# Reactions of *N*-Cinnamoylaziridines by Generation of Aziridino Ketyls from Homolytic Cleavage of Michael Adducts[1]

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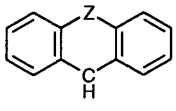
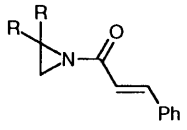
High yields of the pyrrolidinones **2a, b** are obtained from *N*-cinnamoylaziridines **1a, b** and the carbanion 'anthracene hydride' (anion of dihydroanthracene). Aziridino ketyls **3a, b** are intermediates that probably arise by way of base-initiated homolytic fragmentation of an intermediate adduct. From reactions with xanthenyl anion $X^-$ it can be deduced that Michael addition is the first step, perhaps in the absence of steric hindrance (**1a**) accompanied by carbonyl addition. Reversibility of the addition with $X^-$ allows the irreversible nucleophilic ring-opening of **1a** by $X^-$ to dominate in long term runs where the ultimate product is the spiro piperidinone **14**. The trityl anion $Tr^-$ and **1a** form a Michael adduct **26** that slowly homolyses to **3a** giving finally the *para* substituted triphenylmethanes **22** and **23** which probably result from an $S_{RN}1$ chain reaction.

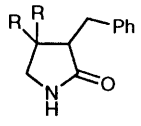
A preliminary paper[2] described the conversion of *N*-cinnamoylaziridines **1a, b** into the pyrrolidones **2a, b** by treatment with the radical anion of naphthalene or with the carbanion 'anthracene hydride' $AH^-$. Laurent *et al.*[3] reported full details for the reaction of **1a, b** with naphthalenide. High yields of **2a, b** were also obtained from **1a, b** with tributyltin hydride–AIBN.[4]



**AH** Z = $CH_2$
**X** Z = O
$AH^-$, $X^-$ = carbanions

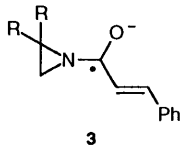


**1**



**2**

| 1–9 | R |
|---|---|
| a | H |
| b | Me |



**3**

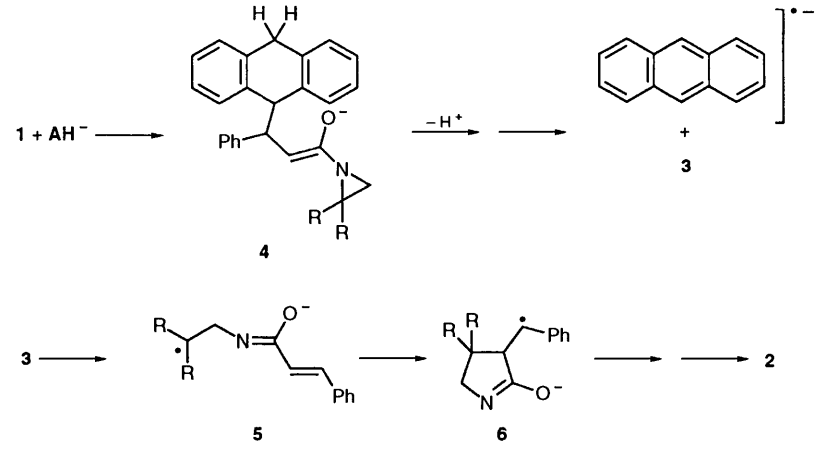
A factor common to all these reactions is homolytic cleavage of the aziridine ring to generate an amidatoalkyl radical that cyclizes by addition to the C=C double bond. Homolytic ring-opening of **1a, b** requires a radical precursor with sufficient spin density at the carbonyl carbon. Such precursors, **3a, b**, arise in the reactions of **1a, b** with anionic reagents. Generation of **3a, b** by direct single electron transfer (SET) from a radical anion to **1a, b** poses no mechanistic problem. However, general principles[5] concerning driving forces and competing polar reactions are not well in accord with the analogous outer-sphere SET from $AH^-$ or similar carbanions proposed in the preliminary paper.[2] This direct path to the ketyl is particularly unlikely for **1a** considering the general reactivity of other acylaziridines. On the other hand **1b** is more easily reduced (0.3 V) to the ketyl than its benzoyl analogue for instance.[3] This situation prompted the present reactivity study of **1a, b** whose main outcome are an alternative path to **3a, b** and an unexpected path to **3a** in a special case.

It has been shown[6] that in reactions with $AH^-$ a special type of inner-sphere SET can easily generate analogous ketyls derived from *N*-aroylaziridines. The initial product is formed by addition of $AH^-$ to the carbonyl group. Deprotonation of this adduct by an excess of $AH^-$ triggers off a homolytic fragmentation yielding anthracenide $A^{\bullet-}$ and the respective ketyl. An analogous 'benzylic fragmentation' to yield another type of ketyl has been described[6] for various Michael adducts of $AH^-$.

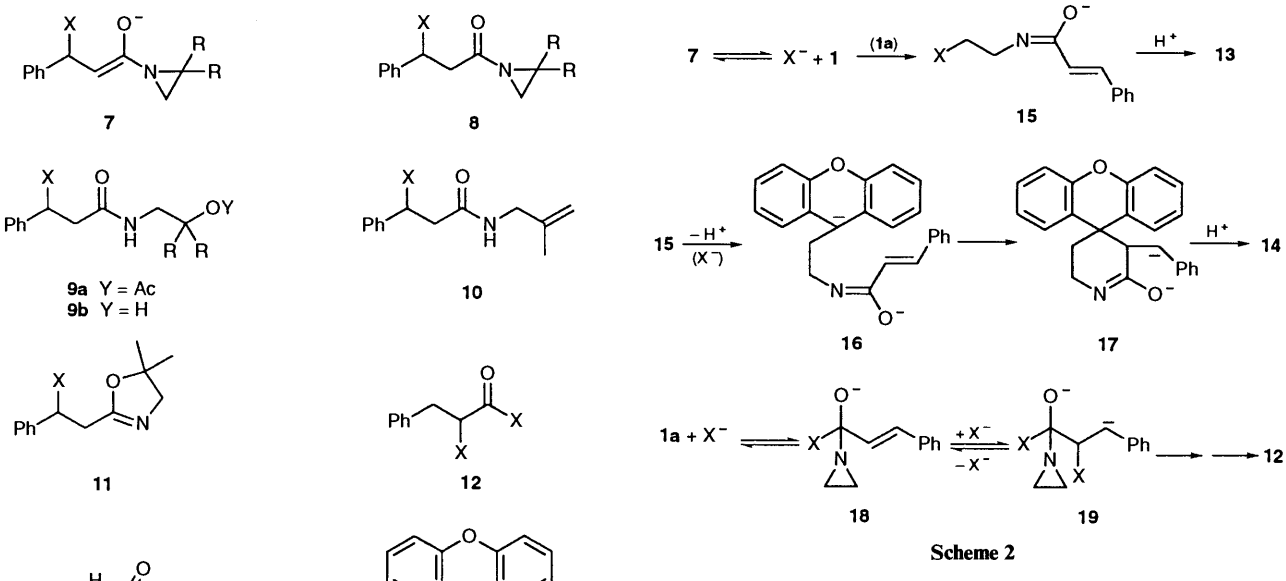
## Results and Discussion

Reaction of **1a, b** with an excess of $AH^-$ provided **2a** (86%) and **2b** (78%). By analogy with benzoylaziridines[6] one may conclude that essential steps are the formation of an adduct and its base-induced fragmentation to give the ketyls **3a, b**. The respective reaction sequence is shown in Scheme 1 for the more likely intermediate Michael addition although a carbonyl addition has to be considered too. Deprotonation of the anionic Michael adduct **4a, b** (or the respective carbonyl adduct) by $AH^-$ followed by benzylic fragmentation provides ketyl **3a, b**, anthracenide $A^{\bullet-}$, and dihydroanthracene $AH_2$ in equimolar quantities. Homolysis of **3a, b** results in radicals **5a, b** that cyclize to the isomeric radicals **6a, b**. The hydrogen to be attached to the benzylic carbon of **6a, b** is provided by $AH_2$ as can be concluded by analogy from an isotope experiment with a benzoylaziridine.[7] Probably, at least a part of this attachment is a multi-step process consisting of radical combination of the benzylic radical **6a, b** with $A^{\bullet-}$ followed by spontaneous heterolytic fragmentation to yield anthracene and the carbanion corresponding to **6a, b** (*cf.* ref. 8). Irrespective of such details, the essentials of the whole reaction sequence are a rapid trapping of the aziridine **1** at the beginning and a lack of high concentrations of strong reductants as, *e.g.*, $N^{\bullet-}$ or ketyl **3**, in the subsequent steps. This may be the reason for the high yields of **2a, b** and the failure to detect those by-products that had been formed by further reduction of radicals **5a, b** in outer-sphere SET with a radical anion.[2,3] It appears that no other reaction of the amidatoalkyl radicals **5a, b** can compete with the cyclization that forms **6a, b**.

The general reactivity of **1a, b** toward carbanions of type $AH^-$ has been studied by reactions with xanthenyl anion $X^-$, the oxa analogue of $AH^-$. With $X^-$ no base-induced fragmentations are possible. The results of these reactions with **1a** are shown in Scheme 2 and Table 1. Michael addition was the main reaction in runs 1 and 2. Isolation of the adduct **8a** was restricted by its reaction with the acetic acid (artifact **9a**) employed to quench the reaction. About 25% of nucleophilic ring-opening (product **13**) in runs 1 and 2 do not exclude a preceding reversible addition reaction. Preceding reversible additions are known[9] for ring-opening of benzoylaziridine by $X^-$ and by $AH^-$. Moreover, reversibility of addition reactions is demonstrated by the long term runs 3 and 4. A further product was the ketone **12** whose structure requires a two-fold



Scheme 1



Scheme 2

**Table 1** Reactions of **1a** with the xanthenyl anion $X^-$ in THF at room temperature.

| | Reagents (mmol)[a] | | | Yields (%) of products | | | | |
|---|---|---|---|---|---|---|---|---|
| Run | **1a** | $X^-$ | Time[b] | **8a** | **9a** | **12** | **13** | **14** |
| 1 | 20 | 25 | 5 min | 31 | 12 | 31 | 23 | |
| 2 | 20 | 25 | 5 min[c] | – | 43 | 28 | 25 | |
| 3 | 20 | 25 | 1 d | – | 15 | 13 | 35 | 32 |
| 4 | 10 | 12.5 | 7 d | – | – | – | – | 79 |

[a] In THF (100 $cm^3$ each). $X^-$ was generated by means of BuLi from 1.25 equiv. of xanthene **XH**. [b] The time required for the addition of **1a** was about 30 s in runs 1 and 2, *ca.* 30 min in runs 3 and 4. All runs were quenched with acetic acid. [c] Run 2 was stirred for 1 d after addition of acetic acid.

attack of $X^-$ on the cinnamoyl moiety of **1a**, *i.e.* one attack on the carbonyl group. A possible reaction sequence starting with the carbonyl addition **1a**→**18** is shown in Scheme 2. Thus, carbonyl addition may also play a certain role in the reactions of **1a** with $AH^-$.

The irreversibly formed amidoethylated xanthene **13** or rather its anion **15** is not the ultimate product. This is the spiro piperidinone **14** as shown by runs 3 and 4. The formation of **14** is not clear apart from the intermediacy of **15**. The following path deserves consideration. The anion **15** of **13** will partially be deprotonated by an excess of $X^-$. Cyclization of dianion **16** yields the dianion **17** of the spiro pyrrolidone **14**. One should be aware that the carbanions in Schemes 1 and 2 actually are organolithium compounds. The latter structure may explain the formation of less-stable carbanions by addition of a more stable one in the steps **16**→**17** and **18**→**19**, since the benzyllithium structure of **17** and of **19** can be stabilized by coordination to the aziridine nitrogen or to the xanthenyl oxygen. One referee, however, proposed a radical ring-closure. Once a small amount of carbanion **16** has been oxidized (by **1a**) to the respective radical, this, reversibly, cyclizes to yield the benzylic radical corresponding to the benzylic anion **17**. This abstracts a hydrogen atom from the xanthenyl moiety of the next molecule **15** and starts a chain reaction. The problem that the cyclization goes again from a more stable to a less stable species may be overcome by the irreversibility of the hydrogen abstraction. Preference can be given neither to the radical nor to the carbanion path. The crucial step may differ from the crucial step in the formation of diketone **12**, since **19** must rapidly, although reversibly, be stabilized by intramolecular proton transfer from a xanthenyl moiety.

In reactions of $X^-$ with **1b** (Table 2) we observed only Michael addition. The adduct **8b** is much more labile than the adduct **8a**. Thermal[10] and acidic isomerizations of 1-acyl-2,2-dimethylaziridines to the respective *N*-methallyl amides are

**Table 2** Reactions of **1b** (20 mmol[a]) with the xanthenyl anion $X^-$ (25 mmol[b]) in THF at room temperature[c]

| Run | Quenched with acetic acid | Chromatography | Yields (%) of products[d] 8b | 9b | 10 | 11 |
|---|---|---|---|---|---|---|
| 1 | + | + | – | – | 96 | – |
| 2 | – | + | – | 17 | 65 | 10 |
| 3 | –[e] | –[e] | (77) | – | (23) | – |

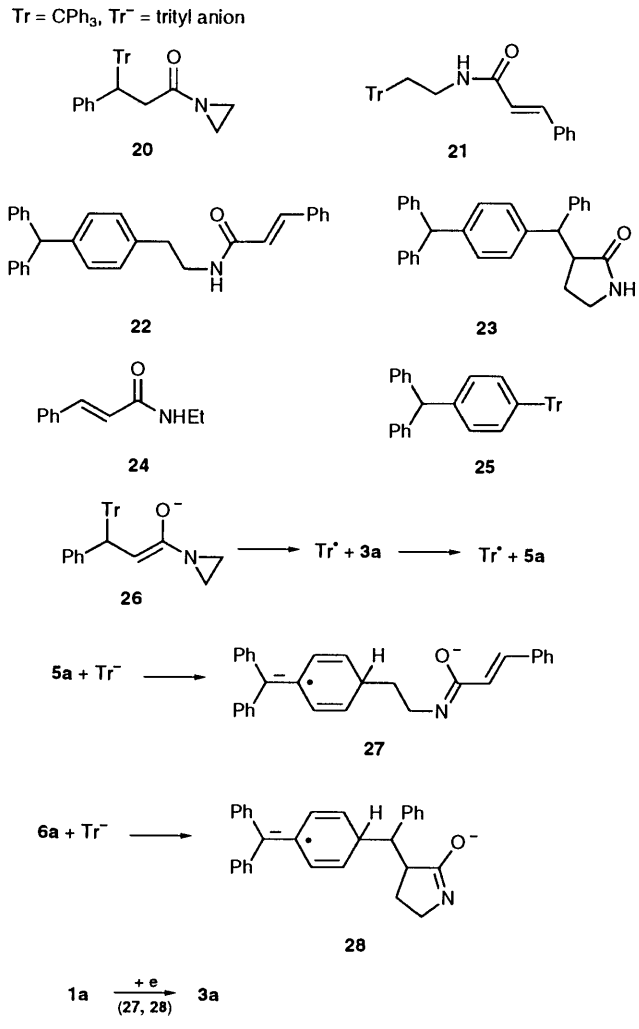
[a] In THF (100 $cm^3$). [b] Generated with BuLi from xanthene **XH** in THF (100 $cm^3$). [c] Reaction time 1 d. [d] Yields in parentheses are relative yields estimated from the $^1H$ NMR spectrum. [e] Evaporation (*ca.* 10 min) of THF at a bath temperature not exceeding 45 °C. Subsequent treatment with $CH_2Cl_2$–water and evaporation (*ca.* 10 min) of the organic layer at a bath temperature not exceeding 40 °C changed the ratio **8b**:**10** to 62:38.

known. Chromatography on silica gel is able to convert such an aziridine into a mixture of the methallyl amide, of the respective 5,5-dimethyloxazoline, and of the product of hydrolytic ring-opening.[11] The results of run 1 and run 2 of Table 2 with the products **9b**, **10** and **11** are, therefore, well understandable. They indicate that the primary Michael adduct **8b** is sensitive to work-up procedures. Avoiding acid treatment, chromatography and high temperatures, we were able to detect the elusive **8b** in $^1H$ NMR spectra of the mixtures obtained with its artifact **10** (run 3).

The common feature of all the above reactions is a very fast addition of the carbanion to the cinnamoyl group. Any reactivity difference between **1a** and **1b** in reactions with $AH^-$ becomes blurred by the subsequent rather fast fragmentation. This makes the type of addition and other reaction paths unimportant for the final result. The difference between **1a** and **1b** in reactions with $X^-$ is not surprising when one considers steric hindrance and the change from a primary to a tertiary alkyl group.

The reaction of the trityl anion $Tr^-$ with **1a** (Table 3, run 1) resulted in Michael addition (product **20**) and a small amount of nucleophilic ring-opening by the carbanion (product **21**). We expected that a longer reaction time would favour the latter reaction owing to the reversibility of the former. The result of a long term run was surprising: in run 2 the yield of **21** increased from 2% to only 8% and no **20** was detected. Four unexpected products were the two *para* substituted triphenylmethanes **22** and **23**, the ethylamide **24** and the triphenyl dimer **25**. Formation of these four products requires an SET mechanism that includes the intermediacy of **3a** and **5a** for the first three products and the intermediacy of **6a** for **23**.

SET from $Tr^-$ to acylaziridines is known[12] but is restricted to sufficient steric hindrance of direct nucleophilic attack as, *e.g.*, by 2,2-dimethyl substitution. Removing both[13] or one[1c] of the methyl groups allows nucleophilic ring-opening by the carbanionic centre of $Tr^-$ giving high yields of the respective products; even a *p*-phenylbenzoyl group, that is comparable to a cinnamoyl group in reducibility, did not show any indication of SET.[1c] One may, therefore, expect that an electron transfer from $Tr^-$ to **1a** would not be able to compete with the nucleophilic ring-opening. A reasonable alternative mechanism is spontaneous homolytic fragmentation of the anionic Michael adduct **26** into trityl radical $Tr^\bullet$ and ketyl **3a** (Scheme 3). A similar homolytic dissociation of a carbonyl adduct was probably responsible for the formation of some *N*-ethylbenzamide in long term reactions of $X^-$ with benzoylaziridine.[9] A spontaneous homolysis should occur even more easily with the Michael adduct **26** due to the greater thermodynamic stabilities of the generated radical products. A small amount of homolysis would be sufficient for the result of run 2 in Table 3 when an $S_{RN}1$ chain as shown in Scheme 3 can build up.




**Scheme 3**

Radicals **5a** and **6a**, respectively, would add to a *para* position of the excess of $Tr^-$ in analogy to the behaviour of methyl radical.[14] The radical anions **27** and **28** arising should be able to reduce **1a** to its ketyl **3a** and start the next propagation circle. The necessary aziridine **1a** will be available from the reversal **26**→**1a** + $Tr^-$ of the Michael addition. This sequence explains the *para* substitution in **22**. If the sterically undemanding radical **5a** were to combine with $Tr^\bullet$, it should attack the *ortho* position.[12] Moreover, the radical anions **27** and **28** will also be able to reduce a part of radical **5a** to the respective carbanion, the precursor of the ethylamide **24** obtained. The products formed from **27** and **28** by detachment of an electron would rearomatize[12] and finally yield **22** and **23**.

The reaction of **1b** with $Tr^-$ will be described in another paper together with outer-sphere SET reactions of $Tr^-$ with other 1-acyl-2,2-dimethylaziridines.

## Experimental

Characterization of products was accomplished by $^1H$ NMR (Bruker W 250 spectrometer, $CDCl_3$ solution unless otherwise stated, multiplicity given, *J* values in Hz), IR (Perkin-Elmer 283 spectrometer, KBr tablets unless otherwise stated), and mass spectroscopy (Varian MAT 311-A instrument). Light petroleum refers to the fraction boiling in the range 50–70 °C. Aziridines **1a**, **b** are known compounds.[4]

All reactions were performed under dry nitrogen in dry THF with continuous stirring. The reactions were either

**Table 3** Reaction of **1a** with trityl anion $Tr^-$ in THF at room temperature[a]

| Run | Time | Yields (%) of products[b] | | | | | |
|---|---|---|---|---|---|---|---|
| | | **20** | **21** | **22** | **23**[c] | **24** | **25** |
| 1 | 20 min | (96) | 2 | – | – | – | – |
| 2 | 4 d | – | 8 | 4 | (15) | (10) | (3) |

[a] A solution of **1a** (5 mmol) in THF (20 $cm^3$) was dropwise added within 2 min to a solution prepared by addition of BuLi (10 mmol, hexane solution) to a solution of triphenylmethane (12.5 mmol) in THF (100 $cm^3$). The reactions were quenched with acetic acid. [b] Yields in parentheses are from $^1H$ NMR analyses. [c] Mixture (*ca.* 1:1) of diastereoisomers α-**23** and β-**23**.

quenched or not quenched as stated either below or in Tables 1–3. Evaporation provided a residue that was taken up in dichloromethane. This solution was washed with water. Evaporation of the organic layer yielded a residue, which was subjected to column chromatography (silica gel Merck, 0.063–0.2 mm, other details are given with each run).

*Reaction of* **1a** *with* $AH^-$.—A solution of **1a** (1.73 g, 10 mmol) in THF (100 $cm^3$) was added within *ca.* 30 s to a solution of $AH^-$, that had been prepared by addition of butyllithium (hexane solution, 12.5 mmol) to the solution of 9,10-dihydroanthracene $AH_2$ (2.71 g, 15 mmol) in THF (100 $cm^3$). After 5 min the reaction was quenched with acetic acid. Chromatography with light petroleum removed the hydrocarbons and elution with ethyl acetate provided a residue whose chromatography (ethyl acetate) yielded **2a** (1.51 g, 86%, characterized in ref. 4).

*Reaction of* **1b** *with* $AH^-$.—The reaction of **1b** (2.01 g, 10 mmol) with $AH^-$ was performed as described above for **1a**, except that the reaction was not quenched. Work-up in the same manner as above yielded **2b** (1.58 g, 78%, characterized in ref. 4).

Reactions with $X^-$ were performed as described in Tables 1 and 2.

*Run 1, Table 1.* Chromatography with light petroleum removed xanthene and xanthenone. Continued elution (toluene) yielded **12** (2.30 g, 31%); m.p. 144–145 °C (Found: C, 85.0; H, 5.4. $C_{35}H_{26}O_3$ requires C, 85.0; H, 5.3%); $\nu_{max}/cm^{-1}$ 1703 (C=O) and 1260 (C–O–C); δ 2.50 (dd, *J* 18.5 and 6.2, C*H*H), 2.87 (dd, *J* 18.5 and 8.6, 1 H of C*H*H), 3.36 (ddd, *J* 8.6 and 6.2 and 4.0, O=CCH), 3.93 (d, *J* 4.0, O=CCCH), 4.93 (s, O=CCH of xanthenyl), 6.02–6.05 (m, 2 H of xanthenyl), 6.14–6.17 (m, 1 H of xanthenyl) and 6.72–7.52 (m, 18 ArH).

Continued elution (ethyl acetate) provided a mixture whose chromatography (3.5 × 45) yielded (dichloromethane) **8a** (2.20 g, 31%); m.p. 127–128 °C (Found: C, 81.1; H, 5.8; N, 4.0. $C_{24}H_{21}NO_2$ requires C, 81.1; H, 6.0; N, 3.9%); $\nu_{max}/cm^{-1}$ 1688 (C=O) and 1254 (C–O–C); δ 2.00–2.03 (m, 2 H of aziridine), 2.09–2.12 (m, 2 H of aziridine), 2.70 (dd, *J* 15.9 and 8.8, O=CC*H*H), 2.86 (dd, *J* 15.9 and 6.7, 1 H of O=C$CH_2$), 3.65 (ddd, *J* 8.8 and 6.7 and 4.8, O=CCCH), 4.28 (d, *J* 4.8, 9-H of xanthenyl), 6.57–6.61 (m, 2 H of xanthenyl) and 6.91–7.77 (m, 11 ArH).

Further elution (dichloromethane) of the second column yielded **13** (1.38 g, 23%); m.p. 142–143 °C (Found: C, 80.9; H, 5.9; N, 3.9. $C_{24}H_{21}NO_2$ requires C, 81.1; H, 6.0; N, 3.9%); $\nu_{max}/cm^{-1}$ 3300 (NH), 1656 (amide I), 1538 (amide II) and 1254 (C–O–C); δ 2.00 (q, *J* 5.7, $NCCH_2$), 3.28 (dt, *J* 5.4 and 5.7, $NCH_2$), 4.12 (t, *J* 5.7, 9-H of xanthenyl), 5.61 (t br, *J* 5.5, NH), 6.16 (d, *J* 15.6, O=C–CH=C), 7.03–7.09 (m, 4 H of xanthenyl), 7.10–7.25 (m, 4 H of xanthenyl), 7.31–7.33 (m, *m*-H and *p*-H of Ph), 7.40–7.44 (m, *o*-H of Ph) and 7.47 (d, *J* 15.6, O=C–C=CH).

Further elution (ethyl acetate) of the second column yielded **9a** (0.96 g, 12%); m.p. 140–141 °C (Found: C, 75.0; H, 6.2; N, 3.5. $C_{25}H_{25}NO_4$ requires C, 75.2; H, 6.1; N, 3.4%); $\nu_{max}/cm^{-1}$ 3320 (NH), 1740 (ester), 1661 (amide I), 1545 (amide II) and 1265 (C–O–C); δ 1.91 (s, Me), 2.40 (dd, *J* 14.8 and 9.6, 1 H of O=C$CH_2$), 2.59 (dd, *J* 14.8 and 6.1, 1 H of O=C$CH_2$), 3.25 (m, $NCH_2$), 3.47 (ddd, *J* 9.6 and 6.1 and 4.8, O=CCCH), 3.75–3.92 (m, $NCCH_2$), 4.20 (d, *J* 4.8, 9-H of xanthenyl), 6.02 (t br, *J* 5.6, NH), 6.55–6.58 (m, 2 H of xanthenyl) and 6.88–7.20 (m, 11 ArH).

*Run 2, Table 1.* Chromatography with light petroleum removed xanthene. Continued elution provided (toluene) **12** (2.30 g, 31%) and (ethyl acetate) a mixture whose chromatography yielded (dichloromethane) **13** (1.80 g, 25%) and (ethyl acetate) **9a** (3.45 g, 43%).

*Run 3, Table 1.* Chromatography with light petroleum removed xanthene and xanthenone. Continued elution provided (toluene) **12** (0.96 g, 13%) and (ethyl acetate) a mixture whose chromatography yielded (dichloromethane) **13** (2.10 g, 35%) and (ethyl acetate) **14** (2.27 g, 32%); m.p. 152–153 °C (Found: C, 81.1; H, 5.9; N, 3.8. $C_{24}H_{21}NO_2$ requires C, 81.1; H, 6.0; N, 3.9%); $\nu_{max}/cm^{-1}$ 3210 (NH), 1670 (amide) and 1240 (C–O–C); δ 2.22–2.27 (m, $NCCH_2$), 2.40 (dd, *J* 14.7 and 2.4, 1 H of O=CCC$H_2$), 3.22–3.31 (m, 1 H of $NCH_2$, 1 H of O=CCC$H_2$), 3.34–3.42 (m, O=CCH, 1 H of $NCH_2$), 6.36 (s br, NH) and 7.00–7.38 (m, 13 ArH); δ($CDCl_3$–$CF_3CO_2D$) 2.40–2.45 (m, $NCCH_2$), 2.72 (dd, *J* 14.8 and 3.3, 1 H of O=CCC$H_2$), 3.12 (dd, *J* 14.8 and 7.9, 1 H of O=CCC$H_2$), 3.64–3.69 (m, $NCH_2$), 3.79 (dd, *J* 7.9 and 3.3, O=CCH), 6.90–6.93 (m, 2 ArH) and 7.11–7.45 (m, 11 ArH).

Further elution (ethyl acetate) provided **9a** (1.20 g, 15%).

*Run 4, Table 1.* Chromatography with light petroleum removed xanthene. Elution with ethyl acetate provided a mixture whose chromatography yielded (dichloromethane) a mixture of xanthene and xanthenone followed (ethyl acetate) by **14** (2.81 g, 79%).

*Run 1, Table 2.* Chromatography (dichloromethane) provided a mixture of xanthene and xanthenone followed by **10** (7.36 g, 96%); m.p. 109–110 °C (Found: C, 81.6; H, 6.5; N, 3.7. $C_{26}H_{25}NO_2$ requires C, 81.4; H, 6.6; N, 3.7%); $\nu_{max}/cm^{-1}$ 3400 (NH), 1647 (amide I), 1541 (amide II) and 1253 (C–O–C); δ 1.47 (s, Me), 2.47 (dd, *J* 14.7 and 10.0, 1 H of O=C$CH_2$), 2.68 (dd, *J* 14.7 and 5.7, 1 H of O=C$CH_2$), 3.52 (ddd, *J* 10.1 and 5.7 and 4.7, O=CCCH), 3.54 (dd, *J* 15.7 and 6.6, 1 H of $NCH_2$), 3.68 (dd, *J* 15.7 and 5.5, 1 H of $NCH_2$), 4.25 (d, *J* 4.7, 9-H of xanthenyl), 4.44 (s br, 1 H of C=C$H_2$), 4.58 (t, *J* 1.2, 1 H of C=C$H_2$), 5.35 (t br, *J* 6, NH), 5.56–6.60 (m, 2 ArH) and 6.89–7.25 (m, 11 ArH).

*Run 2, Table 2.* Chromatography (dichloromethane) provided a mixture of xanthene and xanthenone followed by **10** (4.98 g, 65%). Elution with ethyl acetate yielded **11** (0.77 g, 10%); oil (Found: C, 81.4; H, 6.9; N, 3.6. $C_{26}H_{25}NO_2$ requires C, 81.4; H, 6.6; N, 3.7%); $\nu_{max}/cm^{-1}$(film) 1663 (C=N) and 1267 (C–O–C); δ 1.03 (s, 1 Me), 1.09 (s, 1 Me), 2.56 (dd, *J* 14.8 and 9.5, 1 H of N=C$CH_2$), 2.67 (dd, *J* 14.8 and 7.3, 1 H of N=C$CH_2$), 3.32–3.44 (m, $NCH_2$, N=CCCH), 6.53–6.56 (m, 2 ArH) and 6.88–7.16 (m, 11 ArH). Further elution (ethyl acetate) yielded **9b** (1.37 g, 17%); m.p. 123–124 °C (Found: C, 77.8; H, 6.7; N, 3.7. $C_{26}H_{27}NO_3$ requires C, 77.8; H, 6.8; N, 3.5%); $\nu_{max}/cm^{-1}$ 3300 (NH), 1637 (amide I), 1534 (amide II) and 1251 (C–O–C); δ 0.86 (s, 1 Me), 0.94 (s, 1 Me), 2.15 (s br, OH), 2.49 (dd, *J* 14.6 and 10.5, 1 H of O=C$CH_2$), 2.67 (dd, *J* 14.6 and 5.5, 1 H of O=C$CH_2$), 2.93 (dd, *J* 13.8 and 5.6, 1 H of $NCH_2$), 3.10 (dd, *J* 13.8 and 6.6, 1 H of $NCH_2$), 3.48 (ddd, *J* 10.5 and 5.5 and 4.8, O=CCCH), 4.22 (d, *J* 4.8, 9-H of xanthenyl), 5.80 (t br, *J* 6, NH), 6.58–6.61 (m, 2 ArH) and 6.89–7.26 (m, 11 ArH).

*Run 3, Table 2.* The THF solution (original reaction solution) was gently (*ca.* 10 min, bath temp. < 45 °C) evaporated. The

residue consisted ($^1$H NMR) of **8b** and **10** in the molar ratio 77:23. The residue was taken up in dichloromethane, washed with water and gently evaporated (*ca.* 10 min, bath temp. < 40 °C). The molar ratio **8b**:**10** had changed to 62:38. **8b**: $\delta$ 1.16 (s, 1 Me), 1.25 (s, 1 Me), 2.02 (s, 1 H of $NCH_2$), 2.09 (s, 1 H of $NCH_2$), 2.52 (dd, *J* 15.6 and 8.4, 1 H of O=$CCH_2$), 2.78 (dd, *J* 15.7 and 7.5, 1 H of O=$CCH_2$), 3.53–3.74 (m, O=CCCH), 4.31 (d, *J* 4.6, O=CCCCH), 6.53–6.60 (m, 2 H of xanthenyl) and 6.85–7.24 (m, 11 ArH).

*Reactions with* $\mathbf{Tr}^-$.—These reactions were performed as described in Table 3.

*Run 1, Table 3.* Chromatography (dichloromethane–ethyl acetate, 25:1) provided a mixture (2.47 g) consisting ($^1$H NMR) of triphenylmethane (1.53 g) and **20** (0.95 g). Continued elution yielded **20** (1.05 g, total 2.00 g corresponding to 96%); m.p. 153–155 °C (Found: C, 86.5; H, 6.8; N, 3.5. $C_{30}H_{27}NO$ requires C, 86.3; H, 6.5; N, 3.4%); $\nu_{max}$/cm$^{-1}$ 1664 (C=O); $\delta$ 1.58–1.70 (m, 2 H of aziridine), 1.85–1.96 (m, 2 H of aziridine), 2.60 (dd, *J* 15.6 and 11.5, 1 H of O=$CCH_2$), 3.17 (dd, *J* 15.7 and 1.7, 1 H of O=$CCH_2$), 5.23 (dd, *J* 11.5 and 1.6, O=CCCH), 6.58–6.73 (m, 2 *o*-H of single Ph), 6.94–7.09 (m, *m*-H and *p*-H of single Ph), 7.10–7.33 (m, 6 *m*-H and 3 *p*-H of trityl) and 7.41 (m, 6 *o*-H of trityl); *m*/*z* 417 (0.05, $M^+$), 243 (100, trityl) and 165 (33, fluorenyl).

Further elution yielded **21** (49 mg, 2%); m.p. 215–217 °C (Found: C, 86.3; H, 6.6; N, 3.3. $C_{30}H_{27}NO$ requires C, 86.3; H, 6.5; N, 3.4%); $\nu_{max}$/cm$^{-1}$ 3240 (NH), 1654 (amide I), 1618 (C=C) and 1561 (amide II); $\delta$ 2.85–2.95 (m, $NCCH_2$), 3.12–3.27 (m, $NCH_2$), 5.30 (t br, *J* 5.1, NH), 6.18 (d, *J* 15.6, O=CCH=C), 7.15–7.42 (m, 18 ArH), 7.42–7.51 (m, 2 *o*-H of C=CPh) and 7.58 (d, *J* 15.6, O=CC=CH).

*Run 2, Table 3.* Chromatography (dichloromethane–ethyl acetate, 25:1) provided a mixture (2.084 g) consisting ($^1$H NMR) of triphenylmethane (2.047 g) and **25** (37 mg, 3%). After a small fraction of triphenylmethanol had been eluted, further elution (dichloromethane–ethyl acetate, 10:1) yielded **21** (159 mg, 8%) and **22** (81 mg, 4%); m.p. 158–160 °C (Found: C, 86.4; H, 6.4; N, 3.4. $C_{30}H_{27}NO$ requires C, 86.3; H, 6.5; N, 3.4%); $\nu_{max}$/cm$^{-1}$ 3330 (NH), 3310 (NH), 1662 (amide I), 1623 (C=C) and 1553 (amide II); $\delta$ 2.85 (t, *J* 6.9, $NCCH_2$), 3.58–3.70 (m, $NCH_2$), 5.52 (s, CH), 5.68 (t br, *J* 5.5, NH), 6.32 (d, *J* 15.6, O=CCH=C), 7.02–7.18 (m, 8 ArH), 7.18–7.42 (m, 9 ArH), 7.42–7.53 (m, 2 *o*-H of C=CPh) and 7.62 (d, *J* 15.6, O=CC=CH); *m*/*z* 417 (16%, $M^+$), 270 (100, M − cinnamamide), 167 (6, benzhydryl), 165 (12, fluorenyl), 148 (18, cinnamamide + H), 131 (95, cinnamoyl) and 103 (36, styryl).

Further elution (ethyl acetate) provided unidentified products (271 mg) and a mixture (408 mg) consisting ($^1$H NMR) of **24** (89 mg, 10%, characterization ref. 4) and **23** (319 mg, 15%, *ca.* 1:1 mixture diastereoisomers α-**23** and β-**23** (Found: $M^+$, 417.2091. $C_{30}H_{27}NO$ requires *M*, 417.2092); $\nu_{max}$/cm$^{-1}$ 3270 (NH), 3260 (NH) and 1697 (amide); $\delta$ 1.94–2.13 (m, NCC*H*H), 2.25–2.43 (m, NCC*H*H), 2.69–2.88 (m, NC*H*H), 3.10–3.30 (m, 1 H of NC*H*H, O=CC*H*) and 6.94–7.40 (m, 14 ArH); $\delta$(α-**23**) 4.17 (d, *J* 4.0, O=CCCH), 5.48 (s, α-H of benzhydryl), 5.78 (s br, NH); $\delta$(β-**23**) 4.75 (d, *J* 3.9, O=CCCH), 5.52 (s, α-H of benzhydryl) and 5.82 (s br, NH); *m*/*z* 417 (36, $M^+$), 333 (100, benzyltriphenylmethane − H), 167 (32, benzhydryl) and 165 (20, fluorenyl).

Further elution with methanol provided unidentified products (0.65 g).

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