Three positional isomers of substituted triphenylmethanes from reactions of trityl anion with 1-acyl-2,2-dimethylaziridines[1]

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Ring opening of aziridines 4a–d in reactions with trityl anion Tr^- proceeds exclusively by cleavage of the $NCMe_2$ bond. Substitution of the benzylic carbon of Tr^- leads to 'central' products 10a–d in yields of 0–5%. This is ascribed to an S_N2 reaction with borderline character, as is well known from reactions of aziridines 4a–d with other nucleophiles. All remaining ring-opening reactions result from single-electron transfer (SET). This is direct SET from Tr^- to aziridines 4a–c. For compound 4d (acyl = cinnamoyl), the SET reaction is of the innersphere type and proceeds *via* Michael addition, at least in part. Homolytic ring opening of the generated aziridino ketyls 5 forms the tertiary amidatoalkyl radicals 6. Main reaction of radicals 6a–c is transfer of a hydrogen atom from one of its two methyl groups to the generated trityl radical Tr'. Methallylamides 7 and enamides 8 are the final products. *ortho*-Substituted triphenylmethanes 12 and/or its olefinic precursors 13 arise in ~20% yield. A mechanism for the formation of these unique products is proposed that first converts the radicals 6 into the corresponding carbanions 16 which undergo an S_N2' reaction with one allylic system TrCHCH=CH* of the dimer 14 of Tr'. The leaving group Tr^- is eliminated from this partial structure when carbanions 16 attack the marked carbon converting it finally into the substituted *ortho* carbon of compounds 12. Addition of radicals 6 to Tr^- is probably the way to the *para*-substituted triphenylmethanes 11, which arise in yields of only 0–1% from aziridines 4a,b (acyl = 4-benzoyl, pivaloyl). Higher yields of *para*-substituted compounds 11 are obtained from aziridines 4c (acyl = 4-phenylbenzoyl) and 4d. This is ascribed, at least for substrate 4c, to a chain reaction because ketyl 5c must be formed more rapidly than ketyls 5a,b. A substantial part of radical 6d cyclizes, ending up as the triphenylmethane compound 26 that carries a pyrrolidone ring in the *para* position.

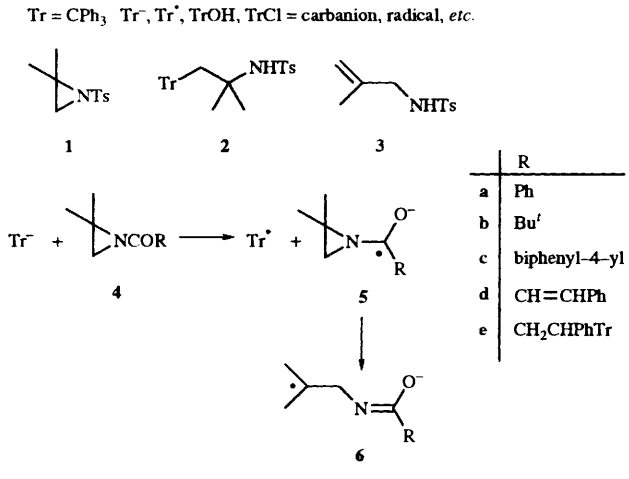
Introduction

A preliminary paper[2] reported on single-electron transfer (SET) from trityl anion Tr^- to the acyl group of 1-acyl-2,2-dimethylaziridines **4** (Scheme 1). The generated aziridino ketyls **5** undergo homolytic ring opening to form the tertiary amidatoalkyl radicals **6**. The most interesting product was seemingly formed by combination of radical **6** with one *ortho* position of trityl radical Tr'. We now propose a mechanistic modification of this surprising '*ortho* combination' and we add further results and new products to the previous short report.

Redox potentials in the literature range from −0.73 V to −0.96 V for the carbanion[3] and from −2.2 V to −3 V for *N*-acylaziridines[4] with −2.5 V for **4a** and −2.2 V for **4d**. The difference between the reactants is so large that one needs not bother about conversions that relate all these measurements to a common basis (compare ref. 3). The initial SET step is clearly endergonic and requires rapid exergonic follow-up reactions as well as retardations of competing reactions, especially of nucleophilic ring opening. The latter is the only reaction with Tr^- when the aziridine ring carries no substituents[5] or one methyl group only.[6] With two geminal methyl groups, as in compounds **4a–d**, other nucleophiles strongly prefer to attack the tertiary carbon, and this results in abnormal ring opening.[7] So, the reported[2] by-products **10** of the SET reaction with Tr^- may possibly arise from a competing borderline S_N2 process.

Results and discussion

The results of the reactions of Tr^- with activated 2,2-dimethylaziridines are listed in Table 1. Solutions of Tr^- in tetrahydrofuran (THF) were generated from triphenylmethane either with BuLi (hexane, low temperature) or with sodium naphthalenide.



Scheme 1

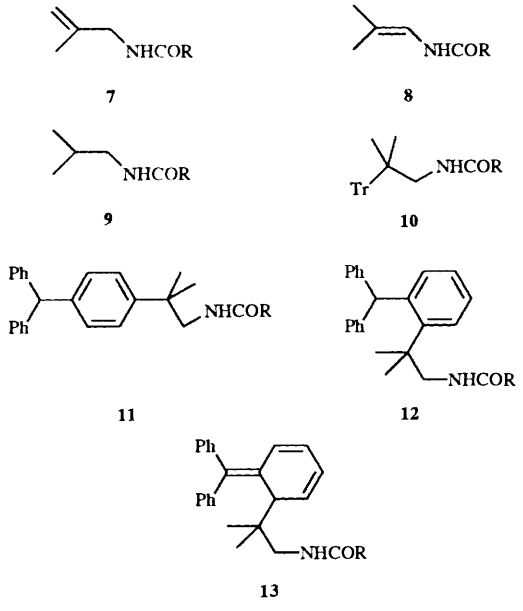
The reaction of the sulfonylaziridine **1** (run 1) is included in Table 1 to illustrate the fact that the rates of possible reactions with Tr^-, SET and nucleophilic ring opening, have the same order of magnitude for activated 2,2-dimethylaziridines. Compound **1** has a better leaving group than do acyl compounds **4a–d**. This allows a classical S_N2 reaction of compound **1**, *i.e.* normal ring opening to form compound **2** as main product. No isomer of product **2** was detected in run 1. However, the poor material balance may point to some SET reaction that cleaves the N–S bond.[8] The products formed from the two fragments of substrate **1** easily escape detection.[8] So, it is likely that the two competing reactions have similar rates with compound **1**. The poorer leaving groups of acylaziridines **4a–d**

Table 1 Reactions of trityl anion Tr^- with aziridines **1** and **4a–d** in THF[a]

Run	Reagents (mmol)				Time[b]	Yields[c] of products						
	TrH	BuLi	Na[d]	1, 4		7	8	9	10	11	12	Other products
1	12.5	10		**1** (5)	2 days							58 **2**, 11 **3**
2	30	20		**4a** (10)	16 days	30 **7a**	27 **8a**		(5) **10a**	(1) **11a**	21 **12a**	
3	30	20		**4a** (10)	18 days	10 **7a**	54 **8a**	tr **9a**			24 **12a**	
4[e]	11	10		**4a** (8.5)[e]	30 min	(64) **7a**			1 **10a**	tr **11a**		23 **13a**[f]
5	40		20	**4a** (10)	10 days	(23) **7a**	(39) **8a**	(3) **9a**	4 **10a**		22 **12a**	
6	40		20	**4a** (10)	18 days		48 **8a**	13 **9a**	(6) **10a**		20 **12a**	
7	20		7.5	**4a** (5)	13 days		38 **8a**	15 **9a**	2 **10a**		20 **12a**	
8[g]	20		7.5	**4a** (5)	14 days[g]	(55) **7a**	(4) **8a**	(6) **9a**	5 **10a**		26 **12a**	
9	25	20		**4b** (10)	6 days	55 **7b**	(4) **8b**			(0.2) **11b**	22 **12b**	
10	12.5	10		**4b** (5)[h]	15 min	(38) **7b** 25 **7c**			3 **10b**		tr **12b**	(13) **13b**, (2) **20**, (3) **21**, 7 **22**
11	12.5	10		**4c** (5)	6 days	(6) **7d**	(5) **8c**	(2) **9c**	4 **10c**	19 **11c**	(6) **12c**	(3) **13c**
12	12.5	10		**4d** (5)	8 days	(14) **7d**			tr **10d**	(16) **11d**	(3) **12d**	(3) **14**, (38) **26**
13	12.5	10		**4d** (5)	30 min[i]			(1) **9d**	(1) **10d**	(8) **11d**	(0.2) **12d**	6 α-**26**, 5 β-**26**, (3) **27**, (2) **28**, (3) **29**

[a] Tr^- was generated in THF (50–100 cm^3). Substrate **2** or **4**, dissolved in THF (10–20 cm^3, 50 cm^3 in run 4), was added dropwise within 2–5 min or (run 10) rapidly injected. [b] The reactions were quenched with acetic acid except for run 13. [c] Yields in parentheses are from ^1H NMR analysis. Products found in traces (tr) were identified by ^1H NMR signals of mixtures. [d] Together with an equivalent amount of naphthalene. [e] The red colour of the Tr^- solution changed to yellow when compound **4a** (8.5 mmol) was added. The yields of run 4 are based on 69% conversion of acylaziridine **4a** since 31% of starting material **4a** was recovered. [f] See text. [g] The reaction was started under cooling with ice–NaCl. [h] Rapidly injected. [i] The reaction with Tr^- was quenched by dropwise addition of a solution of TrCl (10 mmol) in THF (17 cm^3). Discolouration of the red solution required 5 cm^3. Stirring under nitrogen was continued for 8 days. TrOH (2.9 mmol) was detected by chromatography.

must slow down nucleophilic ring opening and force the S_N2 borderline mechanism that displaces the nitrogen from the tertiary carbon.[7] Assuming similar SET rates for compound **1** and **4** the small yields of products **10** in Table 1 are compatible with a non-SET path. The methallylamide **3** in run 1 is probably an artifact of non-converted compound **1** since the easily recognizable ^1H NMR signals of compound **3** were not detected in the crude reaction mixture.



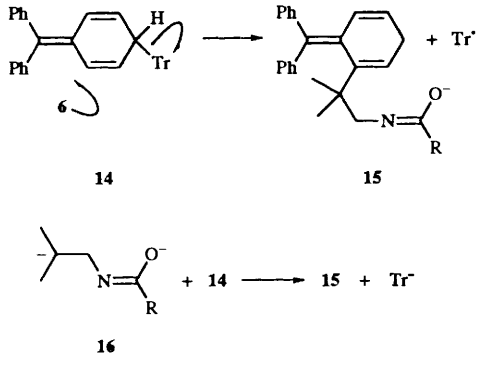
In contrast to run 1, run 2 (and the other runs of Table 1) proceeded nearly exclusively *via* SET. Main products were methallylamide **7a** and the isomeric enamide **8a**. A separate experiment showed that enamide **8a** arises from methallylamide **7a** in a reaction of their amide anions. Similar experiments established the isomerization of methallylamides **7b,c** to enamides **8b,c** in other runs. The progress of this isomerization is clearly recognized from a comparison of run 2 with run 3 and 4. The isomerizations in Table 1 show that the methallylamides **7** are not artifacts of unchanged aziridines **4**. The nitranions of compounds **7** can only arise by hydrogen transfer from radical anions **6** to $Tr^{\cdot}$. The enamides **8** are sensitive to hydrolytic cleavage, as shown by the detection of benzamide in the experiment with compound **7a**.

Three isomeric amidoethylated triphenylmethanes were found in run 2, all formed under abnormal cleavage of the aziridine ring. The main isomer was the *ortho*-substituted triphenylmethane **12a**, an extraordinary result without precedence in the chemistry of both $Tr^{\cdot}$ and Tr^-. The structure of product **12a** was conclusively established by ^1H NMR spectroscopy and was supported by the detection of precursor **13a** in run 4. Structure assignment for compounds **12** and *para* isomers **11** is primarily based on the chemical shifts for the benzylic proton (α-H) of the trityl moiety. For *para*-compound **11a** (and **11b–d**) this is δ 5.54 (δ 5.53–5.55), in very good agreement with triphenylmethane (δ 5.54), pointing to an identical propeller conformation. For *ortho*-compound **12a** (and **12b–d**), however, this chemical shift is δ 6.36 (δ 6.30–6.37), in accord with steeper conformations of the propeller blades caused by the voluminous *ortho* substituent. A similar downfield shift has been described by Kessler *et al.*:[9] δ 6.01 for tris(2,4,6-trimethylphenyl)methane and δ 6.52 for tris(2,6-dimethoxyphenyl)methane. The conformation of compound **12a** induces also a downfield shift for the methyl signal: δ 1.59 (δ 1.51–1.60 for **12b–d**) as compared with δ 1.38 for the *para* isomer **11a** (δ 1.31–1.41 for **11b–d**). Nuclear Overhauser enhancement (NOE) experiments clearly established for compound **12a** (and analogously for compound **12b**) the short distance between the two methyl groups (frequency irradiated) and the α-H as well as between the NCH_2 group and (especially strong NOE) the one neighbouring aryl H at δ 7.42–7.51. For compound **11c** there was no NOE observed between the methyl group and the α-H but instead a clear NOE between methyl (frequency irradiated) and the two neighbouring aryl H and the NCH_2 group. Irradiation at the frequency of the α-H provided also the expected NOE for both compounds **12a** and **12b**.

Run 3 needs no comment apart from the advanced conversion of methalylamide **7a** into enamide **8a**. The short-term run 4 shows the opposite effect, *i.e.* no formation of enamide **8a** at all. More important in this run, compound **12a** was replaced by a corresponding yield of its precursor **13a** as calculated from the ^1H NMR spectrum of the crude product mixture with the help of internal calibration. An attempt to

isolate compound **13a** by chromatography was unsuccessful since conjugated triene **13a** was rather unstable and could not be separated either from methallylamide **7a** or from its own unknown secondary products. The structure of compound **13a** was primarily deduced from the absence of compound **12a** in run 4 and the simultaneous appearance of five multiplets of equal intensity, one aliphatic at δ 3.05 and four olefinic ones at δ 5.78–5.88, 6.05–6.14, 6.18–6.27 and 6.42–6.50. These data coincide with the ^{1}H NMR data of the pivaloyl analogue **13b** in run 10 and of the 4-phenylbenzoyl analogue **13c** in run 11.

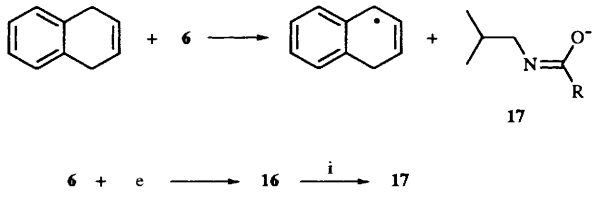
One problem of this work is already visible. It may be analysed and solved before the other results are discussed. How could one understand how a radical **6** combines at the *ortho* position of Tr$^\cdot$ but not, or practically not at all, at the more accessible *para* position? A statistical factor of 2 and a longer conjugation in the *ortho*-product are certainly insufficient to explain the strong *ortho* preference. Collisions of radical **6** with a *para* position of Tr$^\cdot$ must happen and, for steric reasons, this should be the predominating kind of collision. Since detachment of hydrogen is the main reaction of radical **6a**, there can be no doubt about the result of these collisions. It will be hydrogen transfer from one methyl of radical **6** to the *para* position of Tr$^\cdot$. Subsequent conversion of the generated unstable isomer into triphenylmethane is no problem. Base-catalysed migrations of a non-aromatic ring-hydrogen to the α position are known.[10] It follows by analogy that '*ortho* collisions' should also result in hydrogen transfer and not in combination of radicals. Two closely related mechanisms, able to solve the problem, are put up for discussion. The dimer **14** of Tr$^\cdot$ is an excellent candidate for an *ortho* substitution. Compound **14** does not allow '*para reactions*' to occur and it offers an allylic system for *ortho* substitution. The equilibrium between Tr$^\cdot$ and **14** lies strongly in favour of the dimer.[11] An S_H2' substitution of the dimer **14** by radical **6** with Tr$^\cdot$ as the leaving radical (Scheme 2) can easily explain the formation of the *ortho* products. This



Scheme 2

leads to a simple but consistent mechanistic picture when hydrogen transfer with the monomeric Tr$^\cdot$ and the radical displacement with the dimer **14** are complemented by abnormal nucleophilic ring opening of acylaziridine **4** by Tr$^-$, forming the central isomer **10**. A very similar picture arises when **Tr**$^-$ is the leaving group in an S_N2' reaction of compound **14** with carbanion **16**. Since free dianon **16** would rapidly be protonated by THF and/or an excess of triphenylmethane, this S_N2' mechanism is possible only when the required species **16** arises and reacts in a solvent cage. The reaction partners of the first in-cage step would then be radical anion **6** and the radical anion of compound **14**, providing by SET the species **16** and **14** for the second step. At least two reasonable paths to the radical anion of compound **14** are conceivable.

The important difference between the **Tr**$^-$Li$^+$ runs 2–4 and the **Tr**$^-$Na$^+$ runs 5–8 with the same aziridine **4a** is the formation of more than a trace of the *N*-isobutylamide **9a** with **Tr**$^-$Na$^+$. This is most likely not caused by an influence of the counter-ion. The applied technique for the generation of **Tr**$^-$Na$^+$ is coupled with the conversion of naphthalenide into dihydronaphthalenes. The latter are good hydrogen donors and should be able to convert radical **6a** directly into the non-radical imidate **17a** as shown in Scheme 3 for one isomer of

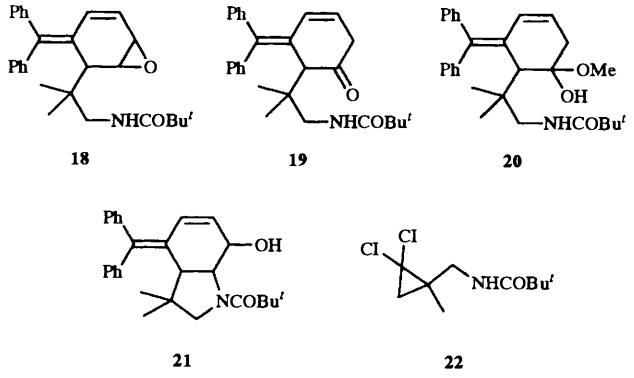


Scheme 3 *Reagent:* i, TrH or THF

dihydronaphthalene. Imidate anion **17a** yields compound **9a** when the reaction is quenched with acid. Comparison of run 5 with runs 6 and 7 shows again the slowness of the methallylamide–enamide isomerization. The unexpectedly low isomerization in run 8 is difficult to understand unless one considers that run 8 deviates from run 7 in two respects which may be interconnected: run 8 was started at a low temperature and the yields of products total 96%. So, one may tentatively assume that, owing to the high conversion, the remaining excess of Tr$^-$ was insufficient to complete the slow isomerization. Summarizing all reactions of the aziridine **4a** and including run 9 with the reaction of compound **4b**, the ratio of products (**7**, **8**, **9**) without an incorporated trityl group to the *ortho* products **12** and **13** is remarkably constant at 2.5–3.0.

The aziridine **4b** is more difficult to reduce than compound **4a**, with a difference in potential of more than 0.5 V[4] but the outcome of run 9 is quite comparable to that of respective runs with the aziridine **4a**. A short-term run should allow us to find the non-aromatized *ortho* product **13b**, that by analogy with compound **13a** in run 4, however, would be difficult to isolate in a pure state. It was hoped to overcome this difficulty by simple experimental modifications that might yield a stable derivative of compound **13b** by addition of dichlorocarbene to a double bond during work-up. Dichlorocarbene is generated in this mixture when the reaction is not quenched with acid and when the hydrolysis of the reaction mixture is performed by shaking with chloroform (in place of dichloromethane) and water. However, only the dichlorocarbene adduct **22** of methallylamide **7b** was detected (in run 10) but no adduct of compound **13b**, although the latter adduct may have been present among the unidentified products. Fortunately, careful chromatography provided a small fraction of compound **13b** sufficiently pure for a clear identification. The yield of compound **13b** in Table 1 was calculated from the ^{1}H NMR spectrum of the crude product mixture isolated directly from the chloroform layer, *i.e.* 7 days prior to chromatography. This calculation was based on the chromatographically isolated yield of the methallylamide **7b** and on the integrals for amides **13b** and **7b** in the crude mixture. This yield of amide **13b** represents (probably) a lower limit of *ortho* products since it is likely that already at this stage of the run a part of compound **13b** had changed to other products.

The chemical shifts given in ref. 2 for compound **13b** are now complemented by the data of the olefinic and aromatic protons: δ 5.78 (1 H, dd, *J* 9.9, 5.2 Hz, 4-H), 6.04 (overlapping with signals of an impurity; approximate analysis: 1 H, dd, *J* 9.3, 6.2 Hz, 2-H), 6.16 (1 H, dd, *J* 9.5, 5.3 Hz, 3-H), 6.44 (1 H, d, *J* 9.9 Hz, 5-H), 7.10–7.40 (m, more than 10 ArH due to impurities). The olefinic signals may be compared with those of compound **13a** given above. Coupling among the protons of the non-aromatic ring was confirmed by 2D homonuclear chemical-shift correlation spectroscopy (COSY). The quantity of additional minor signals pointed to several impurities. A mass spectrum of this chromatographic fraction, taken 10 days later

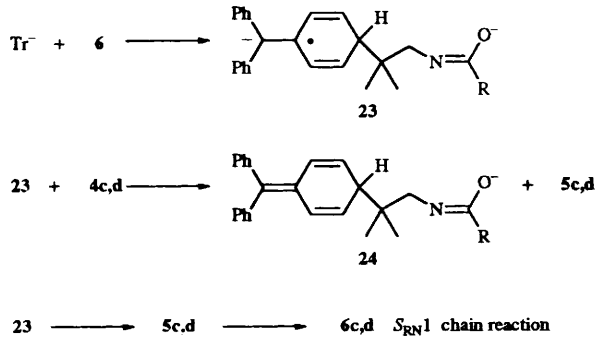


18 19 20 21 22

showed as highest-mass peak m/z 415 with an intensity higher than that of the peak at m/z 399 (M^+ for **13b**). The intensities of these two peaks were 1.8% *vs.* 0.1% at 134 °C, 16% *vs.* 2.7% at 177 °C and *vs.* 2.0% at 186 °C relative to the base peak at m/z 57 (Bu^t). The peak at m/z 415 indicates the incorporation of one oxygen atom into compound **13b**, compatible with structures **18** and **19**. A new ^{1}H NMR spectrum of this fraction, initiated by the MS results, showed only some residual compound **13b** besides unidentified products. The chromatographic fraction following that of compound **13b** was a mixture whose ^{1}H NMR spectrum was difficult to analyse. Attempts to stimulate crystallization by digestion with methanol were partly successful. Some crystals of the hemiketal **20** of the supposed ketone **19** could be picked out manually. More hemiketal **20** was detected by ^{1}H NMR spectroscopy in the mother liquor and in other fractions when they were treated with methanol.

An expected reaction of epoxide **18**, if it is formed, would be an intramolecular ring opening by the amide group. The respective product **21** was indeed found in a fraction consisting mainly of methallylamide **7b**. The very late elution of this trityl-derived product is easily explained by the presence of the hydroxy group. In contrast, the hydroxy-bearing hemiketal **20** can only have been formed after elution of the ketone **19**. The ^{1}H NMR evidence for structure **21** is very convincing. Only two olefinic protons are present (δ 5.45 and 6.82). 1 H multiplets for OCH, NCH and NCCH are observed with reasonable shifts. The diastereotopic character of the NCH_2 group, found in compounds **13b** and **20**, is retained but the two doublets of doublets have changed to two doublets with geminal coupling. This indicates the absence of a proton at the nitrogen. Of course, no NH signal was found. So, we have good reasons to assume that one important first event in the spontaneous transformation of compound **13b**, and analogously of its analogues **13a,c** is the oxidation **13b** ⟶ **18**, possibly initiated by light. Intramolecular ring opening of the epoxide **18** yields compound **21** while, probably acid catalysed, isomerization of compound **18** forms the ketone **19** that is converted into the hemiketal **20** by treatment with methanol.

The aziridine **4c** should be reduced more easily than compound **4a**. From the difference in redox potential[12] between acetophenone and 4-phenylacetophenone one would expect the potential of compound **4c** to be less negative than that of compound **4a** by ~0.3 V. The easier formation of ketyl **5** has a remarkable influence as shown by run 11. The yields of *ortho* products in runs 1–10 were 20–26% apart from the short-term run 10. In these runs, the *para*-product **11** was found in traces only, or not at all, but in run 11 it is the second main product with a yield that is more than twice as high as that of the *ortho*-products **12c** and **13c**. At the same time, it is the first run with more than a trace of isobutylamide **9** in a reaction with the lithium salt. This points to the influence of another mechanism. Tolbert[13] presented evidence that a radical can react with Tr^- by addition to a *para* position and that the generated radical anion is able to propagate a chain reaction of the $S_{RN}1$ type by SET to an electrophile such as bromobenzene. The redox potential of compound **4c** may be estimated to be close to that of bromobenzene. Thus, the *para*-product **11c** is probably the result of an $S_{RN}1$ reaction as shown in Scheme 4.

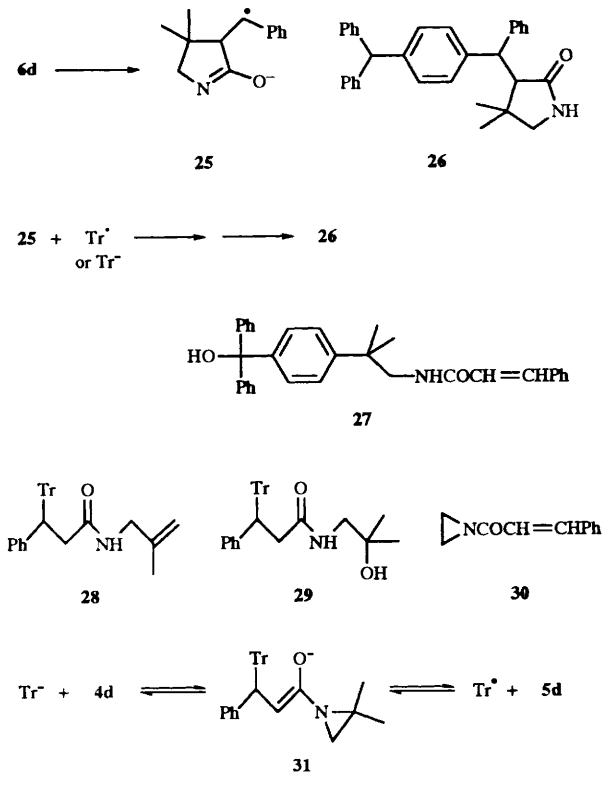


Scheme 4

This chain reaction can only proceed at the expense of other reactions of radical **6**. This is indeed borne out by run 11, especially by the value of only 30% for hydrogen transfer that in runs 1–10 amounted to ~50–60% of product. The $S_{RN}1$ path does not generate any Tr$^\cdot$ that is the pre-requisite for hydrogen transfer. In a side-reaction, radical anion **23** may convert amidatoalkyl radical **6** into the carbanion **16** that is rapidly protonated (Scheme 2, bottom) in the reaction medium, thereby accounting for production of compound **9c**. The mechanistic picture displayed above has to be complemented by reactions *via* radical **23**. The radical anion **23** may arise also in reactions with the aziridines **4a,b** but SET to these compounds **4a,b** is obviously too slow for a chain reaction. When radical **6** or the radicals in Tolbert's work can add to Tr^- one may expect that radical Tr$^\cdot$ will also add to Tr^-, thereby forming the radical anion of dimer **14** that is required for the S_N2' path to compound **12**.

The redox potential of acylaziridine **4d** is 0.3 V less negative than that of **4a**.[4] One would therefore expect a preference for *para* substitution with compound **4d** similar to its analogue **4c** in run 11 but perhaps less clear since the corresponding radical anion **6d** rapidly cyclizes[14,15] to radical **25**, whose behaviour must differ from that of its precursor **6d**. Run 12 with acylaziridine **4d** shows the expected preference for *para* substitution (16% of **11d** *vs.* 3% of **12d**, no **13d**) as well as a great amount of intermediate cyclization of radical **6d**. Addition to a *para* position of Tr^- seems to be the only reaction of radical **25**, in analogy[15] with the behaviour of the demethylated analogue of radical **25**. The pyrrolidinone **26** (diastereoisomers ~1 : 1) was the main product in this run at the expense of products (**7**, **8** and **9**) without the incorporated trityl moiety. The ^{1}H NMR data of both diastereoisomers are nearly identical since the diastereoisomerism originates only from different *para* substituents (benzhydryl or hydrogen) of two otherwise indistinguishable phenyl groups in compound **26**.

It is possible that at least a part of ketyl **5d** is generated by inner-sphere SET, by homolytic disintegration of a first formed Michael adduct, as has been reported[15] for the reaction of Tr^- with the cinnamamide **30**. So, in run 13 the reaction was repeated but now the Tr^- that had not been converted within 30 min was destroyed. A solution of TrCl in THF was added dropwise until the red (colour of Tr^-) solution was discoloured. The mixture was then stirred for 8 days before work-up. The products of run 12 were found again, but a part of *para*-compound **11d** was discovered as its α-hydroxy derivative **27** (see Scheme 5). The latter was obtained in mixture only and was identified by ^{1}H NMR data that nicely correspond to those of compound **11d** except for the absence of the α-H singlet at δ 5.53. The position of compound **27** in the chromatographic sequence is compatible with a hydroxylated derivative of



Scheme 5

compound **11d**. Formation of compound **27** is easily understood, when compound **11d**, or rather its nitranion, exists as a carbanion in equilibrium with Tr^-. Addition of TrCl converted this carbanion into the respective radical that with oxygen finally yielded product **27**. The corresponding oxidation of Tr' is known to form TrOH. Indeed, TrOH was also detected in this run. More importantly, direct evidence for a Michael addition as the first event in the reaction was found. The two products **28** and **29** clearly demonstrate that Michael addition plays a role in the reaction of Tr^- with acylaziridine **4d**. Aziridines **4** undergo abnormal hydrolytic ring opening during chromatography. The products may be called artifacts of compounds **4**, indicating that acylaziridines **4** have formed in a reaction or have survived a reaction. Then, at least compound **29** is an artifact of the generated acylaziridine **4e**, while compound **28** may either be an artifact of its hydrated derivative **4e** or it may be formed directly from the anion **31** in a reaction described by Laurent and co-workers[4] for an analogue of anion **31** in which Tr' is replaced by H.

The results of run 13 pose three questions. Why did a part of compound **31** survive 8 days while the demethylated analogue of compound **31** was completely converted[15] within 4 days, mainly into SET products? The answer may be sought in the reversibility of the homolytic disintegration, since in run 13 the high concentration of Tr', generated by addition of TrCl, may counteract the homolysis **31** ⟶ **5d**. Second, the yields of products in run 13 total only 43%. The last chromatographic fraction was a mixture of unidentified substances that probably contained an artifact of compound **4d** formed by abnormal hydrolytic ring opening. ^1H NMR signals were found at expected positions. How can a part of the aziridine **4d** survive until work-up when no aziridine **30** or an artifact of it had been found[15] in two runs of Tr^- with compound **30**?

Removal of the excess of Tr^- by TrCl liberates the aziridine **4d** from anion **31** due to the reversibility of the Michael addition. The effect may be increased by a less favourable Michael equilibrium for compound **4d** resulting from a flatter and more rapidly inverting nitrogen pyramid as compared with the case for the cinnamamide **30**. Strong Michael acceptors have a non-amidic carbonyl.

The third question: is there any direct indication for inner-sphere SET? Without an excess of Tr^-, *i.e.* when TrCl had been added, no outer-sphere SET is possible. Then, any ketyl **5d** and radical **6d** can arise from only adduct **31**, and radical **6d** can react with only Tr' or its dimer **14**. The reaction of Tr^- with TrCl generates concentrations of species Tr' and **14** substantially higher than in run 12. The increase in yield of methallylamide **7d** from 6% to 14% thus clearly indicates inner-sphere SET for the generation of at least a part of compound **7d**. At the same time, the drop in yield of *ortho*-product **12d** from 3% to 0.2% practically excludes the S_H2' path (upper part of Scheme 2) to imidate anion **15** and thus to *ortho* compounds **13** and **12**. The Tr^- in run 12 can generate the radical anion of compound **14** that is necessary for the S_N2' path (lower part of Scheme 2 and text) to give imidate anion **15**. There seems to be nearly no SET possible from Tr^- to acylaziridine **4d** in run 13, *i.e.* nearly no Tr' will be generated. Rapid Michael addition decreases the concentrations of species **4d** and Tr^-. Only the fast $S_{RN}1$ chain reaction (Scheme 4, bottom) is able to compete. *para* Substitution without intermediate cyclization in the short-term run 13 (**11d**, **27**, together 11%) reaches two-thirds the yields of run 12 (16% **11d**) in accord with the rapidity of a chain reaction that can proceed only as long as sufficient Tr^- is available. No indication of a chain reaction had been observed in the reaction of Tr^- with the cinnamamide **30** due to a practically quantitative trapping of compound **30** by the Michael addition.[15] This prevents any outer-sphere SET.

Experimental

Characterization of products was accomplished by ^1H NMR (Bruker W 250, AC 200 or AC 300 spectrometers, $CDCl_3$ 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 with distillation range 50–70 °C. The concentration of BuLi (hexane solution) was determined by titration with 1 mol dm^{-3} *sec*-butyl alcohol, indicator *o*-phenanthroline (method recommended by the supplier of BuLi, Fluka, Switzerland).

All reactions were performed in dry, continuously stirred THF under dry nitrogen whose quality was secured with a THF solution of sodium naphthalenide.

The aziridines and some products are described in ref. 7: **7b,d**; ref. 16: **1a–c**, **7a,c** and **9a,c**; ref. 17: **3** and **8a**; ref. 18: **1d** and **9b**; ref. 19: **9d** (without spectral data).

Reactions of Table 1

For details see Table 1. Li^+Tr^- was generated by addition of BuLi to a frozen (liquid nitrogen) solution of triphenylmethane in THF (50–100 cm^3) and warming up to room temperature (*ca.* 1 h). Na^+Tr^- was generated by stirring of a solution of naphthalene and triphenylmethane in THF (50–100 cm^3) with sodium pieces for 20–24 h. A solution of acylaziridine **4** in THF (10–20 cm^3, 50 cm^3 in run 4) was added dropwise within 2–5 min, apart from run 10 in which the solution of compound **4b** was rapidly injected by means of a syringe. The reactions were quenched with glacial acetic acid except for run 13. Evaporation yielded a residue, which was taken up in CH_2Cl_2 ($CHCl_3$ in runs 10 and 13) and washed with water. The residue obtained by evaporation was subjected to column chromatography [silica gel (Merck), 0.063–0.2 mm, thickness × length of column in cm and other details are given with each run].

Run 1. Chromatography (3.5 × 45, CH_2Cl_2) provided triphenylmethane and *compound* **2** (1.36 g, 58%), mp 204–205 °C (Found: C, 76.6; H, 6.9; N, 3.3. $C_{30}H_{31}NO_2S$ requires C, 76.7; H, 6.7; N, 3.0%); ν_{max}/cm^{-1} 3255 (NH), 1310, 1305, 1155 and 1133 (all SO_2); δ 0.93 (s, CMe_2), 2.40 (s, Me of Ts), 3.10 (s,

CH_2), 4.70 (s, NH), 7.07–7.53 (m, 17 ArH) and 7.63 (m, 2 *o*-H of Ts).

Continued elution yielded compound **3** (120 mg, 11%).

Run 2. Chromatography (3 × 15, light petroleum) removed the bulk of triphenylmethane. Ethyl acetate provided an eluate that deposited *compound* **12a** (450 mg), mp 235–236 °C (Found: C, 85.7; H, 7.1; N, 3.4. $C_{30}H_{29}NO$ requires C, 85.9; H, 7.0; N, 3.3%); ν_{max}/cm^{-1} 3285 (NH), 1639 (amide I) and 1540 (amide II); δ 1.59 (s, 2 Me), 3.83 (d, *J* 6.2, NCH_2), 5.26 (t br, *J* 6, NH), 6.36 (s, α-H), 7.01–7.09 (m, 4 *o*-H of CPh_2), 7.09–7.14 (m, 1 *o*-H of substituted Ph), 7.15–7.42 (m, 13 ArH) and 7.42–7.51 (m, 1 ArH next to the side-chain).

Evaporation of the mother liquor provided a residue, chromatography of which [3.5 × 50, CH_2Cl_2–ethyl acetate (100:1)] yielded triphenylmethane and mixture A (1.19 g). Elution with CH_2Cl_2–ethyl acetate (10:1) provided compound **7a** (520 mg, 30%). Washing of mixture A with light petroleum left mixture B (600 mg) undissolved. Evaporation of the washing solution yielded mixture C (590 mg). Mixture B consisted (^{1}H NMR) of compounds **12a** (442 mg, total 892 mg, 21%), **8a** (107 mg) and **11a** (51 mg, 1%); δ 1.38 (s, 2 × Me), 3.62 (d, *J* 6.1, NCH_2), 5.54 (s, α-H), 5.80 (s br, NH) and 7.01–7.85 (m, ArH of **11a**, **12a** and **8a**).

Mixture C consisted (^{1}H NMR) of **8a** (373 mg, total 480 mg, 27%) and **10a** (217 mg, 5%). Compound **10a** is characterized below.

Preparation of compound **8a** *by isomerization of compound* **7a**.—A solution of compound **7a** (0.59 mmol) in THF (30 cm^3) was stirred for 4 days with NaH (excess) and a piece of sodium. The usual work-up provided a residue (95 mg) whose ^{1}H NMR spectrum showed the absence of substrate **7a** but the presence of compound **8a** (main component) and of benzamide.

Run 3. Chromatography (3 × 15, light petroleum) removed the bulk of triphenylmethane (5.66 g). Ethyl acetate provided an eluate, chromatography of which [3.5 × 40, CH_2Cl_2–ethyl acetate (100:1)] yielded triphenylmethane (590 mg) and compound **10a** (60 mg), mp 208–210 °C (Found: C, 86.0; H, 7.1; N, 3.4. $C_{30}H_{29}NO$ requires C, 85.9; H, 7.0; N, 3.3%); ν_{max}/cm^{-1} 3320 (NH), 1640 (amide I) and 1554 (amide II); δ 1.44 (s, 2 Me), 3.65 (d, *J* 6.6, NCH_2), 5.86 (t br, *J* 6.7, NH), 7.02–7.54 (m, 18 ArH) and 7.55–7.62 (m, 2 *o*-H of COPh). Continued elution yielded mixture A (2.03 g). Elution with CH_2Cl_2–ethyl acetate (10:1) provided compound **7a** (180 mg, 10%) containing (^{1}H NMR) a trace of compound **9a**. Washing of mixture A with light petroleum (2 × 100 cm^3) left mixture B (1.09 g) undissolved. Evaporation of the washing solution provided compound **8a** (940 mg, 54%). Mixture B consisted (^{1}H NMR) of compounds **12a** (1.016 g, 24%) and **10a** (74 mg, total 134 mg, 3%).

Run 4. ^{1}H NMR analysis (internal standard) of the residue (4.00 g) prior to chromatography indicated the presence of compounds **4a** (464 mg, 31%), **7a** (658 mg, 64%), **10a** (40 mg, 1%) and **13a** (557 mg, 23%; ^{1}H NMR data in the text). Chromatography [3.5 × 50, CH_2Cl_2–ethyl acetate (25:1)] provided triphenylmethane, compound **10a** (38 mg) and a mixture (670 mg) containing (^{1}H NMR) compounds **7a**, **13a** and unknown secondary products probably derived from triene **13a**.

Run 5. Compound **12a** (650 mg) was deposited from the organic layer. Evaporation of the mother liquor provided a residue, chromatography of which (3 × 15, light petroleum) removed the bulk of hydrocarbons. Ethyl acetate provided an eluate, chromatography of which (3.5 × 40, CH_2Cl_2) yielded hydrocarbons, mixture A (445 mg) and mixture B (1.12 g). Washing of mixture A with light petroleum (2 × 100 cm^3) left mixture C (340 mg) undissolved. Evaporation of the washing solution yielded compound **8a** (105 mg). Identical treatment of mixture B provided compound **12a** (80 mg undissolved) and mixture D (1.04 g). Mixture C consisted (^{1}H NMR) of compounds **12a** (170 mg, total 900 mg, 21%) and **10a** (170 mg, 4%). Mixture D consisted (^{1}H NMR) of compounds **7a** (404 mg, 23%), **9a** (59 mg, 3%) and **8a** (578 mg, total 683 mg, 39%).

Run 6. Chromatography (3 × 15, light petroleum) removed the bulk of hydrocarbons. Ethyl acetate provided an eluate that deposited compound **12a** (200 mg). Evaporation of the mother liquor gave a residue, chromatography of which [3.5 × 45, CH_2Cl_2–ethyl acetate (100:1)] yielded hydrocarbons and mixture A (1.76 g). Elution with CH_2Cl_2–ethyl acetate (10:1) provided compound **9a** (230 mg, 13%). Washing of mixture A with light petroleum (2 × 100 cm^3) left mixture B (940 mg) undissolved. Evaporation of the washing solution yielded compound **8a** (820 mg). Mixture B consisted (^{1}H NMR) of compounds **8a** (29 mg, total 849 mg, 48%), **10a** (256 mg, 6%) and **12a** (655 mg, total 855 mg, 20%).

Run 7. Chromatography (3 × 15, light petroleum) removed the bulk of hydrocarbons. Elution with ethyl acetate provided a mixture (1.6 g), chromatography of which [3 × 40, CH_2Cl_2–ethyl acetate (25:1)] yielded hydrocarbons, compound **10a** (35 mg, 2%) and mixture A (760 mg). Elution with CH_2Cl_2–ethyl acetate (10:1) yielded compound **9a** (130 mg, 15%). Washing of mixture A with light petroleum (2 × 100 cm^3) left mixture B (460 mg) undissolved. Evaporation of the washing solution yielded compound **8a** (302 mg). Mixture B consisted (^{1}H NMR) of compounds **8a** (35 mg, total 337 mg, 38%) and **12a** (425 mg, 20%).

Run 8. Chromatography (3 × 18, light petroleum) removed the bulk of hydrocarbons. Elution with ethyl acetate provided a mixture (2.1 g), chromatography of which [3 × 40, CH_2Cl_2–ethyl acetate (25:1)] gave hydrocarbons, compound **10a** (97 mg, 5%), mixture A (577 mg) and then [CH_2Cl_2–ethyl acetate (5:1)] mixture B (540 mg). Mixture A consisted (^{1}H NMR) of compounds **8a** (35 mg, 4%) and **12a** (544 mg, 26%). Mixture B consisted (^{1}H NMR) of compounds **7a** (481 mg, 55%) and **9a** (59 mg, 6%).

Run 9. Chromatography [3.5 × 50, CH_2Cl_2–ethyl acetate (25:1)] removed triphenylmethane. Elution with CH_2Cl_2–ethyl acetate (10:1) provided mixture A (680 mg) and *compound* **12b** (267 mg), mp 207–209 °C (Found: C, 84.3; H, 8.6; N, 3.8. $C_{28}H_{33}NO$ requires C, 84.2; H, 8.3; N, 3.5%); ν_{max}/cm^{-1} 3335 (NH), 1646 (amide I) and 1550 (amide II); δ 0.87 (s, Bu^t), 1.51 (s, 2 × Me), 3.60 (d, *J* 6.0, NCH_2), 4.76 (t br, *J* 6, NH), 6.30 (s, α-H), 6.98–7.08 (m, 4 *o*-H of CPh_2), 7.08–7.13 (m, 1 *o*-H of substituted Ph), 7.16–7.32 (m, 8 × ArH) and 7.38–7.45 (m, 1 ArH next to the side-chain).

Continued elution yielded mixture B (30 mg) and compound **7b** (850 mg, 55%). Mixture A consisted (^{1}H NMR) of compounds **8b** (69 mg, 4%) and **12b** (611 mg). Mixture B consisted (^{1}H NMR) of compounds **12b** (20 mg, total 898 mg, 22%) and **11b** (10 mg, 0.2%); ν_{max}/cm^{-1} 3460 (NH), 1664 (amide I) and 1528 (amide II); δ 1.05 (s, Bu^t), 1.31 (s, 2 × Me), 3.39 (d, *J* 5.9, NCH_2), 5.24 (s br, NH) and 5.54 (s, α-H); ArH signals hidden under signals of compound **12b**.

Preparation of compound **8b** *by isomerization of compound* **7b**.—A solution of triphenylmethane (5.7 mmol), BuLi (5 mmol) and compound **7b** (1.9 mmol) prepared and allowed to react for 9 days as described for reactions reported in Table 1. Chromatography [3 × 15, CH_2Cl_2–ethyl acetate (25:1)] provided triphenylmethane and *compound* **8b** (270 mg, 93%), mp 64–65 °C (Found: C, 69.7; H, 10.9; N, 8.9. $C_9H_{17}NO$ requires C, 69.6; H, 11.0; N, 9.0%); ν_{max}/cm^{-1} 3365 (NH), 1690 (C=C), 1645 (amide I) and 1512 (amide II); δ 1.24 (s, Bu^t), 1.63 (s, 1 × Me), 1.71 (s, 1 × Me), 6.53 (d, *J* 10.1, NCH) and 6.97 (s br, NH).

Run 10. The ^{1}H NMR spectrum of the crude mixture, recorded prior to chromatography, indicated the presence of compounds **7b** and **13b** in the molar ratio 19:6.9. Chromatography [3 × 30, toluene–ethyl acetate, (9:1)] provided triphenylmethane and *compound* **10b** (55 mg, 3%), mp 205–207 °C (Found: C, 84.1; H, 8.2; N, 3.6. $C_{28}H_{33}NO$ requires C, 84.2; H, 8.3; N, 3.5%); ν_{max}/cm^{-1} 3320 (NH), 1635 (amide I)

and 1540 (amide II); δ 1.12 (s, Bu^t), 1.32 (s, CMe_2), 3.41 (d, J 6.7, NCH_2), 5.44 (t br, J 7, NH) and 7.12–7.38 (m, 15 × ArH); m/z (150 °C) 399 (0.02%, M^+), 243 (100, Tr), 165 (29, fluorenyl), 156 (60, M − Tr) and 57 (63, Bu^t).

Continued elution provided impure compound **13b** (46 mg) as an oil; ^{1}H NMR data are given in the text and in ref. 2; while being crystallized compound **13b** underwent chemical transformation (see text).

Further elution yielded a mixture (387 mg) containing compound **13b** and products derived from it as indicated by a relatively strong doublet at δ 6.46, J 10.1. Scratching of this mixture under methanol generated *hemiketal* **20** (28 mg), mp 97–98 °C (Found: M^+, 447.2775. $C_{29}H_{17}NO_3$ requires M, 447.2773); ν_{max}/cm^{-1} 3340 (NH or OH), 3295 (NH or OH), 1660 (amide I) and 1540 (amide II); δ 0.84 (s, 1 × Me of CMe_2), 0.85 (s, 1 × Me of CMe_2), 1.07 (s, Bu^t), 2.32 (m, C≡C–CH_2), 2.91 (dd, J 14.0 and 5.1, NC*H*H), 3.44 (dd, J 14.0 and 7.7, NCH*H*), 3.48 (s, NCCCH), 3.49 (s, OMe), 5.22 (m, NH), 5.80 (ddd, J 10.1, 5.1 and 1.2, C≡CC=CH), 6.46 (d, J 10.2, C≡CCH=C), 7.10 (m, 2 o-H) and 7.17–7.42 (m, 8 × ArH); assignment of C≡CHCH_2 signals was confirmed by decoupling; m/z (197 °C) 447 (2%, M^+), 290 (11, M − H − side-chain), 156 (59, side-chain) and 57 (100, Bu^t).

Continued elution provided mixture A (54 mg), mixture B (42 mg) and *dichloride* **22** (78 mg, 7%), mp 106–108 °C (Found: M^+, 237.0684. $C_{10}H_{17}Cl_2NO$ requires M, 237.0687); ν_{max}/cm^{-1} 3375 (NH), 1638 (amide I) and 1530 (amide II); δ 1.24 (s, Bu^t), 1.31 (d, J 7.4, CCl_2CHH), 1.36 (s, 1 × Me), 1.45 (d, J 7.4, CCl_2CH*H*), 3.02 (dd, J 14.2 and 4.2, NC*H*H) and 4.05 (dd, J 14.2 and 8.3, NCH*H*); m/z (44 °C) 239 (0.3%, M + 2), 237 (0.7, M^+), 204 (3, 239 − Cl), 202 (10, M − Cl), 154 (5, M − CCl_2 − H), 141 (25, M − CH_2=CCl_2), 140 (25, M − CCl_2 − Me), 85 (12, 141 − CH_2=CMe_2), 84 (18, 140 − CH_2=CMe_2) and 57 (100, Bu^t).

Continued elution yielded compound **7b** (168 mg) and a mixture consisting (^{1}H NMR) of compounds **7b** (123 mg, total 291 mg, 38%) and **21** (56 mg, 3%); δ 0.79 (s, 1 × Me), 0.92 (s, 1 × Me), 1.30 (s, Bu^t), 2.86 (d, J 13.9, NC*H*H), 3.14 (d, J 3.0, NCCH), 3.69 (d, J 13.9, CH*H*), 4.15 (m, NCH), 5.01 (m, CHO), 5.45 (dd, J 9.8 and 6.0, C=CHC–O), 6.82 (d, J 9.9, CH=CC–O), 7.17 (d, J 7.8, 4 o-H of 2 × Ph) and 7.20–7.39 (m, 6 × ArH); decoupling, irradiated/changed: 4.15/3.14 and 5.01, 5.01/3.14 and 4.15 and 5.45, 5.45/5.01 and 6.82.

Treatment of mixture A with methanol provided a few crystals (5 mg) and a mother liquor, evaporation of which yielded a mixture (49 mg) containing (^{1}H NMR, internal standard) compounds **12b** (10 mg), **20** (21 mg, total 49 mg, 2%) and a product assumed to be an isomer of epoxide **18**. The crystals consisted (^{1}H NMR) of compounds **12b** (2 mg) and **20** (3 mg, total 31 mg, 1%). Mixture B contained (^{1}H NMR, internal standard) compound **12b** (9 mg, total 21 mg, 0.1%).

Run 11. Chromatography [3.5 × 45, CH_2Cl_2–ethyl acetate (25:1)] provided triphenylmethane and compound **10c** (82 mg) mp 188–190 °C (Found: C, 86.8; H, 6.9; N, 2.7. $C_{36}H_{33}NO$ requires C, 87.2; H, 6.7; N, 2.8%); ν_{max}/cm^{-1} 3440 (NH), 1634 (amide I) and 1549 (amide II); δ 1.46 (s, Bu^t), 3.68 (d, J 6.6, NCH_2), 5.90 (t br, J 6.6, NH), 7.15–7.53 (m, 18 × ArH) and 7.57–7.70 (m, 6 × ArH).

Continued elution yielded mixture A (160 mg), mixture B (501 mg) and mixture C (175 mg). Elution with CH_2Cl_2–ethyl acetate (10:1) provided mixture D (294 mg). Elution with ethyl acetate yielded unknown products (619 mg). The composition (^{1}H NMR) of the mixtures was as follows. Mixture A: compounds **8c** (12 mg), **10c** (15 mg, total 97 mg, 4%), **12c** (66 mg) and **13c** (67 mg); δ 0.92 (s, 1 × Me), 0.94 (s, 1 × Me), 3.06 (dd, J 14.3 and 4.9, NC*H*H), 3.63 (dd, J 14.3 and 8.3, NCH*H*), 5.55 (m, NH), 5.79–5.88 (m, 4-H), 6.04–6.14 (m, 2-H), 6.18–6.27 (m, 3-H), 6.48 (d, J 9, 4, 5-H), 7.03–7.92 (m, ArH for **8c**, **10c**, **12c** and **13c**). Mixture B: compounds **8c** (53 mg, total 65 mg, 5%), **11c** (337 mg), **12c** (94 mg, total 160 mg, 6%) and **13c** (17 mg, total 84 mg, 3%); mixture C: compounds **7c** (42 mg) and **11c** (133 mg, total 470 mg, 19%); mixture D: compounds **7c** (266 mg, total 308 mg, 25%) and **9c** (28 mg, 2%).

Washing of mixture C with light petroleum–CH_2Cl_2 (1:1) left pure *compound* **11c** undissolved, mp 128–129 °C (Found: C, 87.5; H, 6.7; N, 2.6. $C_{36}H_{33}NO$ requires C, 87.2; H, 6.7; N, 2.8%); ν_{max}/cm^{-1} 3460 (NH), 1664 (amide I) and 1528 (amide II); δ 1.41 (s, 2 × Me), 3.65 (d, J 6.0, NCH_2), 5.55 (s, α-H), 5.79 (t br, J 6.0, NH), 7.09–7.18 (m, 6 o-H of trityl moiety, identified by NOE from α-H), 7.20–7.50 (m, 11 × ArH, 2 × ArH of which are shown by NOE from methyl to be neighbours of the side-chain: d at 7.30, J 8.8) and 7.53–7.70 (m, 4 o-H and 2 m-H of p-phenylbenzoyl).

Mixture A was extracted several times with hot light petroleum. Evaporation of the extract provided a residue, washing of which with hot ethanol left a trace of pure compound **12c** undissolved, mp 155–157 °C (Found: C, 87.1; H, 6.8%; M^+, 495.2564. $C_{36}H_{33}NO$ requires C, 87.2; H, 6.7%; M, 495.2563); ν_{max}/cm^{-1} 3420 (NH), 1654 (amide I) and 1541 (amide II); δ 1.60 (s, 2 × Me), 3.85 (d, J 6.1, NCH_2), 5.38 (t br, J 6, NH), 6.37 (s, α-H), 7.03–7.10 (m, 4 o-H of CPh_2), 7.10–7.16 (m, 1 o-H of substituted Ph in trityl moiety), 7.16–7.31 (m, 7 × ArH), 7.35–7.43 (m, 4 × ArH), 7.43–7.50 (m, 3 × ArH) and 7.50–7.60 (m, 4 × ArH).

Recrystallization of mixture D from CH_2Cl_2–light petroleum provided pure compound **7c**, mp 141–143 °C (lit.,[16] 141 °C).

Preparation of compound **8c** *by isomerization of compound* **7c**.—A solution of triphenylmethane (6.5 mmol), BuLi (5 mmol) and compound **7c** (1.35 mmol) in THF (20 cm^{-1}) was prepared and allowed to react for 13 days as described for reactions reported in Table 1. Chromatography [3.5 × 15, CH_2Cl_2–ethyl acetate (25:1)] provided triphenylmethane and compound **8c** (183 mg), mp 149–150 °C (Found: C, 81.5; H, 6.9; N, 5.7. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); ν_{max}/cm^{-1} 3320 (NH), 1695 (C=C), 1641 (amide I) and 1530 (amide II); δ 1.74 (s, 1 × Me), 1.80 (s, 1 × Me), 6.78 (d, J 10.3, NCH), 7.34–7.58 (m, NH, 2 m-H and 1 p-H of Ph), 7.58–7.72 (m, 4 × ArH) and 7.83–7.92 (m, 2 o-H of COAr).

Continued elution provided a mixture (60 mg) consisting (^{1}H NMR) of compound **8c** (52 mg, total 235 mg, 69%) and **7c** (8 mg). Further elution yielded more compound **7c** (94 mg, total 102 mg, 30%).

Run 12. Chromatography [3 × 45, CH_2Cl_2–ethyl acetate (2:1)] provided mixture A (2.206 g) and mixture B (431 mg). Elution with ethyl acetate yielded mixture C (912 mg). The mixtures were composed (^{1}H NMR) as follows. Mixture A: triphenylmethane (2.169 g, 8.9 mmol) and compound **14** (37 mg, 0.15 mmol, 3%); mixture B (Found: C, 85.8; H, 7.1; N, 3.2. Calc. for $C_{32}H_{31}NO$: C, 86.3; H, 7.0; H, 3.1%): compounds **10d** (trace), **11d** (362 mg, 16%) and **12d** (69 mg, 3%); mixture C: compounds **26** (1:1 **α-26** and **β-26**, 851 mg, 38%) and **7d** (61 mg, 6%). Characterization of products **10d**, **11d** and **12d** is presented in run 13.

Run 13. Chromatography [40 × 4, toluene–ethyl acetate (1:1)] provided hydrocarbons, TrOH (744 mg, 2.9 mmol) and compound **10d** (10 mg), mp 209 °C; ν_{max}/cm^{-1} 3310 (NH), 1652 (amide I) and 1538 (amide II); δ 1.38 (s, 2 × Me), 3.54 (d, J 6.6, NCH_2), 5.24 (t br, J 7, NH), 6.14 (d, J 15.6, C=CHCO), 6.98–7.50 (m, 20 × ArH) and 7.58 (d, J 15.6, CH=CCO).

Further elution yielded a mixture (24 mg) consisting (^{1}H NMR) of compounds **10d** (18 mg, total 28 mg, 1%) and **28** (6 mg). Continued elution provided more compound **28** (41 mg), mp 209–210 °C (Found: C, 86.1; H, 6.9; N, 3.0. $C_{32}H_{31}NO$ requires C, 86.3; H, 7.0; H, 3.1%); ν_{max}/cm^{-1} 3290 (NH), 1650 (amide I) and 1545 (amide II); δ 2.07 (dd, J 14.6 and 10.0, C*H*HCO), 3.10 (dd, J 14.6 and 1.9, CH*H*CO), 3.38 (dd, J 15.8 and 4.9, NC*H*H), 3.69 (dd, J 15.8 and 6.2, NCH*H*), 4.20 (s br, =C*H*H), 4.52 (s br, =CH*H*), 5.00 (s br, NH), 5.27 (dd, J 9.8 and 1.7, CHCCO), 6.69 (dd, J 8.0 and 1.9, 2 o-H of a Ph) and

6.99–7.60 (m, 18 × ArH); *m/z* (169 °C) 244 (21%, CPh_3 + 1), 243 (100, CPh_3), 165 (28, fluorenyl) and 55 (8, methallyl).

The next chromatographic fraction (17 mg) consisted (^{1}H NMR) of compound **28** (7 mg, total 54 mg, 2%), **11d** (5 mg) and **12d** (5 mg, 0.2%); 1.54 (s, 2 × Me), 3.77 (d, *J* 6.2, NCH_2), 4.79 (t br, *J* 6.4, NH), 5.93 (d, *J* 15.7, C=CHCO); other signals (m at δ 7.0–7.9, CH=CCO, ArH) overlap with those of compounds **11d** and **28**. Further elution yielded *compound* **11d** (175 mg, total 180 mg, 8%), mp 95 °C (Found: C, 86.7; H, 7.0; N, 3.2. $C_{32}H_{31}NO$ requires C, 86.3; H, 7.0; H, 3.1%); ν_{max}/cm^{-1} 3300 (NH), 1657 (amide I) and 1542 (amide II); δ 1.35 (s, 2 × Me), 3.59 (d, *J* 6.1, NCH_2), 5.32 (t br, *J* 6.4, NH), 5.53 (s, α-H), 6.25 (d, *J* 15.6, C=CHCO), 7.09–7.15 (m, 6 *o*-H of trityl moiety), 7.18–7.35 (m, 12 × ArH), 7.42–7.48 (m, 2 *o*-H of C=CPh) and 7.57 (d, *J* 15.6, CH=CCO); *m/z* (185 °C) 446 (7%, M + 1), 445 (18, M^+), 286 (24), 285 (100, $Ph_2CHC_6H_4CMe_2$), 167 (20, $CHPh_2$), 161 (26, PhCH=CHCONHCH$_2$ + H), 131 (44, PhCH=CHCO) and 103 (14, styryl).

Continued elution yielded a mixture (38 mg) of unknown products: then elution with (toluene–ethyl acetate–methanol (9:1:1) gave compound **7d** (101 mg) and a mixture (120 mg) consisting (^{1}H NMR) of compounds **7d** (45 mg, total 146 mg, 14%), **9d** (15 mg, 1%) and **27** (60 mg, 3%); δ 1.32 (s, 2 × Me), 3.56 (d, *J* 6.1, NCH_2), 5.45 (s br, NH), 6.27 (d, *J* 15.6, C=CHCO), 6.96–7.45 (m, ArH of **27**, **7d** and **9d**) and 7.56 (d, *J* 15.7, CH=CCO). Spectral data (not given in ref. 19) of compounds **9d** (prepared as described in ref. 18): ν_{max}/cm^{-1} 3280 (NH), 1659 (amide I), 1620 (C=C) and 1559 (amide II); δ 0.96 (d, *J* 6.6, 2 × Me), 1.85 (m, NCCH), 3.23 (dd, *J* 6.7 and 6.3, NCH_2), 5.87 (s br, NH), 6.44 (d, *J* 15.6, C=CHCO), 7.31–7.42 (m, 3 × ArH), 7.43–7.53 (m, 2 *o*-H of Ph) and 7.63 (d, *J* 15.6, CH=CCO).

The next fraction was impure *pyrrolidinone* α-**26** (142 mg, 6%), mp 216–218 °C (Found: C, 86.2; H, 6.9; N, 3.3. $C_{32}H_{31}NO$ requires C, 86.3; H, 7.0; H, 3.1%); ν_{max}/cm^{-1} 3210 (NH) and 1700 (C=O); δ 0.82 (s, 1 × Me), 1.05 (s, 1 × Me), 2.85 (d, *J* 9.4, NC*H*H), 2.97 (d, *J* 9.4, NCH*H*), 3.07 (d, *J* 9.9, CHCO), 4.10 (d, *J* 9.9, CHCCO), 5.46 (s, α-H of trityl moiety), 5.50 (s br, NH), 6.97 (d, *J* 8.2, 2 *o*-H of O=CCCPh), 7.09 (m, 4 *o*-H of 2 × Ph), 7.13–7.28 (m, 11 × ArH) and 7.35–7.40 (m, 2 × ArH).

Further elution yielded impure *compound* **29** (78 mg, 3%) as an oil (Found: M^+, 463.2513. $C_{32}H_{33}NO_2$ requires M, 463.2511); ν_{max}/cm^{-1} 3300 (NH, OH), 1651 (amide I) and 1542 (amide II); δ 0.72 (s, 1 × Me), 0.86 (s, 1 × Me), 2.08 (dd, *J* 14.0 and 11.8, C*H*HCO), 2.73 (dd, *J* 13.8 and 5.0, NC*H*H), 3.09 (dd, *J* 14.0 and 1.7, CH*H*CO), 3.16 (dd, *J* 13.8 and 7.2, NCH*H*), 5.25 (dd, *J* 11.5 and 1.6, NCCCH), 5.46 (t br, *J* 6, NH), 6.70 (m, 2 *o*-H of NCCCPh), 6.91–7.05 (m, *m*-H and *p*-H of NCCCPh), 7.05–7.40 (m, 9 × ArH) and 7.42 (m, 6 *o*-H of trityl moiety); *m/z* (199 °C) 463 (0.1%, M^+), 448 (0.4, M − Me), 445 (0.3, M − H_2O), 405 (0.5, M − acetone), 333 (1, $PhCHCPh_3$), 243 (100, CPh_3) and 165 (24, fluorenyl).

Continued elution provided *pyrrolidinone* β-**26** (107 mg, 5%), mp 210–211 °C (Found: C, 86.2; H, 6.9; N, 3.3%); ν_{max}/cm^{-1} 3215 (NH) and 1700 (C=O); δ 0.82 (s, 1 × Me), 1.04 (s, 1 × Me), 2.79 (d, *J* 9.4, NC*H*H), 2.91 (d, *J* 9.4, NCH*H*), 3.07 (d, *J* 9.6, CHCO), 4.08 (d, *J* 9.6, CHCCO), 5.32 (s br, NH), 5.47 (s, α-H of trityl moiety), 6.99 (d, *J* 8.1, 2 *o*-H of O=CCCPh), 7.09 (m, 4 *o*-H of 2 × Ph), 7.13–7.28 (m, 11 × ArH) and 7.35–7.40 (m, 2 × ArH).

Elution with ethyl acetate provided a mixture (432 mg) of unknown products containing (^{1}H NMR) as major component probably *N*-(2-hydroxy-2-methylpropyl)cinnamamide as indicated by the following ^{1}H NMR signals: δ 1.21 (s, CMe_2), 3.37 (d, *J* 6.1, NCH_2), 6.48 (d, *J* 15.6, C=CHCO), 6.65 (t br, *J* 7, NH) and 7.61 (d, *J* 15.6, CH=CCO).

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