Radical Combination in the *ortho* Position of Trityl Radical Observed in Single-electron Transfer Reactions of Trityl Anion

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Single-electron transfer reactions between trityl anion and 1-acyl-2,2-dimethylaziridines provide, among other products, the methallyl amides **7** and the triphenylmethanes **8** carrying an amidoethyl chain attached with the tertiary carbon *ortho* to the triphenylmethane.

Trityl radical (Tr = CPh_3) $Tr^•$ combines with radicals in the *para* position; only radicals of low steric demand add to the central carbon.[1] Combination in the *ortho* position has not been reported to the best of our knowledge. Space-filling models show that attack upon an *ortho* carbon should be possible for t-butyl or radicals of similar steric demand. *para*-Central ambidenticity and steric control[2] is also known for trityl anion Tr^- with possible[2] or proved[3,4] involvement of single-electron transfer (SET).

Ketyl **2**, generated by electron attachment to **1**, forms the radical **3** which can react further.[5] When the electron source is a nucleophile, this SET reaction is not possible unless the competing S_N2 attack is sufficiently slow. Unhindered S_N2 reaction of Tr^- with **4** exclusively yields the central products **5**.[6] We now find that the reaction of Tr^- with **1a–c** can yield all three substitution products **6**, **8** and **9**. Compounds **8** are the first *ortho* products that are the major products of reactions of **1a** and **b** while the central product **6** is always the minor product. Compound **8** arises most probably from a combination of $Tr^•$ with radical **3**.

The main products in all runs are the methallylamides **7** which slowly isomerize to the corresponding enamides under base catalysis.[5] This isomerization guarantees that **7** or rather the amide anions derived from **7** arise prior to work-up. There can be no doubt that **7** is formed *via* transfer of a hydrogen atom from radical **3** to $Tr^•$. Thus, the main products indicate an SET mechanism. The second most important products obtained from **1a,b** are the *ortho* products **8a,b** (runs 1 and 2). The *para* products **9a,b** could only be identified from ^1H NMR spectroscopic signals.† The central product **6a** was not found, *cf.* **6b**. Structure assignment for **8** and **9** was based primarily on the chemical shift data (6.3–6.4 ppm) for the methine proton in the trityl moiety. In the common propeller conformation of triphenylmethanes the methine singlet appears at 5.5 ± 0.1 ppm.[2,4,7] The downfield shift in **8** indicates a 'steeper' conformation for the propeller blades caused by the ortho substituent.[7] Structure **8** was proved by NOE (**8b**) and by the isolation of the non-aromatized precursor **10a** of **8a** in a nearly pure state, when a repetition of run 1 was quenched after 15 min. Structure **10a** follows from the ^1H NMR multiplets of the five spin system 1-H to 5-H (supported by COSY) and from a pronounced diastereotopic NCH_2 group.†

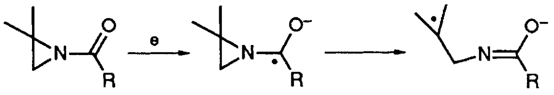
There can be little doubt that **10** and hence **8** arise by combination of the two radicals $Tr^•$ and **3**, which is probably favoured by a rather low steric demand and high selectivity of **3**. Attachment of a hydrogen atom to **3** (final product **11** formed at the expense of **7**) was observed only when Tr^- was generated from triphenylmethane by means of sodium naphthalenide. Dihydronaphthalene resulting from this technique is a good donor of hydrogen atoms.

Reaction of **1c** with Li^+Tr^- markedly changed the composi-

Table 1 Reactions of trityllithium with aziridines **1a–c** in THF[a]

Run	Aziridine	Time/ days	Products [yields (%)]
1	**1a**	6	**6a** (0) **7a**[b] (59) **8a** (22) **9a** (trace)
2	**1b**	16	**6b** (5) **7b**[b] (57) **8b** (21) **9b** (1)
3	**1c**	6	**6c** (4) **7c**[b] (30) **8c** (6) **9c** (19) **10c** (3) **11c** (2)

[a] Reactions with two equivalents of Tr^- at room temperature. Li^+Tr^- was generated from triphenylmethane (small excess) and butyllithium (hexane) in THF. [b] In part isomerized to the respective enamide $RCONHCH{=}CMe_2$: 4% in run 1, 27% in run 2, 5% in run 3.



1 **2** **3**

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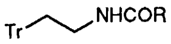

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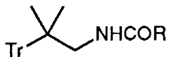

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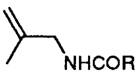

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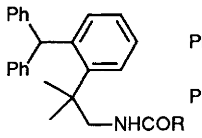

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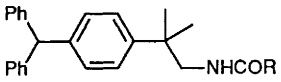

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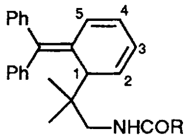

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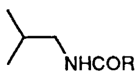

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a; R = Bu^t
b; R = Ph
c; R = 4-biphenylyl

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† An example of characterisation for **8a**, **9a** and **10a**. **8a**: m.p. 207–209 °C. IR (KBr) ν = 3335 cm^{-1} (NH), 1646 (amide I), 1550 (amide II). ^1H NMR (250 MHz, $CDCl_3$) δ = 0.87 (s, 9H, Bu^t), 1.51 (s, 6H, CMe_2), 3.60 (d, *J* 6.0 Hz, 2H, CH_2), 4.76 (t, br, *J* 6 Hz, 1H, NH), 6.30 (s, 1H, methine-H), 6.98–7.08 (m, 4H, *o*-H of 2 Ph), 7.08–7.13 (m, 1H, *o'*-H of C_6H_4), 7.16–7.32 (m, 8 aromatic H), 7.38–7.45 (m, 1H, *m*-H of C_6H_4).

9a (only in mixture with **8a**): ^1H NMR (250 MHz, $CDCl_3$) δ = 1.05 (s, 9H, Bu^t), 1.31 (s, 6H, CMe_2), 3.39 (d, *J* 5.9 Hz, 2H, CH_2), 5.24 (s, br, 1H, NH), 5.54 (s, 1H, methine-H), the signals of the aromatic H are hidden under signals of **8a**.

10a: Oil. IR (film) ν = 3370 cm^{-1} (NH), 1654 (amide I), 1518 (amide II). ^1H NMR (500 MHz, $CDCl_3$) δ 0.79 (s, 3H, 1 Me of CMe_2), 0.80 (s, 3H, 1 Me of CMe_2), 1.04 (s, 9H, Bu^t), 2.88 (dd, *J* 13.8, 5.1 Hz, 1H of CH_2). 3.38 (dd, *J* 13.8, 7.5 Hz, 1H of CH_2), 3.60 (d, *J* 6.0 Hz, 1H, 1-H), 5.25 (t, br, *J* 6 Hz, 1H, NH), 5.78 (dd, *J* 9.9, 5.2 Hz, 1H, 4-H).

tion of the product mixture (run 3). The yield of the *para* product (**9c**) increased at the expense of **7** and **8**. Besides, 2% of **11c** was found. A non-SET ring opening by the nucleophile Tr^- should lead to virtually identical results with **1b** and **1c**. However, the reduction potential[8] for **1b** and the difference in potentials (*ca.* 0.3 V) for acetophenone and 4-phenylacetophenone[9] allow us to conclude that the reduction potential of **1c** is close to the potential of bromobenzene. The Tolbert mechanism (radical addition to Tr^-) takes on chain character in the reaction of Tr^- with bromobenzene.[4] Thus, we assume that the *para* adduct (a radical anion of the *para* analogue of **10** type) formed by addition of **3** to Tr^- is able to sustain a chain reaction by SET to **1c** but not to **1a,b**. SET to **3c** may be responsible for the formation of **11c**.

A tertiary radical of pronounced steric demand greater than **3** cannot add to an *ortho* position of $Tr^\bullet$ as is shown by the reaction of Li^+Tr^- with 1-benzoyl-2-t-butyl-2-phenylaziridine. The corresponding radical (in which two methyl groups in **3b** are replaced by phenyl and t-butyl) adds to the *para* position only (9%).

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