lines, with correlation coefficients better than 0.999; with two exceptions: TRIS at 60 °C ($r = 0.998$) and 0.3 M TRIS ($r = 0.997$). Thermodynamic parameters for the plateau reaction: $\Delta H^{\ddagger} = 90.3 \pm 2.2$ kJ $mol^{-1}$; $\Delta S^{\ddagger} = -40 \pm 6$ J $K^{-1}$ $mol^{-1}$ (25 °C).

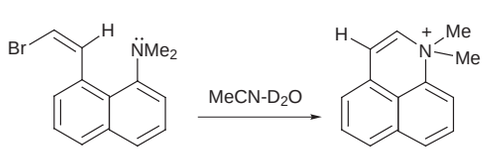
**Table 3** Deuterium kinetic isotope effects on the reaction of vinyl bromide **5***Z* and deuterio-**5***Z* in 50% acetonitrile–water at 60 °C

| Buffer | p*H* (p*D*) | $k_{obs}/10^{-4}$ $s^{-1}$ | $k_H/k_D$ |
|---|---|---|---|
| **5***Z*, 0.1 M Formate–$D_2O$ | (5.03) | 8.77 | 0.96 |
| **5***Z*-*d*, 0.1 M Formate | 4.64 | 8.40 | |
| **5***Z*-*d*, 0.1 M Acetate | 5.54 | 8.78 | |
| **5***Z*-*d*, 0.1 M TRIS | 6.80 | | |

The p$K_a$ of the substrate **5***Z* was measured spectrophotometrically under the conditions used for the kinetic experiments (Table 2), and also in a more aqueous medium (1:4 acetonitrile–water). The measured p$K_a$s were $1.8 \pm 0.1$ and $4.4 \pm 0.4$, respectively. (The lower accuracy of the latter reading is a result of its low solubility in the more aqueous mixture.)

## Discussion

The cyclisation of **5***Z* to **8** is formally a nucleophilic substitution reaction at the sp$^2$ carbon ($S_N(V)$). In acetonitrile as solvent the kinetics are complicated by the demethylation of **8** (to form **7**, Scheme 1), which goes at a similar rate. The complication can be eliminated in two simple ways. Adding 0.1 M NaI to the solution in acetonitrile accelerates the demethylation step and so prevents the build up of the intermediate **8**. Alternatively the cyclisation step can be studied in isolation in unbuffered aqueous–50% acetonitrile solution at UV concentrations: the second, demethylation step is far slower under these conditions, no doubt because the already low concentration of bromide anion is stabilised by solvation.



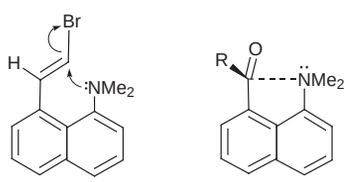

**5***Z* **8**

### Reaction mechanism

Though the formation of the cyclisation products **7** and **8** from **5***Z* is evidently thermodynamically favourable, the mechanism

of the reaction is by no means obvious. We can rule out with some confidence the possibility that the first step is the looked-for elimination of HBr. This would require the rapid 6-*endo*-*dig* cyclisation of the initial product **6** (Scheme 1): a process characterised as favourable in the original Baldwin's rules:[7] though shown to be less favourable than the competing 5-*exo*-*dig* process in related systems.[8]) To test this possibility we ran the reaction in deuteriated solvent (50% acetonitrile–$D_2O$) and found that it is converted cleanly to protiated product **8**, with the proton retained on the original carbon atom, and no evidence for incorporation of deuterium. It seems highly unlikely (though not formally impossible) that the 6-*endo*-*dig* cyclisation of **6**-*d*—involving the *trans*-addition of $NMe_2H^+$—could occur in the deuteriated solvent without exchange of protons for deuterium. (It may also be relevant that the alkyne **6** cannot be made by standard methods for the formation of arylalkynes, although we, like other authors[9] have tried.)

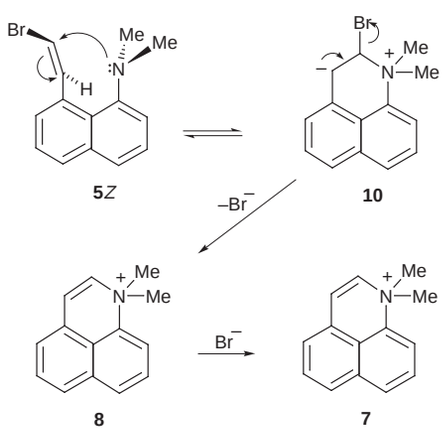
We can also rule out, this time with complete confidence, direct, in-plane concerted displacement of bromide by the dimethylamino group.[10] Though this looks reasonable for the reaction of **5***E* (see **5***E******), which goes with inversion, it is clearly impossible for **5***Z*, yet **5***Z* reacts many times faster, with retention of configuration.




**5***E****** **9**

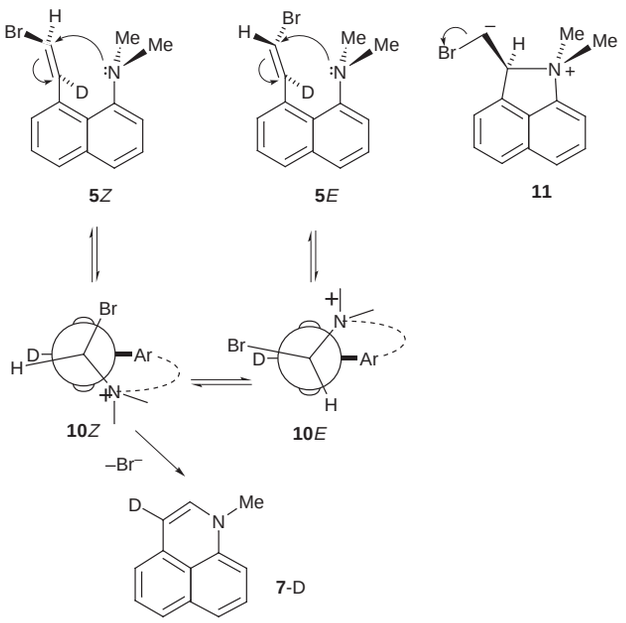
There remain two addition–elimination mechanisms (Schemes 2 and 4, below), in both of which the two steps might be more or less closely coupled. The geometry is favourable, as shown by the crystal structures discussed below: both the $NMe_2$ and alkene groups are rotated out of the plane in the ground state, with the nitrogen lone pair in van der Waals contact with the π-system of the alkene. And the formation of a C–N bond will relieve *peri*-strain, as demonstrated previously for *peri*-substituted systems like the ketone **9** (R = Me), which shows incipient N–C bond formation in the crystal.[11]

The simpler mechanism (Scheme 2) involves a normal




**Scheme 2**

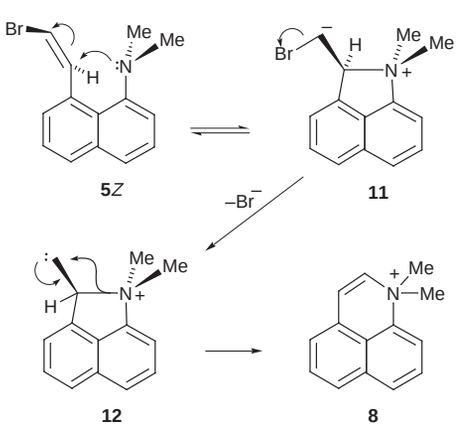
addition–elimination sequence for substitution at the $sp^2$ carbon: 6-*endo*-*trig* addition to the terminal CHBr group of the alkene, followed by—or perhaps concerted with[4]—loss of bromide from the resulting carbanion **10**. It seems clear that N–C bond formation would be rate determining: partially if the reaction were concerted, completely if **10** were a full intermediate, because bromide is a better leaving group than (endocyclic) $NMe_2^+$. 6-*endo*-*trig* addition is stereoelectronically favourable *per se*, but in this system there is little delocalisation possible to stabilise the developing carbanion, at least in the early stages of bond formation, because the alkene is twisted out of the plane of the aromatic ring. To explain the large difference in reactivity between **5***E* and **5***Z*, and the significant effect of changing the leaving group ($k_{Br}/k_{Cl}$ = 6.7 at 40 °C in $CD_3CN$, 4.6 at 60 °C in 50% aqueous MeCN) we consider the structure of the carbanion **10**, which should be closest in structure to the transition state. Carbanion **10** has two possible conformations, **10***E* and **10***Z*, formed initially from **5***E* and **5***Z*, respectively (Scheme 3).




**Scheme 3**

The elimination step requires optimum orbital overlap of the carbanionic centre with $\sigma^*_{C-Br}$, and thus proceeds specifically through conformation **10***Z*. But the same hyperconjugative interaction *stabilises* **10***Z*, and thus also the transition state leading to it. This interaction is not significant in conformation **10***E*, which is therefore formed more slowly from **5***E*. The interaction is stronger for C–Cl (which has a lower energy σ*-orbital) than for C–Br, so the element effect has to be explained in terms of the more stable ground state for the chloro-compound.

Though these arguments can explain both the *relative* reactivities of **5***E* and **5***Z*, and the element effect, there is no doubt that *peri*-strain is reduced more effectively by the (generally more favourable[8]) 5-*exo*-*trig* addition (Scheme 4). This




**Scheme 4**

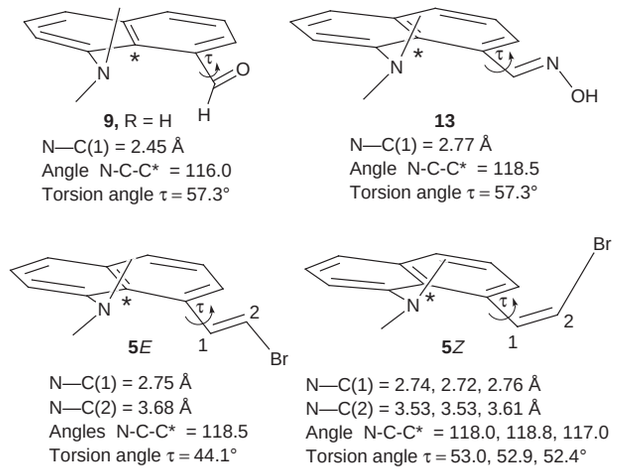
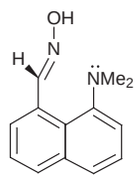



**Fig. 2** Geometries of the interactions between the *peri* groups of the compounds discussed in the text, as revealed by their crystal structures. Details of data collection are summarised in the Experimental section.



**13**

conclusion is based on much precedent, and illustrated by the crystal structures, summarised in Fig. 2. All four compounds, the aldehyde **9**, R = H, its oxime **13** and the *E* and *Z* isomers of **5** have both *peri* substituents twisted out of the plane of the naphthalene ring by some 45°, with the lone pair of the pyramidal nitrogen pointing in the general direction of the $sp^2$ centre 5 atoms away and the N–C–C* angle less than 120°.

This is the pattern originally observed by Dunitz and his co-workers[11] for the acetyl derivative **9**, R = Me, for which the N–C–C* angle was 116°; we find the same angle for the aldehyde **9**, R = H.† The explanation that this is evidence for incipient bond formation is supported by the very short N–C(1) distance, at 2.45 Å well below the sum of the van der Waals radii for the two atoms concerned (and significantly shorter than the 2.56 Å found for the ketone **9**, R = Me). The corresponding interatomic distances (about 2.75 Å), and N–C–C* angles (near 118°) are significantly higher for the alkenes, as expected if bond formation is not so far advanced. (Similar results, up to and including full N–C bond formation, have been found recently by Bell and Wallis for derivatives of **5** with two electron-withdrawing substituents on the terminal alkene carbon.[12]) These short interatomic distances lead to repulsive interactions between the centres involved, which can be relieved by bond formation. In contrast, there is no such close approach between nitrogen and the distal carbon atom of the alkene: the N–C(2) distances (Fig. 2) are over 3.5 Å, and the centres not in van der Waals contact. There is thus correspondingly less relief of ground state strain on the formation of the 6-membered ring.

Full N–C bond formation in the case of **5** would give the carbanion **11**, which would certainly lose bromide quickly to generate the singlet carbene **12**. Related tandem-Michael addition–carbene reactions are well known for alkynyliodonium systems,[13] and recently have been observed also for alkenyliodonium systems.[14] The rigid geometry of **12** precludes other intramolecular reactions of the carbene, and the rearrangement shown, with a 1,2-migration of the $^+NMe_2$ group, is the logical route to a stable product. The rate ratio $k_{Br}/k_{Cl} = 6.7$ is readily explained by the more effective stabilisation of the developing carbanion by α-Br: however the high *E*/*Z* rate ratio is not predicted by this mechanism.

† The structure of **9**, R = H was of interest in connection with Corey's suggestion that aldehyde protons are potential hydrogen-bond donors (E. J. Corey and J. J. Rohde, *Tetrahedron Lett.*, 1997, 37). In practice the nitrogen lone pair finds the aldehyde C=O group more interesting.

## Conclusions

The close proximity of the *peri* substituents in these systems (**5**, **9**, **13**) raises the ground state energies, and thus makes possible their unusual chemistry.[15–18] In the majority of cases where the groups are dialkylamino and unsaturated CH=X this involves initial N–C bond formation. This may be the case (Scheme 4) for the alkenyl bromides **5***E* and **5***Z*, but the evidence is thus far inconclusive, and we cannot at this stage rule out the alternative 6-*endo*-*trig* cyclisation of Scheme 2.

The elimination reaction involving the designed hydrogen-bonding interaction with the CH proton of the CH=X group of the substrates **5** may still be efficient: it is presumably simply overtaken by the even more efficient nucleophilic process observed. However, we have very recently identified the looked-for elimination in a system with exactly the same geometry as **5**, the *syn*-oxime **13** of the aldehyde **9**, R = H. The acetate ester of this oxime is rapidly converted to the nitrile (a *syn*-elimination —typically thousands of times slower than the *anti* equivalent) in a few minutes at 20 °C in 50% aqueous acetonitrile.[19]

## Experimental

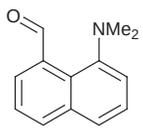
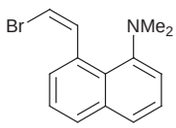
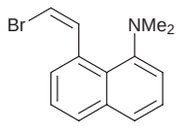
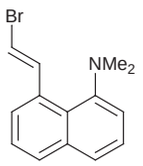
### Materials

Starting materials were obtained commercially (Aldrich). Column chromatography was performed using Merck Kieselgel 60 (230–400 mesh): solvents used were distilled before use. NMR spectra were recorded on Bruker DRX 400 and DPX 250 instruments and IR spectra on a Perkin-Elmer 1600 FT spectrophotometer. Mass spectra were determined on Bruker BIO-APEX II or Kratos MS 890 instruments. UV spectra and kinetic measurements were made in the thermostatted cell compartment of a Varian Cary 3 spectrophotometer.

#### 1-(*N*,*N*-Dimethylamino)-8-[(*Z*)-2-bromoethenyl]naphthalene 5*Z*

Sodium bis(trimethylsilyl)amide (7.4 $cm^3$ of a 1.0 M solution in tetrahydrofuran) was added to a suspension of (bromomethyl)-triphenylphosphonium bromide (3.23 g, 7.40 mmol) in tetrahydrofuran (120 $cm^3$) under argon at −58 °C (dry-ice–chloroform bath) and stirred at −58 °C for 30 minutes to give a yellow solution of ylide. The ylide solution was added *via* a cannula to a solution of 8-(*N*,*N*-dimethylamino)naphthalene-1-carbaldehyde[17] (982 mg, 4.93 mmol) in tetrahydrofuran (80 $cm^3$) at −58 °C under argon and the solution stirred for 30 minutes. The mixture was allowed to warm to 0 °C and stirred for a further 30 minutes. Saturated sodium hydrogen carbonate solution (200 $cm^3$) and water (100 $cm^3$) were added and the mixture stirred for 15 minutes before extraction with diethyl ether (4 × 100 $cm^3$). The ether extracts were combined, washed with water (100 $dm^3$), dried ($Na_2SO_4$) and concentrated *in vacuo*. The residue was chromatographed ($SiO_2$; diethyl ether) to give a mixture of *Z* and *E* isomers. The isomers were separated by repeated crystallisation from light petroleum (bp 30–40 °C) to give pale yellow irregular crystals of the (*Z*)-*vinyl bromide*, mp 58–59 °C; $R_f$ (light petroleum (bp 30–40 °C)) 0.34; $\nu_{max}(CDCl_3)$/$cm^{-1}$ 3054, 2398, 2860, 2828, 2787, 1600 and 1577; $\delta_H$(400 MHz; $CDCl_3$) 7.89 (1H, d, *J* 7.5, vinyl-H), 7.80 (1H, dt, *J* 0.7 and 8.1, ArH), 7.57 (2H, m, ArH), 7.46 (1H, dd, *J* 7.5 and 8.0, ArH), 7.40 (1H, dd, *J* 7.5 and 8.1, ArH), 7.18 (1H, dd, *J* 1.2 and 6.8, ArH), 6.38 (1H, d, *J* 7.5, vinyl-H) and 2.67 (6H, s, $NMe_2$); $\delta_C(CDCl_3)$ 151.8$^-$, 136.9$^+$, 136.0$^-$, 132.1$^-$, 128.9$^+$, 128.7$^+$, 128.3$^-$, 125.7$^+$, 125.2$^+$, 124.1$^+$, 116.7$^+$, 101.8$^+$ and 45.7$^+$

**Table 4** Summary of crystal structure data collection

| | **9**, R = H | **5***Z* | **5***Z* | **5***E* |
|---|---|---|---|---|
| |  |  |  |  |
| Crystallising solvent | Hexanes | Light petroleum (bp 30–40 °C) | Chloroform | Light petroleum (bp 30–40 °C) |
| Empirical formula | $C_{13}H_{13}NO$ | $C_{14}H_{14}BrN$ | $C_{14}H_{14}BrN$ | $C_{14}H_{14}BrN$ |
| Formula weight | 199.24 | 276.17 | 276.17 | 276.17 |
| Temperature/K | 150(2) | 180(2) | 210(2) | 180(2) |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | *P*2(1)/*c* | *P*2(1)/*c* | $P\bar{1}$ | *P*2(1)/*n* |
| Unit cell dimensions | | | | |
| *a*/Å | 8.397(7) | 15.342(3) | 10.562(2) | 7.743(2) |
| *b*/Å | 10.473(12) | 7.545(4) | 15.883(5) | 14.795(3) |
| *c*/Å | 12.712(11) | 10.573(3) | 7.281(2) | 10.956(3) |
| *α*/° | 90 | 90 | 92.82(3) | 90 |
| *β*/° | 109.280(10) | 98.90(2) | 90.24(2) | 100.08(2) |
| *γ*/° | 90 | 90 | 85.89(2) | 90 |
| Volume/Å$^3$ | 1055.2(18) | 1209.1(8) | 1216.8(6) | 1235.7(5) |
| *Z* | 4 | 4 | 4 | 4 |
| Reflections collected | 1963 | 1958 | 7293 | 1637 |
| Independent reflections | 1852 [*R*(int) = 0.0153] | 1880 [*R*(int) = 0.0525] | 4288 [*R*(int) = 0.0446] | 1551 [*R*(int) = 0.0423] |
| Absorption coefficient ($\mu$/mm$^{-1}$) | 0.079 | 3.371 | 3.350 | 4.286 |
| Absn. correction (ψ-scans) | None | 81.70% | 99.70% | 95.40% |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0727$, $wR_2 = 0.1788$ | $R_1 = 0.1046$, $wR_2 = 0.2734$ | $R_1 = 0.0487$, $wR_2 = 0.0897$ | $R_1 = 0.0319$, $wR_2 = 0.0746$ |
| *R* indices (all data) | $R_1 = 0.1321$, $wR_2 = 0.2326$ | $R_1 = 0.1494$, $wR_2 = 0.3144$ | $R_1 = 0.0971$, $wR_2 = 0.1038$ | $R_1 = 0.0402$, $wR_2 = 0.0784$ |
| CCDC Deposition number | 112767 | 112768 | 112769 | 112770 |

(Found: C, 60.74; H, 5.14; N, 5.00%. $C_{14}H_{14}BrN$ requires C, 60.74; H, 5.11; Br, 28.93; N, 5.07%).

### 1-(*N*,*N*-Dimethylamino)-8-[(*E*)-2-bromoethenyl]naphthalene 5*E*

Compound **5***E* was prepared from the mixture of isomers by taking advantage of its lower reactivity. The mixture of *Z* and *E* isomers, prepared as before from 162 mg (0.81 mmol) of aldehyde, was dissolved in acetonitrile (*ca.* 10 cm$^3$) and refluxed for 100 minutes to transform the *Z* isomer to the product. The solvent was removed *in vacuo* and the residue chromatographed ($SiO_2$; light petroleum (bp 30–40 °C)) to give the (*E*)-*vinyl bromide*; $R_f$ (light petroleum (bp 30–40 °C)) 0.34; $\delta_H$(400 MHz; $CD_3CN$) 8.37 (1H, d, *J* 13.6, vinyl-H), 7.81 (1H, dd, *J* 8.1 and 1.3, ArH), 7.56 (1H, dd, *J* 8.1 and 1.0, ArH), 7.44–7.35 (3H, m, ArH), 7.25 (1H, dd, *J* 7.4 and 1.1, ArH), 6.61 (1H, d, *J* 13.6, vinyl-H) and 2.68 (6H, s, $NMe_2$); $\delta_C$($CD_3CN$) 152.6$^-$, 141.3$^+$, 134.9$^-$, 129.8$^-$, 127.2$^+$, 127.0$^-$, 126.4$^+$, 124.7$^+$, 117.7$^+$, 103.2$^+$ and 45.5$^+$.

### 1-(*N*,*N*-Dimethylamino)-8-[(*Z*)-2-chloroethenyl]naphthalene

Sodium bis(trimethylsilyl)amide (1.38 cm$^3$, 1.0 M solution in tetrahydrofuran, 1.38 mmol) was added to a suspension of (chloromethyl)triphenylphosphonium chloride (477.9 mg, 1.38 mmol) in tetrahydrofuran (10 cm$^3$) under argon at 0 °C and stirred for 25 minutes to give a yellow solution of ylide. The ylide solution was added *via* a cannula to a solution of 8-(*N*,*N*-dimethylamino)naphthalene-1-carbaldehyde (182.7 mg, 0.918 mmol) in tetrahydrofuran (10 cm$^3$) at −58 °C under argon and the solution stirred for 1 h at −58 °C. The mixture was allowed to warm to room temperature, brine solution (20 cm$^3$) was added followed by light petroleum (bp 30–40 °C, 20 cm$^3$). The mixture was washed with water–brine (1:1, 50 cm$^3$), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed ($SiO_2$; light petroleum (bp 30–40 °C)) to give a mixture of *Z* and *E* isomers (167.4 mg, 79%). The isomers could be separated by repeated crystallisation from light petroleum (bp 30–40 °C) to give pale yellow irregular crystals of the (*Z*)-*vinyl chloride*, $R_f$ (light petroleum (bp 30–40 °C)) 0.33; $\nu_{max}$($CDCl_3$)/cm$^{-1}$ 2961, 2929, 2858, 2829, 2788, 1609, 1577, 1261, 1097 and 1014; $\delta_H$(400 MHz; $CDCl_3$) 7.77 (1H, dt, *J* 8.2 and 0.6 H, ArH), 7.60 (2H, m, ArH and vinyl-H), 7.55 (1H, dd, *J* 8.1 and 1.0, ArH), 7.46 (1H, t, *J* 7.8, ArH), 7.39 (1H, t, *J* 7.8, ArH), 7.17 (1H, dd, *J* 1.2 and 7.4, ArH), 6.27 (1H, d, *J* 7.7, vinyl-H) and 2.67 (6H, s, $NMe_2$); $\delta_C$($CDCl_3$) 151.8$^-$, 136.0$^-$, 133.7$^+$, 130.8$^-$, 128.8$^+$, 128.7$^+$, 128.3$^-$, 125.6$^+$, 125.2$^+$, 124.0$^+$, 116.5$^+$, 112.5$^+$ and 45.6$^+$.

### 1-(*N*,*N*-Dimethylamino)-8-ethenylnaphthalene

Sodium bis(trimethylsilyl)amide (0.46 cm$^3$, 1.0 M solution in tetrahydrofuran) was added to a suspension of methyltriphenylphosphonium chloride in tetrahydrofuran (5 cm$^3$) under argon at −58 °C (dry-ice–chloroform bath) and stirred at −58 °C for 1 h to give a yellow solution of ylide. The ylide solution was added *via* a cannula to a solution of 8-(*N*,*N*-dimethylamino)naphthalene-1-carbaldehyde (61.1 mg, 0.31 mmol) in tetrahydrofuran (5 cm$^3$) at room temperature, under argon and the solution stirred for 15 minutes. Brine solution was added and the mixture extracted with diethyl ether (3 × 10 cm$^3$). The combined extracts were washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was passed through a plug of silica gel to give the *alkene* (41.8 mg, 68%); $\delta_H$(200 MHz; $CDCl_3$) 8.02 (1H, dd, *J* 17.3 and 10.8, vinyl-H), 7.74 (1H, dd, *J* 7.9 and 1.6, ArH), 7.57–7.35 (4H, m, ArH and vinyl-H), 7.16 (1H, dd, *J* 7.4 and 1.3, ArH), 5.53 (1H, dd, *J* 17.2 and 2.0, vinyl-H) and 2.71 (6H, s, $NMe_2$); $\delta_C$($CDCl_3$) 152.0$^-$, 140.3$^+$, 137.4$^-$, 136.1$^-$, 128.3$^+$, 126.1$^+$, 125.6$^+$, 123.7$^+$, 115.8$^+$, 110.9$^-$ and 45.4$^+$.

### 1-(*N*,*N*-Dimethylamino)-8-(2-bromo-2-methylethenyl)naphthalene

Sodium bis(trimethylsilyl)amide (0.265 cm$^3$ of a 1.0 M solution in tetrahydrofuran) was added to a suspension of (1-bromo-

ethyl)triphenylphosphonium bromide (95.4 mg, 0.212 mmol) in tetrahydrofuran (2 $cm^3$) under argon at −58 °C (dry-ice–chloroform bath) and stirred at −58 °C for 1 h to give an orange solution of ylide. The ylide solution was added *via* a cannula to a solution of 8-(*N,N*-dimethylamino)naphthalene-1-carbaldehyde (35.2 mg, 0.177 mmol) in tetrahydrofuran (1 $cm^3$) at −58 °C under argon and the solution stirred for 30 minutes. The mixture was allowed to warm to room temperature, brine added and the mixture extracted with diethyl ether (5 $cm^3$). The ether extracts were combined, washed with water (3 × 10 $cm^3$), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was passed through a plug of silica gel ($SiO_2$; diethyl ether) to give the *alkenes* (21.2 mg, 67%) as an oily yellow solid which was crystallised by freezing from light petroleum (bp 30–40 °C) to give yellow irregular crystals of one isomer (of undetermined stereochemistry); $\delta_H$(200 MHz; $CDCl_3$) 7.76 (1H, dd, *J* 7.6 and 1.9, ArH), 7.6–7.3 (5H, m, ArH and vinyl-H), 7.16 (1H, dd, *J* 7.4 and 1.3, ArH), 3.58 (3H, d, *J* 1.2, vinyl-Me) and 2.68 (6H, s, $NMe_2$); $\delta_C$($CDCl_3$) 151.8, 135.8, 133.7, 132.2, 129.3, 128.3, 128.2, 125.5, 124.0, 123.1, 116.9, 116.3, 45.6 and 29.4.

#### 1-(*N*,*N*-Dimethylamino)-8-(2-methylethenyl)naphthalene

Sodium bis(trimethylsilyl)amide (1.18 $cm^3$, 1.0 M) solution in tetrahydrofuran (20 $cm^3$) was added to a suspension of ethyltriphenylphosphonium bromide (436.1 mg, 1.18 mmol) in tetrahydrofuran under argon at −58 °C (dry-ice–chloroform bath) and stirred at −58 °C for 1 h to give an orange solution of ylide. The ylide solution was added *via* a cannula to a solution of 8-(*N,N*-dimethylamino)naphthalene-1-carbaldehyde (115.9 mg, 0.783 mmol) in tetrahydrofuran (5 $cm^3$) at −58 °C under argon and the solution stirred for 30 minutes. The mixture was allowed to warm to room temperature, brine was added and the mixture extracted with diethyl ether (20 $dm^3$). The extract was washed with water (3 × 30 $cm^3$), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed ($SiO_2$; light petroleum (bp 30–40 °C)) to give a mixture of the alkenes (111.4 mg, 67%) as an oily yellow solid; $R_f$ (light petroleum (bp 30–40 °C)) 0.35; $\delta_H$(200 MHz; $CDCl_3$) 7.75–7.20 (aromatic and vinyl Hs of mixed isomers), 7.14 (1H, dd, *J* 3.3 and 1.2, ArH), 7.11 (1H, dd, *J* 3.3 and 1.2, ArH′), 6.02 (1H, dq, *J* 15.4 and 6.5, C*H*$CH_3$), 5.68 (1H′, dq, *J* 11.4 and 4.6, C*H*′$CH_3$), 2.72 (6H, s, $NMe_2$), 2.65 (6H′, s, $NMe_2$), 1.96 (3H, dd, *J* 6.5 and 1.8, $CCH_3$) and 1.88 (3H′, dd, *J* 6.9 and 1.8, $CCH_3$).

#### Crystal structures

Determinations were carried out by Dr J. E. Davies and N. Feeder of this Department. Details of data collection are summarised in Table 4 for compounds **5** (two determinations, with crystals obtained from different solvents, giving three independent, almost identical structures) and **9**, R = H. Full details—tables of final fractional atomic co-ordinates, the full list of bond lengths and angles and the list of thermal parameters—have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ. Any request to the CCDC for this material should quote the full literature citation and the reference numbers (112767–112770) which are listed in Table 4 for individual compounds. Details for structure **13** will be published separately.

## Acknowledgements

D. R. W. H. thanks the EPSRC for a Studentship. We are grateful also to Dr J. E. Davies of this Department for help with crystal structure determination, and to Dr J. D. Wallis for information in advance of publication. R. A. R. would have been amused.

## References

1 A. J. Kirby and F. O'Carroll, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 649.
2 A. J. Kirby, *Adv. Phys. Org. Chem.*, 1980, **17**, 183.
3 Y. Ma, unpublished work.
4 Z. Rappoport, *Acc. Chem. Res.*, 1992, 474.
5 C. F. Bernasconi, R. J. Ketner, X. Chen and Z. Rappoport, *J. Am. Chem. Soc.*, 1998, **120**, 7461.
6 P. Flowerday and M. J. Perkins, *J. Chem. Soc. C*, 1970, 298.
7 J. E. Baldwin, *J. Chem. Soc.*, *Chem. Commun.*, 1976, 734.
8 C. M. Evans and A. J. Kirby, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 1269.
9 N. Beydoun and M. Pfeffer, *Synthesis*, 1990, **8**, 729.
10 T. Okuyama and M. Ochiai, *J. Am. Chem. Soc.*, 1997, **119**, 4785.
11 W. B. Schweizer, G. Procter, M. Kaftory and J. D. Dunitz, *Helv. Chim. Acta*, 1978, **61**, 2783.
12 P. C. Bell and J. D. Wallis, *Chem. Commun.*, 1999, 257.
13 P. J. Stang, *Angew. Chem.*, *Int. Ed. Engl.*,1992, **31**, 274.
14 M. Ochiai, Y. Kitagawa, M. Toyonari, K. Uemura, K. Oshima and M. Shiro, *J. Org. Chem.*, 1997, **62**, 8001.
15 R. W. Alder, P. S. Bowman, W. R. S. Steele and D. R. Winterman, *Chem. Commun.*, 1968, 723.
16 A. J. Kirby and J. M. Percy, *Tetrahedron*, 1988, **44**, 6911.
17 A. J. Kirby and J. M. Percy, *Tetrahedron*, 1988, **44**, 6903.
18 H. A. Staab, C. Krieger, G. Hieber and K. Oberdorf, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 1884.
19 D. R. W. Hodgson, PhD Thesis, University of Cambridge, 1999.

*Paper 9/000901*