Aziridines. Part 60.[1] Electron Transfer from Radical Anions to *N*-Alkanoylaziridines. Exocyclic Cleavage of an Aziridino Ketyl

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Reactions of non-aromatic *N*-acylaziridines with radical anions yield products arising from the intermediate β-amidatoalkyl radicals that are generated by homolytic ring opening of the first formed aziridino ketyls. Reduction of these radicals and their combination with the radical anion show a dependence on the nature of the radical anion (naphthalenide, anthracenide) similar to the known reactions of these radical anions with alkyl halides, *i.e.* (nearly) no reduction by anthracenide. This contrasts with the published 37% reduction in the reaction of anthracenide with an *N*-benzoylaziridine. Very rapid mixing of the reagents by an injection technique changes the product mixture in a manner that points to a reduction by the aziridino ketyl which has a very short lifetime if derived from a non-aromatic acyl group. It is shown that an aziridino ketyl can undergo exocyclic cleavage of the bond next to the ketyl carbon provided that the eliminated carbanion (R^- of the acyl group RCO) is stabilized such as by two phenyl groups in the reported example.

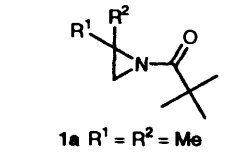
Reactions of *N*-acylaziridines initiated by single-electron transfer (SET) have been reported in several recent papers.[2] The first intermediate, namely the ketyl of the acylaziridine, forms rapidly in a homogeneous solution of radical anions derived from aromatic hydrocarbons. Reduction by an alkali metal is much slower owing to the heterogeneity of such a system. So far, in both types of reductions, only such aziridines have been used whose ketyls were stabilized by spin delocalization. We now report on the formation and reactions of non-stabilized ketyls in homogeneous solution. The short lifetime of such ketyls should make the reactions between radical anions and the aziridine resemble the dissociative SET from the respective radical anions to alkyl halides. The latter reactions provided alkylated dihydroarenes (or arenes) and other products in ratios near 1:1 from naphthalenide[3] $N^{\bullet -}$ and about 9:1 or greater from anthracenide[4] $A^{\bullet -}$ (mainly dialkylated products[5]). In the latter case replacement of the halogen by hydrogen can have played only a negligible role, if any. Why then did the reaction of *N*-benzoylaziridine with $A^{\bullet -}$ afford *N*-ethylbenzamide in 37% yield?[2a] The results presented below allow an answer to this question to be put forward.

The ketyl of an acylaziridine undergoes homolytic ring opening.[2a] Homolytic ring cleavage of an intermediate resembling the ketyl has been studied by addition of a tin radical to the carbonyl oxygen.[6] This study showed that the choice between two non-identical C–N bonds is largely controlled by the stability of the generated radical and by stereoelectronic requirements. Deviating behaviour was observed with 1-benzoyl-2-methylaziridine, since the primary radical was formed under kinetic control. Generally, there is a strong resemblance with the known[7] behaviour of the carba analogues of acylaziridines. In the case of the above aziridine the related *trans*-1-acetyl-2-methylcyclopropane provided the same ratio of isopropyl:propyl products under comparable conditions, *e.g.* ~0.5:1 with 1.6 mole equivalents of tributyltin hydride.

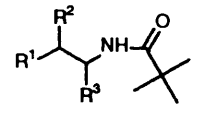
Results and Discussion

Unless otherwise stated, a solution of the aziridine was added dropwise to a stirred solution of the radical anion in tetrahydrofuran (THF) under nitrogen. The counterion was Na^+ unless Li^+ (under argon) is indicated.

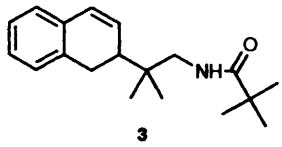
Reaction (1 hour) of $N^{\bullet -}$ (16.2 mmol) with the dimethylaziridine **1a** (6.5 mmol) provided the isobutylamide **2a** (43%)



1a $R^1 = R^2 = Me$
1b $R^1 = R^2 = H$
1c $R^1 = H, R^2 = Me$



2a $R^1 = R^2 = Me, R^3 = H$
2b $R^1 = R^2 = R^3 = H$
2c $R^1 = R^2 = H, R^3 = Me$
2d $R^1 = Me, R^2 = R^3 = H$



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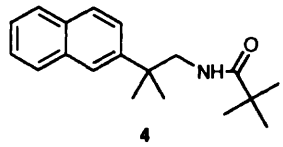

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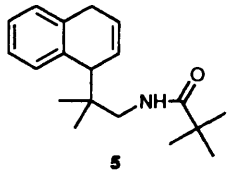

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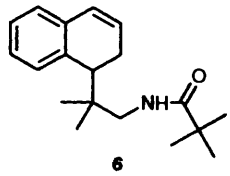

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and amidoethylated dihydronaphthalenes **3**, **5** and **6** (32%). This is in accord with expectation from the classic alkyl halide results. The mixture of isomeric dihydronaphthalenes could not be separated. Isomer **3** was identified by the ^1H NMR spectrum of an enriched mixture. It was partially aromatized to anthracene compound **4** by being heated to 80 °C (3 days) or by long storage (> 1 year) at room temperature. Comparison of the spectra before and after heating allowed us to recognize the signals of the fully aromatic system **4**. The presence of structures **5** and **6** was indicated by signals of the olefinic protons that were sufficiently separated from other signals of the mixture. On the whole, the outcome of the reaction was in line with alkyl halide reactions of $N^{\bullet -}$. Reactions of $A^{\bullet -}$ with the dimethylaziridine **1a** are listed in Table 1. With an excess of $A^{\bullet -}$ only the monoamidoethylated dihydroanthracene **7a** was obtained in high yield after completion of the reaction (run 1) and in only 26% yield after a very short reaction time (run 2). The yield of compound **7a** in a prolonged reaction with an equimolar amount of $A^{\bullet -}$ (run 3) corresponded to the consumption of 66% of $A^{\bullet -}$ although the colour of the solution indicated the complete disappearance of $A^{\bullet -}$. A similar deficit in the

Table 1 Reactions of the aziridine **1a** with anthracenide $A^{\bullet -}$

Run	Reagents (mmol/cm³ THF) $A^{\bullet -}$	**1a**	Time[a] t_1/s	t_2/s	Quenched	Yields[b] of products **7a**	**8**	**9**
1	15/100	5/30	10–20 min	1 d	water	75		
2	4.5/100	2/20	~10 s	0	AcOH	(26)	(9)	(45)
3	5.5/100	5/100	10–20 min	1d	AcOH	33	12	26

[a] t_1 = time required for the addition of **1a**; t_2 = subsequent reaction time. [b] Yields in parentheses were calculated from ^{1}H NMR spectra of product mixtures.

Table 2 Reactions of aziridines **1b** and **1c** with anthracenide $A^{\bullet -}$

Run	Reagents (mmol/cm³ THF) $A^{\bullet -}$	**1b** or **1c**	Time[a] t_1/s	t_2/s	Quenched[b]	Yields[c] of products **10**	**7**	Other products
1	12/100	**1b** 10/100	20–30 min	24 h	–	85 **10a**		
2	5.8/50	**1b** 5/50	15–25 min	6 h	+	73 **10a**	7 **7b**	
3	75/300	**1b** 10/100	20–30 min	24 h	–	8 **10a**[d]	(11)[e] **7b**	
4	20/100	**1b** 10/10	2 s	3 days	+	(26) **10a**	—	(1) **2b**, 4 **11a**, 0.5 **12a**
5	20[f]/100	**1b** 10/10	2 s	3 days	+	(52) **10a**	(7) **7b**	(6) **11a**, tr **12a**, 11 **13a**
6	18/200	**1c** 10/0	1 s	2 days	+	(22) **10b** (27) **10c** (0.5) **10d**	(0.2) **7c** (1.4) **7d**	(0.7) **2c**, (0.4) **2d** 0.9 **11b**, 0.8 **12b**, (0.5) **13b**

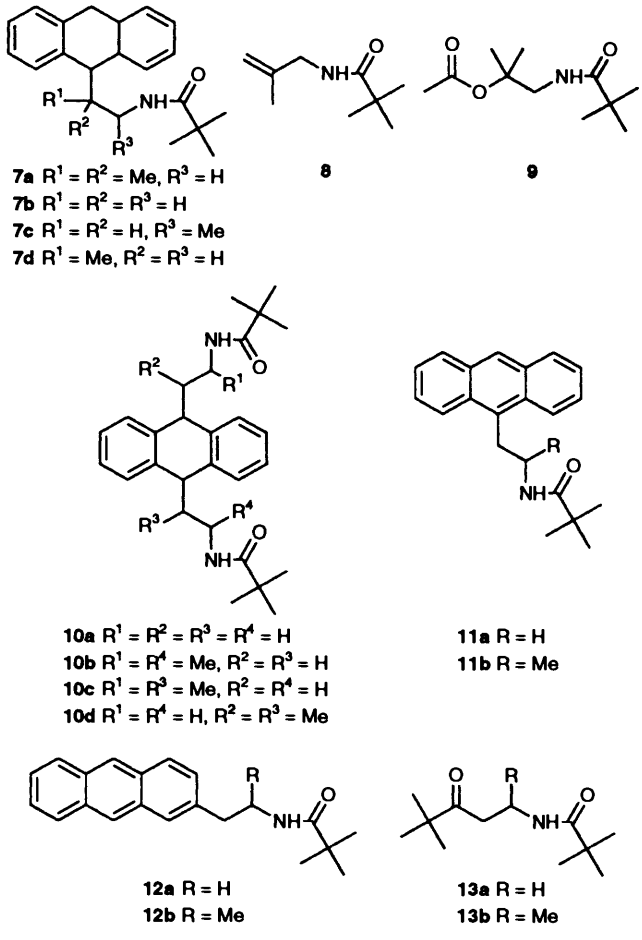
[a] t_1 and t_2: see Table 1. [b] Quenched with acetic acid. [c] Yields in parentheses: see Table 1. [d] 6% *cis* and 75% *trans* isomer. [e] Crude. [f] Counterion Li^+.

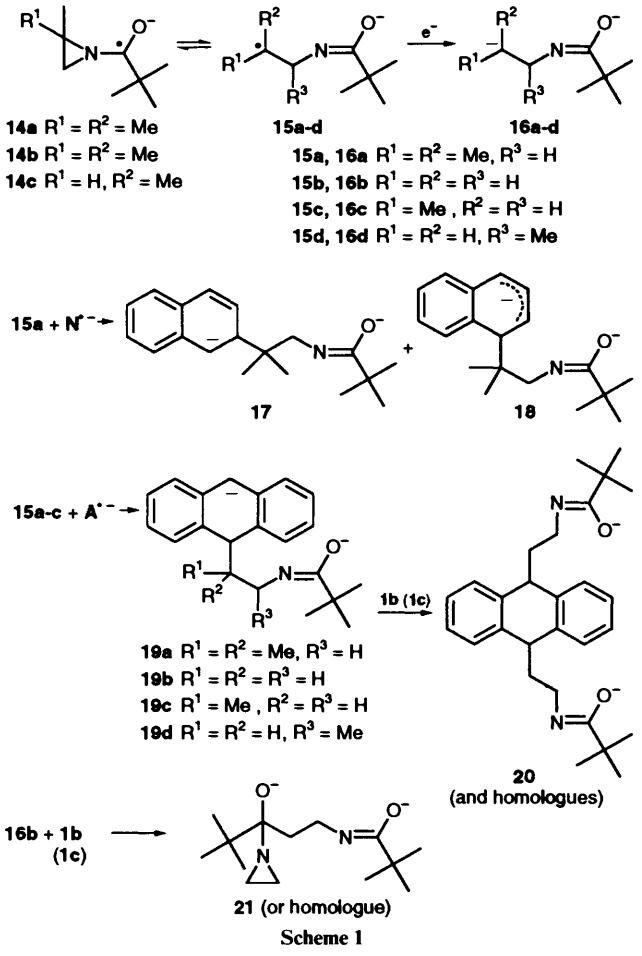
consumption of $A^{\bullet -}$ has been reported for alkylations.[4,8] In a repetition of run 3 a trace of amide **2a** was detected in the isolated methallylamide **8** by ^{1}H NMR spectroscopy. Compound **8** and its acetate **9** are artefacts of unchanged aziridine **1a**, arising when the reaction was quenched with acetic acid.

The results obtained with compound **1a** are interpreted by Scheme 1. Ketyl **14a** is cleaved to radical **15a**. Reaction of this radical with $N^{\bullet -}$ takes the two expected routes of (i) electron transfer, generating dianion **16a**, and of (ii) radical combination, generating carbanions **17** and **18**. In contrast, although in accord with the known behaviour of $A^{\bullet -}$, radical combination seems to be the only reaction of radical **15a** with $A^{\bullet -}$, resulting in dianion **19a**. Combinations with other positions of $A^{\bullet -}$ were not detected but cannot be excluded.

Reactions of $A^{\bullet -}$ with pivaloylaziridine **1b** in runs 1–3 of Table 2 are analogous to the reactions with the aziridine **1a** apart from the further fast S_N2 reaction of carbanion **19b** with a second molecule of substrate **1b** to give bis-imidate **20** (Scheme 1, disubstituted **10a**). Therefore, these results harmonize well with the aforementioned reaction of alkyl halides. Only in runs 2 and 3 was a small amount of the monosubstituted compound **7b** found, one owing to the large excess of $A^{\bullet -}$, one owing to the short reaction time and the concentration dependence of the S_N2 step. The analogous S_N2 reaction of dianion **19a** with the aziridine **1a** seems to be much slower due to steric hindrance exerted by both reactants. Anions of 9-substituted dihydroanthracenes are known to prefer the *cis* configuration[8] that in the present case implies a strong shielding of the carbanionic site due to the boat conformation. As expected, compound **10a** is obtained as the *cis* isomer [nuclear Overhauser enhancement (NOE) experiment]. The *trans* isomer found in run 3 must result from a reversible deprotonation of dianion **20**. Anions of analogues (primary alkyl substituents) of species **20** provide the respective *trans* isomer on protonation.[9] The necessary base in run 3 can be either carbanion **19b** or the dicarbanion formed by reversible dimerization of $A^{\bullet -}$ (see below).

The change from dropwise addition of the aziridine **1b** to its rapid injection (runs 4 and 5) had a surprising influence on the outcome of the reaction. In run 4 the yield of dihydroanthracene **10a** dropped to 26% and the sum of all detected products was less than 33% despite the excess of $A^{\bullet -}$ and the long reaction

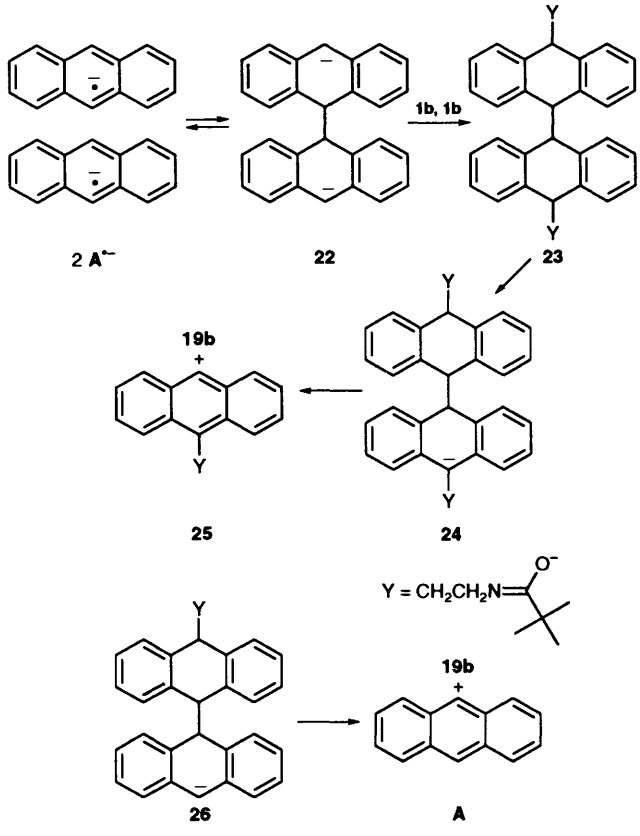




Scheme 1

time. The only reasonable explanation for the deficit is a nearly complete loss of ethylamide **2b** during work-up owing to its volatility and solubility in water.[10] This would push the behaviour of the aziridine **1b** closer to that of *N*-benzoylaziridine in published[2a] and unpublished reactions with $A^{\bullet -}$ under dropwise addition of the aziridine (see above). The formation of the *N*-ethyl amides in both cases is no mechanistic problem if the reducing agent for the amidatoalkyl radical (**15a, b** and analogues) is the ketyl and not $A^{\bullet -}$ [redox potential −1.98 V (ref. 11)]. The redox potentials[2c,*] of *N*-benzoylaziridine (−2.15 V) and of compound **1b** (−2.7 V) reveal their reducing power and show nicely the particularly high energy of the non-stabilized ketyl **14b**. This implies (relatively) slow formation and fast cleavage of ketyl **14b**. Under dropwise addition of the aziridine **1b** the ketyl **14b** cannot build up a sufficient concentration for competition with the relatively high concentration of $A^{\bullet -}$. In contrast, a stabilized aziridino ketyl with a longer lifetime will reach the necessary concentration even under dropwise addition of the aziridine. Formation of the amidoethylated anthracene **11a** is discussed below. Its positional isomer **12a** is assumed to arise from radical combination at position 2 of $A^{\bullet -}$. The respective 1,2-dihydroanthracene will undergo aromatization during work-up or storage much more easily than will a 9,10-dihydroanthracene like **7a**.

The influence of the injection technique is also found in the reaction of the aziridine **1b** with $A^{\bullet -}Li^+$ (run 5). However, the most striking result of this run is the isolation of the β-amido ketone **13a** whose analogue (*tert*-butyl replaced by phenyl) had previously been obtained[2b] from dropwise addition of *N*-benzoylaziridine to $A^{\bullet -}Na^+$. Formation of ketone **13a** and the increased yield of **10a** in run 5 relative to run 4 indicate a special role for the counterion. The influence of the counterion is not novel in the SET reactions with acylaziridines. Inner-sphere SET[13] with *N*-benzoylaziridine had led to exclusive reduction of the amidatoalkyl radical with Na^+, while with Li^+ up to 25% of amidoethylation had been found in addition. These effects can be attributed to the less ionic nature of 'carbanions' with the counterion Li^+. The lithiated carbanion **16b** will survive many collisions with solvent molecules and finally add to the carbonyl group of aziridine **1b** to form dianion **21** (Scheme 1), the precursor of ketone **13a**. An analogous addition to anthracene † may be the reason for the increase in amidoethylation (**7b** and **10b**) relative to run 4.



Scheme 2

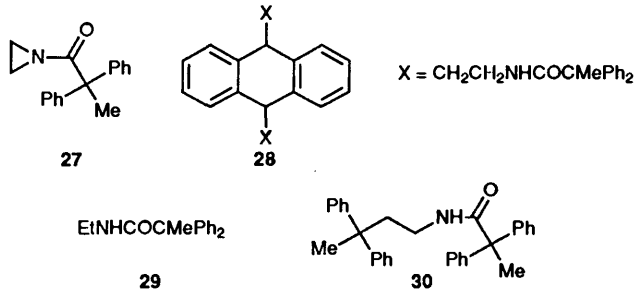
Formation of amidoethylated anthracene **11a** seems also to be connected with the injection technique. This technique may allow a fast formation of dimer **23** by a two-fold S_N2 reaction of the dimer dianion **22** of $A^{\bullet -}$ before it is reconverted into monomeric (solvent separated) $A^{\bullet -}$ ions (Scheme 2). Subsequent deprotonation by one of the available anions forms carbanion **24**, which undergoes benzylic fragmentation[2d,13,‡] to generate species **19b** and **25**, the precursors of **7b** and **11a**. With a low concentration of aziridine **1b**, *i.e.* under dropwise addition, the second amidoethylation of dimer **22** will be too slow to compete with the fragmentation **26** ⟶ **19b** + **A**. This route may always provide some of the product **7b**.

* Relative to saturated calomel (ref. 12).

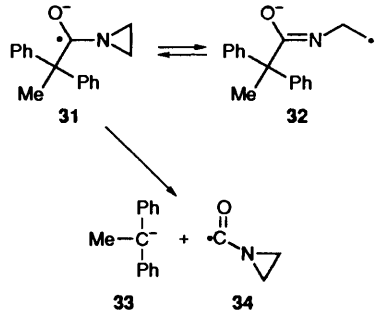
† Addition of alkyllithiums to anthracene is known.[14] A slower initial SET[15] with Li^+ may also lead to more amidoethylation but cannot explain the formation of ketone **13a**.

‡ *Cf.* ref. 16 and refs cited therein. Fragmentation of anion **26** (Y = H) has been described in ref. 16. Fragmentation of an S_N2 product **26** (Y = alkyl) provides a simple explanation for an incomplete racemization[4,5] in the reaction of $A^{\bullet -}$ with an optically active alkylating agent. Benzylic fragmentation seems to be a rather general reaction, that is found even with a simple '1,4-dihydrobenzene'.[17]

Run 6 of Table 2 describes the reaction of $A^{\bullet -}$ with injected monomethylaziridine **1c**. Work-up of this run was cumbersome and lengthy. Some minor products could not be identified and others (**10d** and **13b**) were recognized only by ^1H NMR spectroscopic analysis of mixtures. Monosubstituted dihydroanthracene **7c** is known.[1] Main products were bis-amidoethylated dihydroanthracenes **10b–d**. We assume that each of these disubstituted dihydroanthracenes possesses *cis* configuration although compound **10b** was obtained as a 1:1 mixture of isomers (α and β) that forms a 1:1 crystal with a sharp melting point. Comparison of chemical shifts for the *meso* protons of both isomers with those of *cis*-**10a** and *trans*-**10a** excluded the unlikely *cis–trans* isomerism for α and β forms. Thus, the isomers represent racemic and *meso* forms. The 1:1 ratio demonstrates that the introduction of the second centre of chirality is independent of the first chirality. No such stereoisomers were detected for compounds **10c** and **10d**, indicating a smaller distance between the first centre of chirality and the negatively charged *meso* carbon that reacts in the second amidoethylation (see below). Homolytic[6] as well as nucleophilic[1] ring opening of 1-acyl-2-methylaziridines (**1c** and analogues) is not regiospecific. Hence, the products of run 6 correspond with the products of runs 4 and 5, but they can form isomers by reaction with either the primary (pr) or with the secondary (sec) carbon of the aziridine **1c**. The reaction paths are analogous to those of the aziridine **1b** (Scheme 1). S_N2 Reaction of aziridine **1c** with the anion (**19** devoid of the side-chain) of dihydroanthracene proceeds[1] in the ratio pr:sec 33:1. One can expect a very similar ratio for the second amidoethylation of type **19** ⟶ **20** (Scheme 1). For the disubstituted dihydroanthracenes **10b–d** the total (first and second substitution) ratio pr:sec is 2.5:1. Consequently, the first substitution is, at least in the main, a combination of $A^{\bullet -}$ with the radicals **15c** and **15d**. The total ratio 2.5:1 requires much more combination with the secondary radical **15c** than with the primary one **15d**. These combinations are obviously slow enough to allow an effective equilibration of the isomeric radicals *via* their common ketyl. Formation of the isomeric anthracenes **11b** and **12b** will be analogous to that of their demethyl counterparts **11a** and **12a**. The ^1H NMR spectrum of compound **12b** did not allow us to determine the position of the methyl group. Structure **12b** was given preference on account of a strong peak with m/z = 128 and another peak with m/z = 191 in the mass spectrum. Cleavage at the β-position to the nitrogen can generate both respective ions from structure **12b** but not from its isomer. The formation of ketone **13b** may reflect the greater stability and the smaller steric demand of the primary carbanion. It is likely that the major propylamides **2c** and **2d** are lost during work-up.



In an attempt to isolate the elusive ethylamide **2b** (runs 4 and 5 of Table 2) quantitatively, the acyl group of the starting aziridine **1b** was made 'heavier' without influencing the intrinsic stability of the ketyl. Two methyl groups of compound **1b** were replaced by two phenyl groups. To make sure that there is no difference in reactivity between this aziridine **27** and its congener **1b** a run was performed with dropwise addition to $A^{\bullet -}$ The result was unexpected. Only 55% of the expected bis-amidoethylated dihydroanthracene **28** had been formed and not 80% or more as expected from runs 1–3 of Table 2. The yield (26%) of ethylamide **29** exceeded the highest possible yield (15–18%) of the undetected ethylamide **2b** in runs 1–3 of Table 2. The surprise finding was product **30** (7% yield) whose structure dictates the requirement of a cleavage of a C–CO bond. This can result only from an exocyclic cleavage of ketyl **31** (Scheme 3). Considering the low SET and the high S_N2 reactivity of the 'parent' aziridine **1b**, there can be little doubt that the novel product **30** results from an attack of 1,1-diphenylmethyl anion **33** on the aziridine **27**. We assume that heterolytic cleavage of the ketyl **31** immediately gives carbanion **33**. The second product (**34**) of this cleavage can lead to elusive products only.



Scheme 3

How can the radical **32** be reduced to the respective carbanion (precursor of the ethylamide) under the experimental conditions? The most likely electron source is carbanion **33**. The 1,1-diphenylmethyl radical arising from anion **33** would rapidly be reconverted into **33** by $A^{\bullet -}$, either directly or *via* intermediate combination and subsequent benzylic fragmentation. The missing supporting evidence for reduction by the ketyl would be put in doubt by this alternative reduction. We therefore did not repeat this run with the injection technique. However, the formation of carbanion **33** from the ketyl **31** was confirmed by stirring of the aziridine **27** with metallic sodium in THF. ^1H NMR analysis of the product mixture indicated its composition as 29% **29**, 6% **30**, 49% 1,1-diphenylethane (protonated **33**) and 11% 1,1-diphenylethanol (oxidized **33**). The combined yields (>50%) of the products derived from anion **33** cannot be reached by the alternative formation of anion **33** from amidatoalkyl radical **32**. Comparison of these two experiments with the aziridine **27** indicates the reversibility of homolytic ring cleavage. When the amidatoalkyl radical **32** is not rapidly trapped by $A^{\bullet -}$, the exocyclic cleavage dominates.

Experimental

Characterization of products was accomplished by ^1H NMR (Bruker W 250, Bruker H-X 90, and Varian T 60-A instruments; $CDCl_3$ solution; signal multiplicity given exclusively m_c = multiplet centred at; *J*-values in Hz), IR (Perkin-Elmer 283 instrument; 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.

Starting Materials.—Aziridines **1a**[18] and **1c**[2c] are known. Aziridines **1b** and **27** were prepared from aziridine and the respective acyl chloride by the method described in ref. 19.

1-Pivaloylaziridine **1b**. Yield 76%; b.p. 64 °C at 20 mmHg (Found: C, 65.8; H, 10.2; N, 10.9. $C_7H_{13}NO$ requires C, 66.1; H, 10.3; N, 11.0%); ν_{max}(film)/cm^{-1} 1690 (C=O); δ 1.25 (s, CMe_3) and 2.15 (s, CH_2CH_2).

1-(2,2-*Diphenylpropionyl*)*aziridine* **27**. Yield 68%; m.p. 33–35 °C (Found: C, 80.9; H, 6.9; N, 5.4. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); ν_{max}(film)/cm^{-1} 1690 (C=O); δ 1.86 (s, CH_2CH_2), 1.99 (s, Me) and 7.20 (s, 2 × Ph).

Reactions with Radical Anions.—The solutions of radical anions in THF were prepared and made to react as described in ref. 2*d*. Details for each run are given in Tables 1 and 2 or in the text. The residue obtained by evaporation was taken up in dichloromethane and washed with water. Evaporation provided a residue, which was subjected to chromatography (silica gel Merck, 0.063–0.2 mm, thickness × length of column in cm and other details given with each run).

Reaction of compound **1a** *with* $N^{\bullet -}$. Chromatography (3 × 33; CH_2Cl_2–ethyl acetate 10:1) provided mixture A (139 mg) and mixture B (906 mg). A second chromatography (3 × 30; toluene–ethyl acetate 5:1) of mixture A yielded a mixture (118 mg) consisting (^{1}H NMR) of compounds **3** (main component), **5** and **6**. Heating of this mixture to 80 °C for 3 days converted most of the dihydronaphthalene **3** into the aromatic system **4**. Mixture B consisted (1H NMR) of compound **2a** (437 mg, 43%) and a mixture of compounds **3**, **5** and **6** (469 mg) (total 587 mg = 32%). The isobutylamide **2a** was identified by comparison with an authentic sample.[6]

^{1}H NMR data of compound **3**: δ 1.17 (s, CMe_3), 1.20 (s, CMe_2), 2.31 (m_c, NCCCH) 2.80 (dd, *J* 14.1 and 3.5, 1 H of $NCCCCH_2$), 2.86 (dd, *J* 14.1 and 2.3, 1 H of $NCCCCH_2$), 3.17 (dd, *J* 13.9 and 5.8, 1 H of NCH_2), 3.28 (dd, *J* 13.9 and 5.7, 1 H, of NCH_2), 5.67 (br s, NH), 5.99 (dd, *J* 9.9 and 3.7, NCCCCH=C), 6.53 (dd, *J* 9.9 and 2.3, NCCCC=CH) and 6.98–7.17 (m, Ar H).

^{1}H NMR data of compound **4**: δ 1.02 (s, CMe_3), 1.43 (s, CMe_2), 3.53 (d, *J* 6.0, NCH_2), 5.31 (br s, NH), 7.44–7.54 (m, 3-, 6- and 7-H), 7.74 (d, *J* 1.8, 1-H) and 7.80–7.85 (m, 4-, 5- and 8-H).

Structure **5** was deduced from two multiplets of equal intensity centred at δ 6.11 and 6.17.

Structure **6** was deduced from a multiplet at δ 6.41 with a shape similar to that of the multiplet of its isomer **3** at δ 6.53. There were signals for the remaining protons of isomers **5** and **6** but an assignment was not possible.

Run 1, *Table* 1. Chromatography (3.5 × 45) with toluene provided hydrocarbons (2.03 g). Elution with CH_2Cl_2–ethyl acetate (10:1) yielded compound **7a** (1.259 g, 75%) that has previously[17] been obtained from the aziridine **1a** and the anion of dihydroanthracene.

Run 2, *Table* 1. Chromatography (3 × 20) with toluene removed hydrocarbons (785 mg). Elution with CH_2Cl_2–ethyl acetate (2:3) yielded a mixture (348 mg) and *amide ester* **9** (47 mg); m.p. 71 °C (Found: C, 61.7; H, 9.7; N, 6.2. $C_{11}H_{21}NO_3$ requires C, 61.4; H, 9.8; N, 6.5%); ν_{max}/cm^{-1} 3315 (NH), 1738 (ester) 1640 (amide I) and 1549 (amide II); δ 1.22 (s, CMe_3), 1.41 (s, CMe_2), 2.03 (s, MeCO), 3.49 (d, *J* 6.0, NCH_2) and 6.62 (br s, NH).

The mixture consisted (^{1}H NMR) of compound **7a** (173 mg, 26%), compound **8** (27 mg, 9%) and compound **9** (148 mg) (total 195 mg = 45%).

Run 3, *Table* 1. Chromatography (3 × 40) with CH_2Cl_2 removed anthracene (966 mg). Elution with CH_2Cl_2–ethyl acetate (10:1) provided compound **7a** (560 mg, 33%) and compound **8** (90 mg, 12%); m.p. 72–73 °C (Found: C, 69.9; H, 11.1; N, 9.2. $C_9H_{17}NO$ requires C, 69.6; H, 11.0; N, 9.0%); ν_{max}/cm^{-1} 3340 (NH), 1642 (amide I) and 1532 (amide II); δ 1.23 (s, CMe_3), 1.73 (s, C=CMe), 3.80 (d, *J* 5.9, NCH_2), 4.78–4.88 (m, $C=CH_2$) and 5.75 (s br, NH).

Elution with ethyl acetate yielded compound **9** (286 mg, 26%).

Run 1, *Table* 2. Chromatography (3.5 × 55) with CH_2Cl_2 removed hydrocarbons (0.85 g). Elution with ethyl acetate yielded *diamide* cis-**10a** (1.85 g, 85%); m.p. 199–202 °C (Found: C, 77.7; H, 8.8; N, 6.6. $C_{28}H_{38}N_2O_2$ requires C, 77.4; H, 8.8; N, 6.5%); ν_{max}/cm^{-1} 3330 (NH), 1642 (amide I) and 1534 (amide II); δ 1.10 (s, 2 × CMe_3), 1.97 (dt, *J* 7.2 and 7.1, 2 × $NCCH_2$), 3.41 (dt, *J* 7.2 and 7.1, 2 × NCH_2), 3.98 (t, *J* 7.2, 9- and 10-H), 5.76 (br t, *J* 7, 2 × NH) and 7.20–7.30 (m, 8 × Ar H).

Run 2, *Table* 2. Chromatography (3 × 40) with CH_2Cl_2 removed anthracene (942 mg) (contaminated with some anthraquinone). Elution with CH_2Cl_2–ethyl acetate (10:1) yielded *compound* **7b** (114 mg, 7%); m.p. 116–118 °C (Found: C, 82.1; H, 8.3; N, 4.7. $C_{21}H_{25}NO$ requires C, 82.0; H, 8.2; N, 4.6%); ν_{max}/cm^{-1} 3320 (NH), 1635 (amide I) and 1540 (amide II); δ 1.03 (s, CMe_3), 1.85 (dt, *J* 7.2 and 7.2, $NCCH_2$), 3.26 (dt, *J* 7.2 and 7.2, NCH_2), 3.86 (d, *J* 18.3, 10-H pseudo-eq), 3.98 (t, *J* 7.2, 9-H pseudo-eq), 4.09 (d, *J* 18.3, 10-H pseudo-ax), 5.41 (br t, *J* 7, NH) and 7.15–7.33 (m, 8 × Ar H).

Elution with ethyl acetate provided *cis*-**10a** (790 mg, 73%).

Run 3, *Table* 2. Anthracene (8.62 g) was removed by filtration prior to chromatography. Chromatography (7 × 15; light petroleum) removed hydrocarbons (5.64 g). Elution with ethyl acetate provided a mixture (2.22 g), which was then put on a second column (3.5 × 45). Elution with CH_2Cl_2 yielded *diamide* trans-**10a** (1.63 g, 75%); m.p. 229–231 °C (Found: C, 77.6; H, 8.8; N, 6.5. $C_{28}H_{38}N_2O_2$ requires C, 77.4; H, 8.8; N, 6.5%); ν_{max}/cm^{-1} 3345 (NH), 1638 (amide I) and 1532 (amide II); δ 1.09 (s, 2 × CMe_3), 2.28 (dt, *J* 5.7 and 8.2, 2 × $NCCH_2$), 3.15 (dt, *J* 7.5 and 8.2, 2 × NCH_2), 4.13 (t, *J* 5.7, 9- and 10-H), 7.24–7.31 (m, 4 × Ar H) and 7.43–7.49 (m, 4 × Ar H).

Continued elution provided crude **7a** (0.34 g, 11%) and *cis*-**10a** (0.13 g, 6%).

Run 4, *Table* 2. Chromatography (4 × 45) with toluene–ethyl acetate (9:1) yielded *compound* **11a** (118 mg, 4%) m.p. 227–230 °C (Found: C, 82.5; H, 7.4; N, 4.6. $C_{21}H_{23}NO$ requires C, 82.6; H, 7.6; N, 4.6%); ν_{max}/cm^{-1} 3350 (NH), 1640 (amide I) and 1545 (amide II); δ 1.08 (s, CMe_3), 3.72 (m_c, NCH_2), 3.89 (t, *J* 7.1, $NCCH_2$), 5.73 (br s, NH), 7.51 (m_c 2-, 3-, 6- and 7-H), 8.01 (d, *J* 8.2, 4- and 5-H), 8.35 (d, *J* 8.7, 1- and 8-H) and 8.38 (s, 10-H); *m/z* 305 (M^+, 22%), 204 (100), 191 (51), 85 (9) and 57 (39).

Further elution provided *compound* **12a** (16 mg, 0.5%); m.p. 184–185 °C (Found: M^+, 305.1777. $C_{21}H_{23}NO$ requires *M*, 305.1778); ν_{max}/cm^{-1} 3365 (NH), 1640 (amide I) and 1535 (amide II); δ 1.12 (s, CMe_3), 3.00 (t, *J* 6.7, $NCCH_2$), 3.61 (m_c, NCH_2), 5.71 (br s, NH), 7.44–7.47 (m, 3-, 6- and 7-H), 7.75 (s, 1-H), 7.95–7.98 (m, 4-, 5- and 8-H), 8.34 (s, 9-H) and 8.40 (s, 10-H); *m/z* 305 (M^+, 20%), 204 (100), 191 (54), 85 (12) and 57 (45).

Further elution provided unidentified products (79 mg).

Elution with toluene–ethyl acetate–methanol (9:1:1) gave compound **10a** (450 mg) and a mixture (113 mg) consisting (^{1}H NMR) of compound **10a** (94 mg) and compound **2b** (19 mg, 1%).[6]

Further elution provided a mixture (147 mg) containing (1H NMR, internal standard compound **10a** (30 mg) (total 574 mg = 26%).

Run 5, *Table* 2. Chromatography (4 × 40; CH_2Cl_2–ethyl acetate 10:1) provided compound **11a** (125 mg) and a mixture (486 mg) consisting (^{1}H NMR) of compound **11a** (59 mg) (total 184 mg = 6%), compound **7b** (217 mg, 7%), and traces of compound **12a** and perhaps of its 1,2-dihydro derivative.

Further elution yielded compound **13a** (117 mg, 11%), m.p. 55–57 °C (Found: M^+, 213.1727. $C_{12}H_{23}NO_2$ requires *M*, 213.1728); ν_{max}/cm^{-1} 3370 (NH), 1705 (ketone), 1645 (amide I) and 1530 (amide II); δ 1.13 (s, $NCOCMe_3$), 1.15 (s, $CCOCMe_3$), 2.73 (d, *J* 5.5, $NCCH_2$), 3.47 (q, *J* 5.5, NCH_2) and 6.31 (s br, NH); *m/z* 213 (M^+, 1%), 156 (93), 114 (39), 85 (42) and 57 (100).

Elution with CH_2Cl_2–methanol (9:1) yielded *cis*-**10a** (1.132 g, 52%).

Run 6, *Table* 2. Chromatography (3 × 30) with toluene–ethyl acetate (10:1) provided mixture A (383 mg) and mixture B (43 mg). Elution with CH_2Cl_2–ethyl acetate–methanol (20:2:1)

gave mixture C (1.192 g). Second chromatography (3 × 15; toluene–ethyl acetate 9:1) of mixture A provided a mixture (39 mg) consisting (^{1}H NMR) of compound **7c**[1] (6 mg, 0.2%) and compound **7d**[1b] (33 mg, 1.4%).

Continued elution yielded *compound* **11b** (30 mg, 0.9%); m.p. 210–213 °C (Found: M^+, 319.1936. $C_{22}H_{25}NO$ requires *M*, 319.1936); ν_{max}/cm^{-1} 3360 (NH), 1650 (amide I) and 1540 (amide II); δ 1.08 (s, CMe_3), 1.12 (d, *J* 6.7, Me), 3.64 (dd, *J* 14.0 and 8.7, 1 H of $NCCH_2$), 4.03 (dd, *J* 14.0 and 6.0, 1 H of $NCCH_2$), 4.48 (m_c, NCH), 5.67 (br d, *J* 6, NH), 7.51 (m_c 2-, 3-, 6-and 7-H), 8.00 (d, *J* 8.5, 4- and 5-H), 8.37 (s, 10-H) and 8.49 (d, *J* 8.7, 1- and 8-H); *m*/*z* 319 (M^+, 29%), 218 (32), 191 (41), 128 (65), 85 (55) and 57 (100).

Further elution provided a mixture (130 mg) containing (^{1}H NMR, internal standard) compound **12b** (25 mg, 0.8%). A methanol slurry of this mixture allowed us to pick out a tiny crystal of compound **12b**; m.p. 218–221 °C (Found: M^+, 319.1929. $C_{22}H_{25}NO$ requires *M*, 319.1936); ν_{max}/cm^{-1} 3260 (NH), 1635 (amide I) and 1545 (amide II); δ 1.06 (s, CMe_3), 1.40 (d, *J* 6.8, Me), 3.33 (m_c, 1 H of $NCCH_2$), 3.70 (m_c, 1 H of $NCCH_2$), 3.96 (m_c, NCH), 5.56 (br s, NH), 7.47 (m_c, 3-, 6- and 7-H), 7.77 (s, 1-H), 7.96–8.02 (m, 4-, 5- and 8-H), 8.37 (s, 9-H) and 8.40 (s, 10-H); *m*/*z* 319 (M^+, 26%), 218 (24), 191 (33), 128 (73), 85 (65) and 57 (100).

Mixture B consisted (^{1}H NMR) of compound **2c** (10 mg, 0.7%), compound **2d** (6 mg, 0.4%), compound **10d** (12 mg, 0.5%) and compound **13b** (9 mg, 0.5%) compounds **2c** and **2d** were identified by comparison with authentic material synthesized from isopropylamine or propylamine, respectively, and pivaloyl chloride. Compound **2c**; m.p. 105 °C (Found: C, 67.4; H, 12.1; N, 9.9. Calc. for $C_8H_{17}NO$: C, 67.1; H, 11.9; N, 9.8%); ν_{max}/cm^{-1} 3325 (NH), 1630 (amide I) and 1535 (amide II); δ 1.13 (d, *J* 6.6 Hz, CMe_2), 1.18 (s, CMe_3), 4.07 (oct, *J* 6.5, NCH) and 5.41 (br s, NH). Compound **2d**; m.p. 33 °C (Found: C, 67.3; H, 11.5; N, 9.8%); ν_{max}/cm^{-1} 3360 (NH), 1640 (amide I) and 1540 (amide II); δ 0.92 (t, *J* 7.3, Me), 1.20 (s, CMe_3), 1.48 (sext, *J* 7.2, $NCCH_2$), 3.16 (m_c, NCH_2) and 5.92 (br s, NH).

The structure of compound **10d** followed from the doublet of the *meso* protons and from the aromatic signals: δ 1.08 (d, *J* 6.9, 2 × Me), 1.13 (s, 2 × CMe_3), 1.95 (m_c, 2 × NCCH), 3.13 (m_c, 2 × NCH_2), 3.55 (d, *J* 10.2, 2 × NCCCH), 6.37 (br t, *J* 6, 2 × NH) and 7.11–7.28 (m, Ar H).

Structure **13b** followed from the two doublets of doublets for CH_2 and from the NCH multiplet: δ 1.12 (s, $NCOCMe_3$), 1.17 (s, $CCOCMe_3$), Me hidden, 2.60 (dd, *J* 17.4 and 5.4, 1 H of $NCCH_2$), 2.83 (dd, *J* 17.4 and 4.1, 1 H of $NCCH_2$), 4.27 (m_c, NCH) and 6.61 (br s, NH).

A second chromatography (3 × 30; toluene–ethyl acetate–methanol 20:2:1) of mixture C provided fraction A (689 mg) consisting (^{1}H NMR) of compound **10b** (221 mg) and compound **10c** (508 mg).

Continued elution resulted in fraction B (431 mg) consisting (^{1}H NMR) of further compound **10b** (292 mg) (total 513 mg = 22%) and further compound **10c** (138 mg) (total 646 mg = 27%). TLC (same solvent system) of a sample of fraction A provided a pure sample of *compound* **10c**, m.p. 208–209 °C (Found: C, 77.5; H, 9.0; N, 5.9. $C_{30}H_{42}N_2O_2$ requires C, 77.9; H, 9.2; N, 6.1%); ν_{max}/cm^{-1} 3310 (NH), 1630 (amide I) and 1540 (amide II); δ 1.03 (d, *J* 6.6, NCCMe), 1.07 (s, 1 × CMe_3), 1.08 (s, 1 × CMe_3), 1.24 (d, *J* 6.5, NCMe), 1.86 (m_c, NCCH, 1 H of $NCCH_2$), 2.11 (dt, *J* 14.0 and 8.3, 1 H of $NCCH_2$), 3.20 (t, *J* 6.2, NCH_2), 3.55 (d, *J* 10.0, MeCC*H*), 4.03 (m_c, MeCCC*H*), 4.22 (m_c, NCH), 5.83 (br t, *J* 6, MeCCN*H*), 5.98 (d br, *J* 8, MeCN*H*), 7.13–7.31 (m, 7 × Ar H) and 7.38 (d, *J* 7.5, 1 *peri* H); *m*/*z* 462 (M^+, 18%), 320 (51), 219 (21), 142 (39), 128 (100), 85 (24) and 57 (61).

TLC of a sample of fraction B provided a pure sample of *compound* **10b**, m.p. 215–217 °C (Found: C, 77.7; H, 8.9; N, 5.8%); ν_{max}/cm^{-1} 3370 (NH), 1645, 1635 (both amide I), 1535 and 1520 (both amide II); δ (aromatic signals for α- and β-**10b**) 7.13 (m, 13 H), 7.33–7.38 (m, 2 *peri* H) and 7.42–7.48 (m, 1 peri H); δ (α-**10b**) 1.10 (s, 2 × CMe_3), 1.21 (d, *J* 6.6, 2 × Me), 1.82 (m_c, 1 H of each CH_2), 1.99 (dt, *J* 14.0 and 8.2, 1 H of each CH_2), 3.96 (t, *J* 7.8, 9- and 10-H), 4.18 (m_c, 2 × NCH) and 5.77 (br d, *J* 8.1, 2 × NH); δ (β-**10b**) 1.15 (d, *J* 6.5, 2 × Me), 1.24 (s, 2 × CMe_3), 1.83 (t, *J* 7.0, 2 × CH_2), 3.98 (d, *J* 7.8, 9- and 10-H), 4.28 (m_c, 2 × NCH) and 5.45 (br d, *J* 8.9, 2 × NH).

Reaction of the Aziridine **27** *with Anthracenide* $A^{\bullet-}$.—A solution of compound **27** (822 mg, 3.3 mmol) in THF (20 cm^3) was added dropwise within 7 min to a stirred solution prepared in the usual manner from sodium (188 mg, 8.2 mmol) and anthracene (1.75 g, 9.8 mmol) in THF (120 cm^3). The mixture was stirred for 1 h. The reaction was quenched with acetic acid. Evaporation provided a residue, which was taken up in CH_2Cl_2 and washed with water. Evaporation provided the product mixture, which was subjected to chromatography (3 × 30; benzene–ethyl acetate 10:1). After a forerun of anthracene there was obtained *compound* **30** (89 mg, 12%); m.p. 123–124 °C (Found: C, 85.7; H, 7.2; N, 3.3. $C_{31}H_{31}NO$ requires C, 85.9; H, 7.2; N, 3.2%); ν_{max}/cm^{-1} 3370 (NH), 1630 (amide I) and 1540 (amide II); δ 1.64 (s, NCCCMe), 1.96 (s, O=CCMe), 2.25 (dd, *J* 7.7 and 8.2, $NCCH_2$), 3.09 (m_c, NCH_2), 5.36 (br t, *J* ~ 4, NH) and 7.09–7.34 (m, 20 × Ar H); *m*/*z* 433 (M^+, 4%), 252 (7), 182 (100), 167 (35) and 103 (31).

Continued elution yielded an unknown product (82 mg) and *compound* **28** (214 mg); m.p. 158–160 °C (Found: C, 84.2; H, 7.0; N, 4.1. $C_{48}H_{46}N_2O_2$ requires C, 84.4; H, 6.8; N, 4.1%); ν_{max}/cm^{-1} 3305 (NH), 1665, 1655 (both amide I) and 1515 and 1505 (both amide II); δ 1.78 (q, *J* ~ 7.3, 2 × $NCCH_2$), 1.97 (s, 2 × Me), 3.40 (m_c, 2 × NCH_2), 3.76 (t, *J* 7.6, 9- and 10-H), 5.54 (br t, *J* 5.5, 2 × NH) and 7.04–7.34 (m, 28 × Ar H); *m*/*z* 682 (M^+, 11%), 501 (53), 430 (21) and 181 (100).

Further elution provided a mixture (549 mg) consisting (^{1}H NMR) of compound **29** (165 mg) and compound **28** (384 mg) (total 598 mg = 55%). The last fraction was *compound* **29** (47 mg) (total 212 mg = 26%); m.p. 77–78 °C (Found: C, 80.9; H, 7.4; N, 5.2. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.4; N, 5.5%); ν_{max}/cm^{-1} 3370 (NH), 1640 (amide I) and 1530 (amide II); δ 1.05 (t, *J* 7.2, NCMe), 1.99 (s, O=CCMe), 3.29 (qd, *J* 7.2 and 5.7, NCH_2), 5.42 (br s, NH) 7.21–7.38 (m, 10 × Ar H); *m*/*z* 253 (M^+, 6%), 182 (90), 181 (100) and 167 (69).

Reaction of Compound **27** *with Sodium*.—Sodium (129 mg, 5.6 mmol) and compound **27** (338 mg, 1.34 mmol) were stirred in THF (100 cm^3) for 12 days. The reaction was quenched with an insufficient quantity of acetic acid. Work-up was as in the preceding experiment. Chromatography (3 × 30; toluene–ethyl acetate 9:1) provided a mixture (266 mg) consisting (^{1}H NMR) of 1,1-diphenylethane (120 mg, 49%), 1,1-diphenylethanol (29 mg, 11%), compound **29** (98 mg, 29%) and compound **30** (19 mg, 7%).

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