Tetrahedron Vol. 43, No 5, pp. 923 to 934, 1987
Printed in Great Britain.

0040-4020/87 $3.00 + .00
Pergamon Journals Ltd.

REACTIONS OF CARBAMYL RADICALS: INTRAMOLECULAR HYDROGEN ABSTRACTION REACTIONS

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(*Received in UK* 11 *November* 1986)

Summary - ω-Phenylalkyl-N-methylcarbamyl radicals undergo intermolecular addition to 3,3-dimethylbut-1-ene in preference to intramolecular hydrogen abstraction. Methyl N-(ω-phenylalkyl) carbamyl radicals and methyl N-pentylcarbamyl radicals readily abstract hydrogen through a six membered transition state or a seven membered transition state if the hydrogen is benzylic. The selectivities are interpreted in terms of the electrophilicity of the radical and the stereo-electronic requirements of hydrogen abstraction reactions.

The structure and reactivity of amidyl radicals (1a) have been studied extensively[1,2,3,4], however, their congeners, carbamyl radicals (1b) have received little attention.

$$X\text{-}CO\text{-}\dot{N}\text{-}R$$

(1) (a) X = alkyl, R = H or alkyl
(b) X = RO, R = H or alkyl
(c) X = EtO, R = H
(d) X = R = H

No studies of the trends in hydrogen abstraction by either intramolecular or intermolecular processes have been made and only a limited number of intermolecular additions to olefins have been reported[2,5]. The rates of bimolecular decay for several carbamyl radicals have also been determined[6]. In the same e.s.r. study, Ingold and co-workers have indicated that carbamyl radicals, like amidyl radicals, have a π-ground state in which an N-alkyl substituent eclipses the carbonyl oxygen.

To elaborate further upon the similarities and differences between these closely related species, we have studied the intramolecular hydrogen abstraction reactions of a series of carbamyl radicals.

RESULTS

Intramolecular hydrogen abstraction from the O-alkyl side-chain.

A series of ω-phenylalkyl-N-methylcarbamates (2a-c) were prepared by reacting the corresponding alcohol with methylisocyanate. Attempts to convert (2a) to its N-iodo derivative (2g) with preformed t-butyl hypoiodite[7] or mercuric oxide and iodine[8] were unsuccessful. However, all three carbamates were readily transformed into their N-bromo derivatives (2d-f) with preformed t-butylhypobromite in benzene[9].

$ROC(O)N(CH_3)X$

(2)

(a) $Ph(CH_2)_{2-}$, X = H
(b) $Ph(CH_2)_{3-}$, X = H
(c) $Ph(CH_2)_{4-}$, X = H
(d) $Ph(CH_2)_{2-}$, X = Br
(e) $Ph(CH_2)_{3-}$, X = Br
(f) $Ph(CH_2)_{4-}$, X = Br
(g) $Ph(CH_2)_{2-}$, X = I

$ROC(O)\dot{N}CH_3$

(3)

(a) R = $Ph(CH_2)_{2-}$
(b) R = $Ph(CH_2)_{3-}$
(c) R = $Ph(CH_2)_{4-}$

$PhCHBr(CH_2)_nOC(O)NHCH_3$

(4)

(a) n = 1
(b) n = 2
(c) n = 3

$PhCH_2(CH_2)_nOC(O)N(CH_3)CH_2CHBrBu^t$

(5)

(a) n = 1
(b) n = 2
(c) n = 3

$CH_3OC(O)NXR$

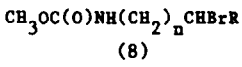
(6)

(a) R = $(CH_2)_3Ph$, X = H
(b) R = $-(CH_2)_4Ph$, X = H
(c) R = $-(CH_2)_5Ph$, X = H
(d) R = $-(CH_2)_4CH_3$, X = H
(e) R = $(CH_2)_3Ph$, X = Br
(f) R = $(CH_2)_4Ph$, X = Br
(g) R = $(CH_2)_5Ph$, X = Br
(h) R = $(CH_4)CH_3$, X = Br

$CH_3OC(O)\dot{N}R$

(7)

(a) R = $(CH_2)_3Ph$
(b) R = $(CH_2)_4Ph$
(c) R = $(CH_2)_5Ph$
(d) R = $(CH_2)_4CH_3$



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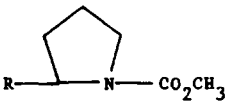
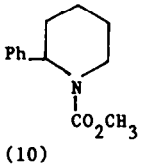


(9)

(a) n = 2, R = Ph
(b) n = 3, R = Ph
(c) n = 4, R = Ph
(d) n = 3, R = CH_3

(a) R = Ph
(b) R = CH_3
(c) R = $PhCH_2$



(10)

Upon photolysis of 2-phenylethyl-N-bromo-N-methylcarbamate (2d) in benzene with a medium pressure ultraviolet lamp, starting material was rapidly consumed and after 0.5h, an aliquot revealed no positive bromine by iodometry. Removal of solvent gave a nearly quantitative yield of 2-bromo-2-phenylethyl-N-methylcarbamate (4a) (Table 1). N-bromocarbamates (2e) and (2f) similarly gave the benzylic brominated products (4b) and (4c) respectively (Table 1). Benzylic bromination could arise by intramolecular hydrogen abstraction by the carbamyl radical (Scheme 1) or intermolecular hydrogen abstraction by bromine atoms (Schemes 2 and 3). To distinguish between these two pathways, the photolyses were repeated in the presence of 3,3-dimethylbut-1-ene which is a good bromine atom scavenger and thereby inhibits bromine chain processes[10]. The products were mainly the parent carbamates (2a-c) and ω-phenylalkyl N-(2-bromo-3,3-dimethylbutyl)- N-methylcarbamates (5a-c) which were isolated by preparative t.l.c. (Table 1). High field (500 MHz) ^{13}C and ^{1}H n.m.r. spectral analysis of the adducts established[11] that they were formed by regiospecific addition of carbamyl radicals (3a-c) to the least hindered position of 3,3-dimethylbut-1-ene.

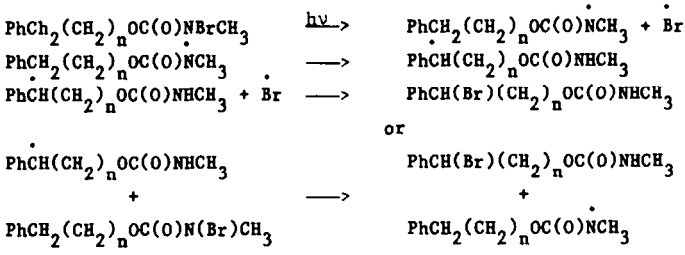
In addition, low but similar yields of benzylic bromides (4a-c) were obtained (Table 1). Formation of these could be due to hydrogen abstraction by nitrogen (according to Scheme 1) or inefficient trapping of bromine atoms by 3,3-dimethylbut-1-ene resulting in some bromine chain halogenation (Schemes 2 and 3). Since intramolecular hydrogen abstraction via a highly disfavoured eight membered cyclic transition structure was deemed unlikely in formation of (4c) from (3c), we favour the latter process. Furthermore, increasing the ratio of 3,3-dimethylbut-1-ene to (2f) from 0,5 to 10 rapidly reduced the extent of benzylic bromination but failed to eliminate it altogether. The similarity in yields of benzylic brominated products (4a-c) from (2d-f) suggests that the more favourable seven and six membered cyclic transition structures for intramolecular hydrogen abstraction by (3a) and (3b) do not play a significant role and that bromides (4a) and (4b) are likewise formed by bromine atom chain reactions.

Table 1: Products form irradiation of N-bromocarbamates for 0.5h in benzene

Substrate	TBE/ equivalent	benzylic bromide[b]	adduct[a]	carbamate[a]
2(d)	0	4a (98)		nd
2(e)	0	4b (97)		nd
2(f)	0	4c (85)		nd
2(d)	10	4a (6)	5a (44)	2a (26)
2(e)	10	4b (9)	5b (28)	2b (33)
2(f)	10	4c (10)	5c (34)	2c (37)
2(f)	0,5	4c (60)	nd	nd
	1,0	(56)	nd	nd
	2,0	(42)	nd	nd
	5,0	(31)	nd	nd
	10,0	(10)	nd	nd
6(e)	0	8a (85)	-	nd
6(f)	0	8b (98)	-	nd
6(g)	0	8c (88)	-	nd
6(e)	10	8a (9)	nd	6a (76)
6(f)	12	8b (93)	nd	nd
6(g)	12	8c (>61)	nd	nd

nd not determined
a isolated yield
b by analytical h.p.l.c.

Scheme 1



Scheme 2

$$PhCH_2(CH_2)_nOC(O)NBrCH_3 \xrightarrow{h\nu} PhCH_2(CH_2)_nOC(O)\dot{N}CH_3 + \dot{B}r$$

$$\dot{B}r + PhCH_2(CH_2)_nOC(O)N(Br)CH_3 \longrightarrow Ph\dot{C}H(CH_2)_nOC(O)N(Br)CH_3 + HBr$$

$$Ph\dot{C}H(CH_2)_nOC(O)N(Br)CH_3 + PhCH_2(CH_2)_nOC(O)N(Br)CH_3 \longrightarrow PhCHBr(CH_2)_nOC(O)N(Br)CH_3 + PhCH_2(CH_2)_nOC(O)\dot{N}CH_3$$

$$PhCH_2(CH_2)_nOC(O)\dot{N}CH_3 + HBr \longrightarrow PhCH_2(CH_2)_nOC(O)NHCH_3 + \dot{B}r$$

Scheme 3

$$PhCH_2(CH_2)_nOC(O)NBrCH_3 \xrightarrow{h\nu} PhCH_2(CH_2)_nOC(O)\dot{N}CH_3 + \dot{B}r$$

$$\dot{B}r + PhCH_2(CH_2)_nOC(O)N(Br)CH_3 \longrightarrow Ph\dot{C}H(CH_2)_nOC(O)N(Br)CH_3 + HBr$$

$$H\dot{B}r + PhCH_2(CH_2)_nOC(O)N(Br)CH_3 \longrightarrow PhCH_2(CH_2)_nOC(O)NHCH_3 + Br_2$$

$$PhCH(CH_2)_nOC(O)N(Br)CH_3 + Br_2 \longrightarrow PhCH(Br)(CH_2)_nOC(O)N(Br)CH_3 + \dot{B}r$$

Intramolecular hydrogen abstraction from the N-alkyl side chain

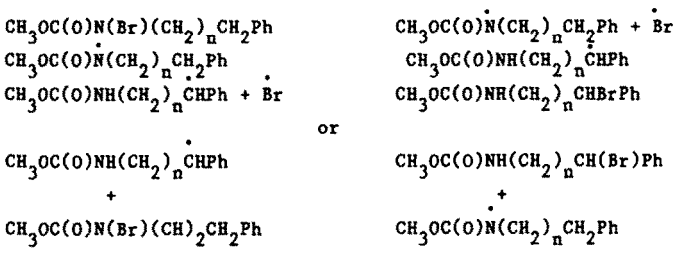
A series of methyl N-(ω-phenylalkyl)carbamates (6a-c), as well as methyl-N-pentylcarbamate (6d), were synthesised and converted to their N-bromo derivatives (6e-h).

Irradiation of (6e-g) in benzene for 0,5h gave nearly complete conversion to the corresponding benzylic bromides (8a-c) (Table 1). (8b) was unstable and rearranged quantitatively to N-carbomethoxy-2-phenylpyrrolidine (9a) with loss of hydrogen bromide. Methyl N-(4-bromo-4-phenylbutyl)carbamate (8c) underwent a slower cyclisation upon standing to N-carbomethyoxy-2-phenylpiperidine (10). The cyclisation was also effected by treatment of (8c) with silver perchlorate. Treatment of benzylic bromide (8a) with silver perchlorate did not give the corresponding azetidine. These results reflect the relative ease of four, five and six membered ring formation.

Irradiation of methyl-N-bromo-N-(3-phenylpropyl)carbamate (6e) in the presence of 3,3-dimethylbut-1-ene gave mainly parent carbamate (6a) and some residual benzylic bromination (8a) (Table 1). In the presence of 3,3-dimethylbut-1-ene, N-bromo-N-(4-phenylbutyl)carbamate (6f) gave upon irradiation an excellent conversion to the benzylic bromide (8b) which rearranged to pyrrolidine (9a) (Table 1). Since the presence of olefin during photolysis of (2d-f) and (6e) resulted in the elimination of most bromine atom mediated benzylic hydrogen abstraction, the formation of (8b) from (6f) is ascribed to intramolecular hydrogen abstraction by carbamyl radical (7b) according to Scheme 4 (n = 3). Such a process would involve benzylic hydrogen abstraction via a six membered cyclic transition state.

When methyl N-bromo-N-(5-phenylpentyl)carbamate (6g) was irradiated in the presence of 3,3-dimethylbut-1-ene, an unstable mixture was obtained which, upon treatment with silver perchlorate in benzene, gave the piperidine (10, 61%) and parent carbamate (6c, 39%). The formation of (10) implies the presence of benzylic bromide (8c) with a yield of $\geq$ 61% in the crude reaction mixture from the photolysis experiment. Furthermore, since no N-carbomethoxy-2-(benzyl)pyrrolidine (9c) was obtained, hydrogen abstraction via a six membered cyclic transition state by the carbamyl radical from the unactivated 3-position on the N-alkyl side chain did not take place. Clearly intramolecular benzylic hydrogen abstraction via a seven membered cyclic transition state (Scheme 4, n = 4) occurs at a much faster rate.

Scheme 4



Irradiation of methyl-N-bromo-N-pentylcarbamate (6h) in the presence of bromine scavenger resulted in quantitative conversion to methyl N-(4-bromopentyl)carbamate (8d) which was stable at room temperature but rearranged upon heating to N-carbomethoxy-2-methylpyrrolidine (9b). In the absence of an activating phenyl substituent, hydrogen abstraction via a six membered cyclic transition state (Scheme 4, n = 3, Ph = CH_3) predominates over abstraction from the terminal position.

DISCUSSION

The relative yields of 1,2-olefin addition products from the reactions of N-chloroamides and N-chlorocarbamates with simple olefins suggest that carbamyl radicals (1b) are more electrophilic than amidyls (1a).[12] MNDO calculations (half electron method) predict the SOMO of ethyl carbamyl radical (1c, X = EtO, R = H) to be lower in energy (-7, 136 eV) than that for formamidyl radical (1d, X = R = H) (-6, 92 eV) and the former should be more electrophilic.[13] Although amidyl radicals abstract hydrogen preferentially from the N-alkyl rather than the N-acyl side-chain,[14,15] γ-hydrogen abstraction from the acyl side-chain occurs readily when a suitable hydrogen is not available on the N-alkyl side-chain[7,14,15,16,17] and particularly when there is a t-butyl substituent on nitrogen[14,15] or rigidity in the system.[18] This contrasts markedly with carbamyl radicals in which there is no competitive intramolecular hydrogen

abstraction from the O-alkyl side-chain despite its greater electrophilicity. Since intramolecular hydrogen abstraction from the N-alkyl side-chain competes favourably with addition to 3,3-dimethylbut-1-ene, β-hydrogen abstraction from the O-alkyl side-chain in carbamyl radicals must be very much slower than abstraction from the N-alkyl side-chain. Furthermore, although abstraction via an eight-membered cyclic transition structure is highly unfavourable,[19] benzylic hydrogen abstraction via seven and six-membered transition structures, which occur readily on the N-alkyl side-chain, are also disfavoured when abstraction is from the O-alkyl side-chain.

An MNDO calculation on ethylcarbamyl radical (1c) predicts a planar conformation with ethyl trans to the carbamyl oxygen and the odd electron in a $2p_z$ orbital on nitrogen (coefficient 0.898) in concurrence with e.s.r. data[6] (Figure 1a). π-bond orders for the N-C, C=O and C-OEt bonds were 0,43, 0,79 and 0,37 respectively.

As a consequence, impaired rotation about the O-CO bond should reduce the flexibility in the acyl side chain relative to amidyls and should facilitate β-hydrogen abstraction.[18] However, for hydrogen transfer reactions, optimum orbital overlap requires colinearity between the semi-occupied orbital and the relevant CH bond. While this is possible for abstraction from the N-alkyl side-chain in both amidyls[14,15] and carbamyls (Figure 1b), for β-hydrogen abstraction to occur from the O-alkyl side-chain, of carbamyls such colinearity would require complete loss of the π-overlap between oxygen and the carbonyl (Figure 1c).

This argument presupposes that the radical exists in a $2p_z$ orbital on nitrogen which is not twisted significantly about the N-CO bond. The results suggest that the E_A for hydrogen abstraction processes involving rotation of either O-alkyl substituent about the O-CO bond or the $N2p_z$ orbital about the N-CO bond are greater than E_A for intramolecular addition of olefins. Since there would be no significant stereoelectronic barrier to hydrogen abstraction by the Σ-state of carbamyl (Figure 1d) the reorganisation of electrons to this configuration must also require greater energy than the E_A for the intramolecular addition. These stereoelectronic requirements would to a lesser extent, impede hydrogen abstraction via a seven-membered transition structure which, in addition, would be disfavoured by the loss of one more rotational degree of freedom.

Hydrogen abstraction from the N-alkyl side-chain via a six-membered cyclic transition state, occurs readily in both (7b) and (7d). In both radicals there are no barriers to attaining maximum orbital overlap via a six-membered transition structure. However, since no hydrogen abstraction via a six-membered cyclic transition state occurs in carbamyl (7c), phenyl substitution at the site of abstraction is a major stabilising factor in the transition state for abstraction. Enthalpic factors predominate over entropic factors resulting in a seven-membered cyclic structure. Phenyl could stabilize developing radical character in a late transition state of an endothermic process or a developing positive charge due to polar separation in an early transition state of an exothermic process[19]. A polar effect in hydrogen abstraction reactions of amidyls has been reported[20] and since carbamyl radicals are probably more electrophilic than amidyls, as well as the facility with which hydrogen abstraction takes place, we favour an exothermic hydrogen abstraction with a polar transition state structure.

The stereoelectronic requirements for abstraction, namely co-linearity between the semi-occupied orbital and the C-H σ-bond cannot be accommodated in a five-membered transition structure and the enthalpic stabilisation by the 3-phenyl substituent in (7a) is unimportant.

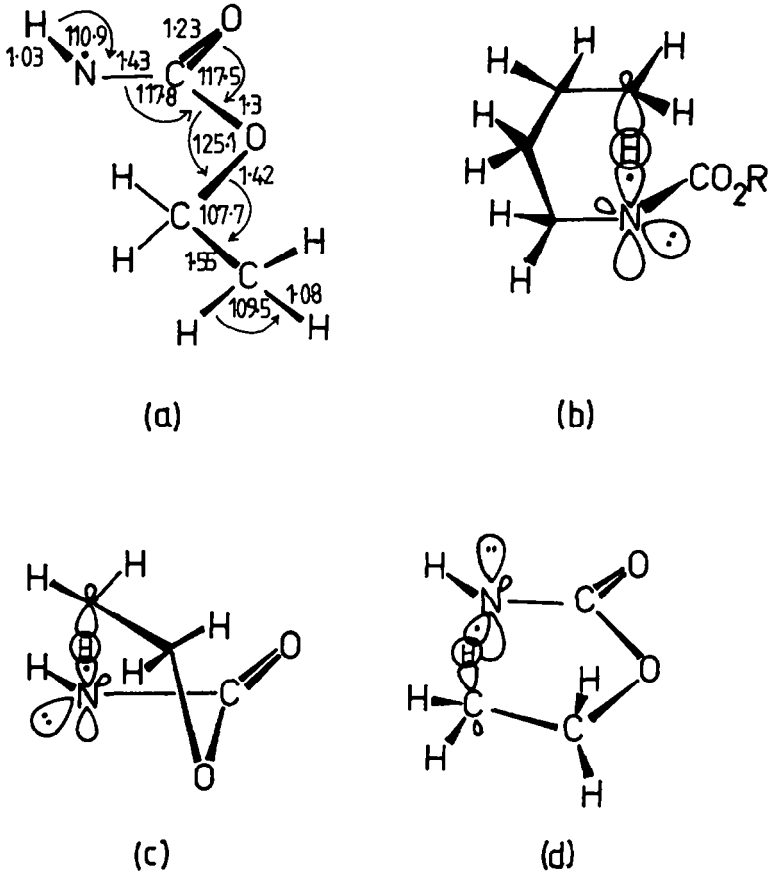


Figure 1. (a) MNDO optimised geometry for (1c); (b) stereoelectronic requirements for hydrogen abstraction from N-alkyl side-chain by π-state carbamyl radicals; (c) stereoelectronic requirements for hydrogen abstraction from the alkoxy side-chain by π-state carbamyl radicals; (d) stereoelectronic requirements for hydrogen abstraction from the alkoxy side-chain by Σ-state carbamyl radicals.

EXPERIMENTAL

M.p.'s. were determined on a Kofler hot stage and are uncorrected. I.r. spectra were recorded with a Perkin Elmer 297 spectrometer. ^{1}H n.m.r. spectra were recorded on a Perkin Elmer R12A n.m.r. spectrometer with tetramethylsilane as internal standard. MNDO calculations were carried out on a Burroughs 6800 computer by use of the QCPE version of MNDO by W Thiel[21].

The synthesis of[11] N-methylcarbamates (2a-c) and their N-bromo adducts (2d-f) have been described elsewhere[11].

Methyl N-(3-phenylpropyl)carbamate (6a)

Freshly distilled 4-phenylbutyroyl chloride (50 mmol) in acetone (37,5 ml) was added dropwise to a well stirred solution of sodium azide (154 mmol) in water (37,5 ml) maintained at 10-15°. After 1h, the organic layer was separated and dried over Na_2SO_4 to give 4-phenylbutyroyl azide; ν_{max} ($CHCl_3$) 2145 cm^{-1}. The azide in benzene was refluxed until evolution of nitrogen ceased. Concentration gave 3-phenylpropyl isocyanate; ν_{max} ($CHCl_3$) 2275 cm^{-1}. The isocyanate in excess methanol was refluxed for 12h. The mixture was concentrated under reduced pressure to give methyl N-(3-phenylpropyl) carbamate (6a) as an oil, b.p. 170-173°/2 mm; δ($CDCl_3$) 1,78 (2H,p), 2,65 (2H,t) 3,15 (2H, d of t), 3,65 (3H,s), 5,05 (1H, br), 7,20 (5H,s); ν_{max} ($CHCl_3$) 3460, 2950, 1720 and 1510 cm^{-1}. (Found: C, 68,0; H, 7,8; N, 7,3%. $C_{11}H_{15}NO_2$ requires: C, 68,4; H, 7,8 and N, 7,3%).

Methyl N-(4-phenylbutyl)carbamate (6b) was prepared similarly as an oil, b.p. 154-155°/1,5 mm; δ($CDCl_3$) 1,25-1,80 (4H,m), 2,6 (2H,t), 3,15 (2H, d of t), 3,60 (3H,s), 4,75 (1H,br), 7,2 (5H,s); ν_{max} ($CHCl_3$) 3460, 2950, 1720 and 1510 cm^{-1}. (Found: C, 69,6; H, 8,1; N, 6,6%. $C_{12}H_{17}NO_2$ requires: C, 69,5; H, 8,3; N, 6,8%).

Methyl N-(5-phenylpentyl)carbamate (6c)

A solution of 6-phenylhexamide (81 mmol) in methanol dioxane mixture was added dropwise to methylhypobromite prepared by the dropwise addition of bromine to sodium methoxide in methanol at -45°. The reaction mixture was warmed to 60° for 0,25h then cooled, acidified with acetic acid and concentrated under reduced pressure. The residue was added to water which was extracted with ether. Ethereal extracts were washed successively with water, saturated sodium chloride solutions and dried over Na_2SO_4. Concentration under reduced pressure gave methyl N-(5-phenylpentyl) carbamate (6c) (40 mmol) as an oil, b.p. 165-167°/7 mm; δ($CDCl_3$) 1,13-1,85 (6H,m), 2,60 (2H,t), 3,15 (2H, d of t) 3,68 (3H,s), 4,7 (1H,br), 7,21 (5H,s); ν_{max} ($CHCl_3$) 3475, 2950, 1720 and 1520 cm^{-1}. (Found: C, 70,4; H, 8,6; N, 6,3%. $C_{13}H_{19}NO_2$ requires: C, 70,6; H, 8,7; N, 6,3%).

Methyl N-pentylcarbamate (6d) was prepared similarly as an oil, b.p. 127-130°/9 mm; δ($CDCl_3$) 0,9 (3H,t), 1,1-1,7 (6H,m), 3,13 (2H, d of t), 3,63 (3H,s), 5,19 (1H,br); ν_{max} ($CHCl_3$) 3450, 2950, 1720 and 1510 cm^{-1}. (Found: C, 57,7; H, 10,3; N, 9,6%. $C_7H_{15}NO_2$ requires: C, 57,9; H, 10,4; N, 9,6%).

Carbamates (6a-d) were converted to their N-bromo forms (6e-h) with t-butylhypobromite by a previously reported method[11].

Methyl N-bromo-N-(3-phenylpropyl)carbamate (6e) was an oil; δ($CDCl_3$) 1,95 (2H,p), 2,60 (2H,t), 3,55 (2H,t), 3,65 (3H,s), 7,15 (5H,s); ν_{max} ($CHCl_3$) 1700 cm^{-1}. (Found: Br, 27,01%. $C_{11}H_{14}BrNO_2$ requires: Br, 29,41%).

Methyl N-bromo-N-(4-phenylbutyl)carbamate (6f) was an oil; δ($CDCl_3$) 1,40-1,80 (4H,m), 2,6 (2H,t), 3,55 (2H,t), 3,70 (3H,s), 7,18 (5H,s); ν_{max} ($CHCl_3$) 1700 cm^{-1}. (Found: Br, 26,52%. $C_{12}H_{16}BrNO_2$ requires Br, 27.97%).

Methyl N-bromo-N-(5-phenylpentyl)carbamate (6g) was an oil; δ($CDCl_3$) 1,3-2,0 (6H,m), 2,6 (2H,t), 3,55 (2H,t), 3,68 (3H,s), 7,15 (5H,s); ν_{max} ($CHCl_3$) 1700 cm^{-1}. (Found: Br, 25,29%. $C_{13}H_{18}BrNO_2$ requires: Br, 26,67%).

Methyl N-bromo-N-pentylcarbamate (6h) was an oil; δ($CDCl_3$) 0,9 (3H,t), 1,1-1,75 (6H,m), 3,58 (2H,t), 3,75 (3H,s); ν_{max} ($CHCl_3$) 1690 cm^{-1}. (Found: Br, 34,59%. $C_7H_{14}BrNO_2$ requires: Br, 35,71%).

Photolysis of N-bromocarbamates (no olefin present)

A solution of the N-bromocarbamate (0.2 mmol) in dry benzene (15 ml) was irradiated at room temperature with a medium pressure mercury lamp through pyrex (>300 nm) until aliquots no longer liberated IBr upon treatment with aqueous potassium iodide-acetic acid solution. The reaction mixture was concentrated and separated on silica gel by preparative h.p.l.c.. The relatively labile benzylic bromides 4a, 4b, 4c and 8a were characterised by i.r. and n.m.r. spectroscopy. Yields of the bromides were determined by analytical h.p.l.c. analysis of crude reaction mixtures.

2-Bromo-2-phenylethyl-N-methylcarbamate (4a) was formed in 98% yield and was isolated as an oil, ν_{max} ($CHCl_3$) 3475, 2950, 1720 and 1510 cm^{-1}; δ($CDCl_3$) 2,72 (3H,d,N-Me), 4,500 (2H,d,CH_2-O), 4.8 (1H,br,NH), 5,12 (1H,t,-CH(Br)Ph) and 7,39 (5H,s,ArH).

3-Bromo-3-phenylpropyl-N-methylcarbamate (4b) was formed in 97% yield and was isolated as an oil, ν_{max} ($CHCl_3$) 3475, 3000, 1725 cm^{-1}; δ($CDCl_3$) 2,22-2,55 (2H,m,CH_2), 2,68 (3H,d,N-Me), 4,10 (2H,t,CH_2-O), 5,0 (1H,t,CH(Br)Ph), 5,3 (1H,br,NH) and 7,28 (5H,s,ArH).

4-Bromo-4-phenylbutyl-N-methylcarbamate (4c) was formed in 94% yield and isolated as an oil, ν_{max} ($CHCl_3$) 3475, 2950 and 1720 cm^{-1}; δ($CDCl_3$) 1,4-1,95 (2H,m,-CH_2-), 2,0-2,5 (2H,m,-CH_2-), 2,69 (3H,d,N-Me), 4,05 (2H,t,-CH_2-O), 4,94 (1H,t,-CH(Br)Ph) and 5,3 (1H,br,NH) and 7,3 (5H,s,ArH).

Methyl N-(3-bromo-3-phenylpropyl)carbamate (8a) was formed in 85% yield and isolated as an oil, ν_{max} ($CHCl_3$) 3460, 2950 and 1720 cm^{-1}; δ($CDCl_3$) 2,4 (2H,t,CH_2-N), 3,2 (2H,q,-CH_2-) 3,62 (3H,s,OMe), 5,0 (1H,t,-CH(Br)Ph), 5,45 (1H,br,NH) and 7,3 (5H,s,ArH)

Methyl N-(4-bromo-4-phenylbutyl)carbamate (8b) formed in 98% yield was isolated as an oil, ν_{max} ($CHCl_3$) 3450, 3000, 2950 and 1720 cm^{-1}; δ($CDCl_3$) 1,2-1,8 (2H,m,-CH_2-), 1,95-2,4 (2H,m,-CH_2-), 3,14 (2H,t,-CH_2-N), 3,6 (3H,s,OMe), 4,95 (1H,t,-CH(Br)Ph), 5,75 (1H,br,NH) and 7,35 (5H,s,ArH). The oil rearranged quantitatively upon standing to N-carbomethoxy-2-phenylpyrrolidine (9a) which was purified by preparative plate chromatography and was an oil, ν_{max} ($CHCl_3$) 2950, 1685, 1450 and 1385 cm^{-1}; δ($CDCl_3$) 1,5-2,4 (4H,m,-CH_2's), 3,42-3,8 (2H,m,-CH_2-N), 4,70-5,1 (1H,m,-CH(Ph)N-), 7,18 (5H,s); $^m/_z$ 205 (M^+), 146, 128 and 69 (Found: C, 69,9, H, 7,4; N, 6,8%. $C_{12}H_{15}NO_2$ requires: C, 70,2; H, 7,4 and N, 6,8%).

Methyl N-(5-bromo-5-phenylpentyl)carbamate (8c) formed in 88% yield was isolated as an oil, ν_{max} ($CHCl_3$) 3460, 2950 and 1720 cm^{-1}; δ($CDCl_3$) 1,2-1,8 (6H,m,-CH_2's-), 3,08 (2H,CH_2-N), 3,6 (3H,s,OMe), 4,9 (1H,t,-CH(Br)Ph), 5,0 (1H,br,NH) and 7,3 (5H,s,ArH). The oil rearranged at room temperature upon standing or upon treatment with $AlClO_4$ in benzene to N-carbomethoxy-2-phenyl-piperidine which was purified by preparative plate chromatography and was an oil, ν_{max} ($CHCl_3$) 2950, 1680, 1450 and 1410 cm^{-1}; δ($CDCl_3$) 1,3-1,8 (4H,m,-CH_2's), 1,8-3,10 (4H,m,CH_2's),

3,72 (3H,s,OMe), 5,38-5,65 (1H,m,-CH(Ph)N-) and 7,3 (5H,s,ArH); $^{m}/z$ 219 (M^{+}), 160, 142 (Found: C,70,8; H, 7,7; N, 6,2%. $C_{13}H_{17}NO_2$ requires: C, 71,2; H, 7,8 and N, 6,4%).

Photolysis of N-bromocarbamates in the presence of 3,3-dimethylbut-1-ene

The photolysis of N-bromocarbamates (1,75 mmol) in benzene (15 ml) were repeated in the presence of a 10 molar excess of 3,3-dimethylbut-1-ene. Aliquots of the reaction mixture were analysed for benzylic bromination products by h.p.l.c. prior to work-up.

2-Phenylethyl N-bromo-N-methylcarbamate (2d) gave after 0,5h a mixture which contained 2-bromo-2-phenylethyl N-methylcarbamate (4a, 6%). Concentration afforded an oil which was separated on silica gel plates into (4a), 2-phenylethyl N-methylcarbamate (2a, 26%) and 2-phenylethyl N-(2-bromo-3,3-dimethylbutyl)-N-methylcarbamate (5a, 44%), ν_{max} ($CHCl_3$) 2950 and 1690 cm^{-1}; $^{m}/z$ 192, 148 and 105. The structure of (5a) has been confirmed by 500 MHz n.m.r. spectroscopy[11].

3-Phenylpropyl N-bromo-N-methylcarbamate (2c) gave after 0,5h, a mixture which contained 3-bromo-3-phenylpropyl N-methylcarbamate (4b, 9%). Concentration afforded an oil which was separated by plate chromatography into (4b), 3-phenylpropyl N-methylcarbamate (2b, 33%) and 3-phenylpropyl N-(2-bromo-3,3-dimethylbutyl) N-methylcarbamate (5b, 28%), ν_{max} ($CHCl_3$) 2950, 1695 cm^{-1}; $^{m}/z$ 357 (M^{+}), 206, 118 and 91. The structure of (5b) was confirmed by 500 MHz n.m.r. spectroscopy[11].

4-Phenylbutyl N-bromo-N-methylcarbamate (2f) gave after 0,5h a mixture which contained 4-bromo-4-phenylbutyl N-methylcarbamate (4c, 10%). Concentration afforded an oil which was separated by preparative plate chromatography into (4c), 4-phenylbutyl N-methylcarbamate (2c, 37%) and 4-phenylbutyl N-(2-bromo-3,3-dimethylbutyl)-N-methylcarbamate (5c, 34%), ν_{max} ($CHCl_3$) 2950, 1690 cm^{-1}; $^{m}/z$ 369, 220, 133 and 91. The structure of (5c) was confirmed by 500 MHz n.m.r. spectroscopy[11].

Methyl N-bromo-N-(3-phenylpropyl)carbamate (6e) gave after 0,5h a mixture which contained methyl N-(3-bromo-3-phenylpropyl)carbamate (8a, 9%). Concentration gave an oil which was chromatographed on silica gel plates to afford (8a) and methyl N-(3-phenylpropyl)carbamate (6a, 76%).

Methyl N-bromo-N-(4-phenylbutyl)carbamate (6f) gave after 0,5h an oil which was shown by analytical h.p.l.c. and n.m.r. to contain methyl N-(4-bromo-4-phenylbutyl)carbamate (8b, 93%). The oil decomposed rapidly to give N-carbomethoxy-2-phenylpyrrolidine (9a) which was identical to authentic material.

Methyl N-bromo-N-(5-phenylpentyl)carbamate (6g) gave after 0,5h an oil which, from n.m.r. analysis, contained a mixture of methyl N-(5-phenylpentyl)carbamate (6c) and methyl N-(5-bromo-5-phenylpentyl)carbamate (8c). The mixture was treated with $AgClO_4$ in benzene in the dark at room temperature. Work-up afforded an oil which consisted of carbamate (6c, 39%) and N-carbomethoxy-2-phenylpiperidine (10, 61%).

Methyl N-bromo-N-pentylcarbamate (6b) (1,5 g, 6,7 mmol) and 3,3-dimethylbut-1-ene (5,63 g, 67 mmol) in dry benzene (25 ml) were irradiated for 0,5h. Concentration afforded an oil which contained only methyl N-4-bromopentylcarbamate (8d) which was purified on silica gel plates as an oil, ν_{max} ($CHCl_3$) 3450, 2950, 1720 and 1510 cm^{-1}; $\delta(CDCl_3)$ 1,7 (3H,d,-CH-CH$_3$), 1,8-2,15 (4H,m), 3,15 (2H, d of t, CH$_2$-NH), 3,6 (3H,s,OMe), 3,9-4,48 (1H,m,-CH(Br)CH$_3$) and 5,28 (1H,br,NH), (Found: C, 38,0; H, 6,3; N, 6,2%. $C_7H_{14}NO_2$ requires: C,37,5; H, 6,3; N, 6,3%). The oil cyclised upon neat pyrolysis (140-150°) to N-carbomethoxy-2-methylpyrrolidine (9b) which was

an oil, ν_{max} ($CHCl_3$) 2950, 1680, 1460 and 1390 cm^{-1}; δ($CDCl_3$) 1,18 (3H,d,$\underline{CH_3}$-CH), 1,42-2,08 (4H,m), 2,98-3,55 (3H,m,N-$\underline{CH}$ and N-$\underline{CH_2}$) and 3,68 (3H,s).

Acknowledgements

The authors are grateful to the South African CSIR and MINTEK (PFD) for financial support.

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