Direct and Bromine-atom Initiated Photodecompositions of *N*-acetyl-*N*-bromohexanamide

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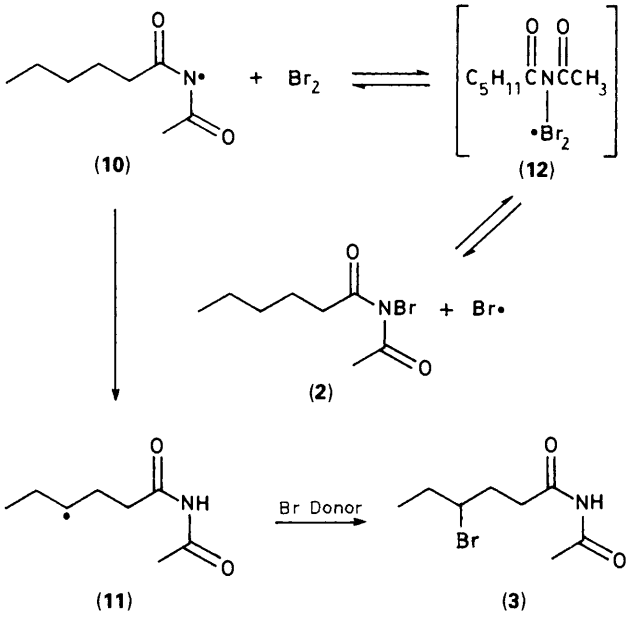
Photolysis of *N*-acetyl-*N*-bromohexanamide in the presence of an alkene (which scavenges bromine) gives high yields of *N*-acetyl-4-bromohexanamide (C_4-bromide) through efficient intramolecular H-atom transfer in the corresponding imidyl radical. Bromine, in a mixture with the *N*-bromoimide was irradiated selectively to generate bromine atoms that interact with the *N*-bromoimide to give the imidyl radical and the C_4-bromide. For such a mixture, irradiation of both *N*-bromoimide and bromine generates both bromine atoms and the imidyl radical and gives a product distribution similar to that obtained by a bromine-atom initiated reaction. These observations are best explained in terms of an equilibrium involving a bromine atom, an imidyl radical, and a bromine–radical complex. Possible reactions of such a radical complex are discussed.

While *N*-bromosuccinimide (NBS) has been extensively used to generate the succinimidyl radical (S$^\cdot$) by thermolysis and photolysis,[1] the utilization of acyclic *N*-halo imides to generate open-chain imidyl radicals has rarely been studied except for one reported case some 25 years ago.[2] In recent years, the photodecomposition of NBS and other cyclic *N*-bromo imides has attracted intensive investigation[3–12] undoubtedly owing to questions concerning the structure and reactivities of amine centred radicals,[13–19] imidyl radicals. During this period, the presence of two varieties of the succinimidyl radical with Σ and Π configurations was proposed;[3–7] the proposal was later shown to be erroneous[10–12] and was withdrawn.[8] Irrespective of this episode, there exists a long-standing question about the type of reactive intermediate involved in the photolysis of a mixture of NBS (or an *N*-bromo imide, in general) and bromine.[8,10,12,20,21]

Using a selective-excitation technique, we have shown that NBS could be photoexcited to give the succinimidyl radical which undergoes ring-opening efficiently even from its precursor state,[20,21] and that the photolysis of a mixture of the *N*-bromo imide and bromine generates an equilibrium system of the imidyl radical,[20–23] a bromine atom, and an intermediary radical complex as shown in Scheme 1. It should be noted that the succinimidyl radical undergoes a unimolecular ring-opening reaction which serves nicely as a guide for the elucidation the equilibrium.[20–23] In this report, we wish to exploit the specific intramolecular hydrogen–bromine exchange *via* an imidyl radical intermediate as a reference reaction (*i.e.*, a radical clock)[24] in the photodecomposition of *N*-bromo-*N*-acetylhexanamide (2) and to show the presence of such an equilibrium and the bromine radical complex for the corresponding reaction. Such atom-exchange reactions have been demonstrated many times in the photolysis of *N*-halo- and *N*-nitrosoamides[14,17] and at least once in that of *N*-chloro imides;[2] they appear to occur from their amidyl or imidyl radical *via* specific intramolecular H-atom transfer from the C–H bond at the fifth position to the nitrogen radical centre.[14]



Scheme 1.

Results

N-Bromoimide (2) was prepared from the corresponding imide (1) and at [(2)] = 0.04 mol dm^{-3} it showed u.v. absorptions of $A = 1$ at 320 nm which attenuated rapidly to weak absorptions in the range of 340–380 nm. The photolysis of (2) in methylene chloride or benzene in the presence of an alkene gave excellent yields of *N*-acetyl-4-bromohexanamide (3) and small percentages of imide (1) and an unidentified compound (X) (Table 1). Other *C*-brominated compounds were barely detected, and the addition products to an alkene (*e.g.*, 3,3-dimethylbut-1-ene) and to benzene were not detected. In the absence of an alkene, the yield of (3) (Table 1, experiment 3) decreased significantly owing to the lack of scavenging of bromine and bromine atoms.[20] The C_4-bromide (3) was easily isolated by chromatography and its structure was determined from its spectroscopic data (see below).

A mixture of the *N*-bromo imide (2) and bromine was irradiated with a light source >400 nm to generate Br$^\cdot$ from bromine without the excitation of (2). In two series of experiments (experiments 5–10), as the concentrations of bromine increased in the range 0.002–0.2 mol dm^{-3} region, the percentage yields of the C_4-bromide (3) remained remarkably high but decreased with concurrent increases in those of the C_2-bromide (4), C_5-bromide (5), *N*-bromoacetylhexanamide (6) and the parent imide (1). A similar bromine-atom initiated

Table 1. Direct and indirect photodecomposition of *N*-bromo imide 2[a] at 0 °C.

Experiment	Additive/ mmol dm^{-3}	Product (%) (3)	(1)	(4)	(5)	(6)	(X)	Δ5
1	DMB (100)[b,e]	83	8.5	—[c]	—[c]	0	6.5	—
2	DCE (100)[d,e]	82	8.8	—[c]	—[c]	0	6.4	—
3	—[e]	68	16	1.1	4.0	—[c]	2.0	3.6
4	Br_2 (20)[e]	55	19	7.0	8.2	0.8	2.1	5.9
5	Br_2 (2)[f]	65	17	2.1	6.3	—[c]	2.7	5.6
6	Br_2 (20)[f]	52	20	7.3	9.0	0.7	3.4	6.6
7	Br_2 (200)[f]	27	34	17	11	1.6	3.9	5.3
8	Br_2 (2)[g]	55	27	1	6.2	—[c]	1.6	5.9
9	Br_2 (20)[g]	51	28	4.7	7.2	0.6	1.7	5.6
10	Br_2 (200)[g]	26	45	12	7.8	1.5	1.8	3.8
11	Br_2 (20)[h]	53	26	5.9	7.9	0.7	2.1	5.9

[a] General conditions: unless specified otherwise a solution of (**2**) (0.04 mol dm^{-3}) and an additive in CCl_4 (except experiments 1 and 2) was irradiated through a Pyrex filter (experiments 1–4) or a filter solution (cut-off ≥400 nm) (experiments 5–11) at 0 °C. [b] The reaction was run in CH_2Cl_2 in the presence of 3,3-dimethylbut-1-ene (DMB). [c] Detected by g.c. but could not be integrated owing to their low yields. [d] The reaction was run in benzene in the presence of 1,2-dichloroethane (DCE). [e] These four reactions used a Pyrex filter but other reactions used a filter solution (>400 nm). [f] The conversion of (**2**) was ≤85%. [g] [(**2**)] = 0.12 mol dm^{-3}. The conversion of (**2**) was ≤85%. [h] The conversion of (**2**) was 80% at temperature = −20 ± 2 °C.

Table 2. Photobrominations[a] of imide (**1**) at 0 °C.

Reagents [Br_2]/ mol dm^{-3}	Others	*h*ν/ min	Conversion of (**1**)(%)	Products (relative yield) (3)	(4)	(5)	(6)
10	K_2CO_3[b]	160	5	0.0	2.9	1.0	0.0
2	NBS[c]	75	10	0.5	3.0	1.0	0.3
20	NBS[c]	40	8	0.4	3.1	1.0	0.2
200	NBS[c]	35	6	0.4	3.1	1.0	0.3
20	NBS[d]	32	22	0.5	2.7	1.0	0.3
200	NBS[d]	30	20	0.5	2.8	1.0	0.2

[a] For the general conditions see the Experimental; the concentration of (**1**) was 0.04 mol dm^{-3} except in the first experiment in which [(**1**)] = 0.02 mol dm^{-3} was used. [b] A heterogeneous mixture of Br_2 and K_2CO_3 (molar ratio <1:5) in CCl_4 was vigorously stirred. [c] A heterogeneous mixture of Br_2 and NBS (0.08 mol dm^{-3}) in CCl_4 was vigorously stirred. [d] A solution of (**1**) and NBS (0.11 mol dm^{-3}) in CH_2Cl_2 was photolysed.

Table 3. ^{1}H N.m.r. parameters of *C*-bromides in $CDCl_3$.

Compound	Chemical shift (ppm)	Coupling constant/Hz
(**3**)	1.07 (3 H, t, H_6), 1.89 (2 H, m, H_5), 2.07 (1 H, m, $H_{3'}$), 2.23 (1 H, m, H_3), 2.35 (3 H, s), 2.78 (2 H, m, H_2), 4.03 (1 H, m, H_4), 7.88 (br s, NH)	$J_{5.6}$ 7.5, $J_{4.5}$ 5.0, $J_{2.3'} \simeq 8$, $J_{4.3'} \simeq 6$, $J_{3.3'}$ 14.0, $J_{2.3}$ 7.0, $J_{3.4}$ 3.5, $J_{4.x}$ 1.6
(**4**)	0.915 (3 H, t, H_6), 1.38 (4 H, m, H_4 and H_5), 2.0 (1 H, m, H_3), 2.1 (1 H, m, H_3), 2.45 (3 H, s), 4.43 (1 H, t, H_2), 8.57 (br s, NH)	$J_{5.6}$ 7.5, $J_{2.3}$ 5.0, $J_{2.3}$ 5.0, $J_{3.x}$ 4.0, $J_{3'y}$ 7.5, $J_{3.z}$ 6.0
(**5**)	1.76 (3 H, d, H_6), 1.86 (4 H, m, H_3 and H_4), 2.38 (3 H, s), 2.60 (2 H, t, H_2), 4.01 (1 H, m, H_5), 8.23 (br s, NH).	$J_{5.6}$ 6.7, $J_{3.2}$ 6.5, $J_{5.4}$ 6.0
(**6**)	0.92 (3 H, t, H_6), 1.35 (4 H, m, H_5 and H_4), 1.67 (2 H, m, H_3), 2.59 (2 H, t, H_2), 4.18 (2 H, s), 8.38 (br s, NH).	$J_{5.6}$ 6.5, $J_{2.3}$ 7.1
(**8**)	0.92 (3 H, t, H_6), 1.36 (4 H, m, H_4 and H_5), 2.07 (1 H, m, H_3 or $H_{3'}$), 2.16 (1 H, m, $H_{3'}$ or H_3), 2.43 (3 H, s), 3.28 (3 H, s, NCH_3), 5.10 (1 H, dd, H_2)	$J_{5.6}$ 6.0, $J_{2.3}$ 5.0, $J_{2.3'}$ 5.5
(**9**)	1.73 (3 H, d, H_6), 1.77 (4 H, m, H_3 and H_4), 2.42 (3 H, s), 2.75 (2 H, t, H_2), 3.22 (3 H, s, NCH_3), 4.15 (1 H, m, H_5)	$J_{5.6}$ 6.5, $J_{2.3}$ 6.0, $J_{5.4}$ 6.0

Table 4. ^{13}C N.m.r. chemical shifts in $CDCl_3$.

Compound	Chemical shifts (ppm)
(**3**)	172.59, 171.24, 58.71, 34.42, 32.95, 32.41, 25.01, 12.01
(**6**)	173.38, 166.37, 37.25, 31.15, 29.36, 23.90, 22.30, 13.79
(**8**)	173.35, 172.49, 47.61, 34.32, 32.08, 29.55, 26.11, 22.13, 13.78
(**9**)	175.53, 173.23, 50.82, 40.41, 37.32, 31.57, 26.53, 26.35, 22.97

Table 5. FTIR parameters in CH_2Cl_2.

Compounds	ν/cm^{-1} (relative intensity)
(**3**)	3 423(w), 2 980(w), 2 945(w), 1 736(s), 1 684(w), 1 458(m), 1 379(w), 1 253(m), 1 202(m), 1 024(w), 972(w), 667(w), 627(w)
(**6**)[a]	3 230(m), 3 180(m), 1 735(s), 1 510(m), 1 170(m)
(**8**)	2 968(m), 2 880(w), 1 763(w), 1 720(s), 1 690(m), 1 448(w), 1 375(m), 1 306(m), 1 261(m), 1 138(w), 1 057(w)
(**9**)	2 945(w), 1 722(s), 1 373(m), 1 303(m), 1 261(m), 1 140(w), 1 082(17)

[a] A regular i.r. spectrum recorded from Nujol mull.

decomposition of *N*-bromo imide (**2**) was also carried out at a low temperature (−20 °C, experiment 11) and gave virtually the same product distribution as compared with that of experiment 9. However, the photolysis of a mixture of the *N*-bromo imide (**2**) and bromine (2 × 10^{-2} mol dm^{-3}) through a Pyrex filter (experiment 4) caused the photoexcitation of both (**2**) and Br_2 and generated the imidyl radical and bromine atoms; the fact that it gave a product distribution similar to that for the corresponding experiment using >400 nm photolysis (see experiment 6) is noteworthy. These photodecompositions were relatively fast and proceeded to 80–90% completion in less than 10–15 min, suggesting a radical-chain reaction. The unidentified compound (**X**) was also formed in these experiments and appeared to be derived from the C_4-bromide (**3**) since the percentage yields of these two products varied in approximate proportion.

The imide (**1**) was photolytically brominated with Br_2 in the presence of K_2CO_3 or with a mixture of NBS and bromine to give *C*-brominated products (**3**), (**4**), (**5**), and (**6**) in the relative yields shown in Table 2 as determined by g.c. analysis. The former method has been shown to involve bromine atoms as the propagating radical and K_2CO_3 serves as a HBr scavenger. The latter method brominates faster than the former and has been shown to involve the corresponding bromine radical complex and bromine atoms as the propagating species.[22,23] In these

Table 6. Mass spectroscopic data.

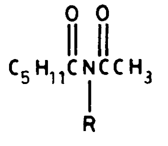
Compound	*m*/*z* (% rel. intensity)
(**3**)	(EI) 156(22), 140(25), 114(87), 101(100), 84(21), 69(43), 55(28), 43(62) (CI) 238(24), 236(25), 156(100)
(**4**)	(EI) 181(20), 179(18), 114(18), 100(20), 55(24), 43(100) (CI) 238(28), 236(30), 158(55), 165(100)
(**5**)	(EI) 156(27), 114(100), 97(40), 60(57), 59(56), 55(30), 43(90) (CI) 238(41), 236(41), 156(100)
(**6**)	(EI) 237(5), 235(4), 208(66), 206(68), 194(20), 193 (18), 181(33), 179(31), 156(55), 140(32), 138(35), 100(100), 99(80), 72(30), 55(18)
(**8**)	(EI) 170(82), 128(100), 97(47), 86(20), 74(87), 56(23), 43(21)
(**9**)	(EI) 170(70), 128(12), 114(13), 97(17), 69(22), 55(36), 43(100)

Table 7. Elemental analysis.

Calcd. for $C_8H_{14}NBr$	C: 40.68	H, 5.93	N: 5.93
(**3**) Found	C: 40.89	H: 6.20	N: 5.70
(**4**) Found	C: 40.86	H: 6.23	N: 5.69
(**5**) Found	C: 40.78	H: 6.21	N: 5.65
(**6**)Found	C: 40.87	H: 6.12	N: 5.81
Calcd. for $C_9H_{16}NBr$	C: 43.20	H: 6.40	N: 5.60
(**8**) Found	C: 43.41	H: 6.69	N: 5.32
(**9**) Found	C: 43.38	H: 6.65	N: 5.33

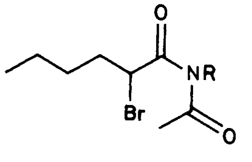
photobrominations, the C_2-bromide (**4**) and C_5-bromide (**5**) were the major products (Table 2), and their ratios deviated very little from 3:1 regardless of the methods of photobromination. The C_5-bromide (**5**) was isolated from one of these photolysates through extensive chromatography. Authentic samples of C_2-bromides (**4**) and (**6**) were prepared from α-bromoacetyl bromide and α-bromohexanoyl chloride as the starting materials according to routine reactions (see the Experimental section). The structures of these products were determined from their spectroscopic data as shown in Tables 3–7; in particular, ^1H n.m.r. spectra and their decoupling experiments enabled us to decide the position of the bromine atom in each *C*-bromide. The C_5-bromide (**5**) showed the proton of the CHBr group coupled to the terminal methyl group of the hexanoyl moiety. Both (**4**) and (**6**) exhibited the protons of the CHBr and CH_2Br groups as a triplet and singlet respectively with chemical shifts in agreement with the structures. In C_4-bromide (**3**), both the CH_3 (triplet) and CHBr groups were shown to be coupled to two diastereotopic protons at the C_5-position (1.8–1.9 ppm).

As comparative experiments, *N*-acetyl-*N*-methylhexanamide (**7**) was photobrominated with Br_2–K_2CO_3, Br_2–NBS, and a mixture of *N*-acetyl-*N*-bromoacetamide and Br_2 under similar conditions to those described in the footnotes to Table 2. The major products were *N*-acetyl-*N*-methyl-2-bromohexanamide (**8**) and *N*-acetyl-*N*-methyl-5-bromohexanamide (**9**) in the ratios of 2.5–3.5 to 1. Compound (**8**) has been shown to give two g.c. peaks; one of them is due to (**8**) itself, and the other (which has a shorter retention time) is due to a derivative arising from the elimination of HBr from (**8**) as shown by the M^+ peak in g.c.–m.s. analysis. The percentage yields of (**8**) were calculated from the sum of these two peaks. The C_2-bromide (**4**) also shows slight dehydrobromination under the g.c. conditions to give the corresponding g.c. peak; the extent was, however, insignificant.

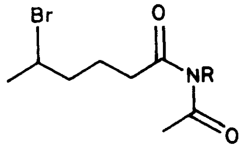


$$\mathrm{C_5H_{11}\overset{\overset{O}{\|}}{C}\underset{\underset{R}{|}}{N}\overset{\overset{O}{\|}}{C}CH_3}$$

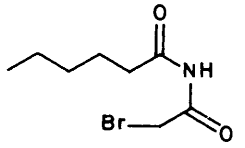
(**1**) (R = H); (**7**)(R = CH_3)



(**4**)(R = H);(**8**)(R = CH_3)



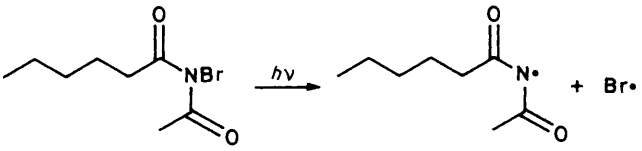
(**5**)(R = H);(**9**)(R = CH_3)



(**6**)

Discussion

The near exclusive formation of C_4-bromide (**3**) in the photolysis of *N*-bromo imide (**2**) is an excellent demonstration of the generation of the imidyl radical and the well known specific functionalization of the fifth position from a nitrogen radical centre through intramolecular H-atom transfer in imidyl radicals, *i.e.* (**10**)→(**11**)→(**3**) in Scheme 1. By analogy with the similar intramolecular functionalization of *N*-bromoamides and *N*-nitrosoamides,[14] the 1,5-H-atom transfer for the imidyl radical (**10**) is so efficient that the reaction products that may be formed from the addition of (**10**) to benzene or an alkene[21,25] are not obtained. It should be recalled that the unimolecular ring-opening reaction of the succinimidyl radical is not as fast and can be quenched by benzene or 3,3-dimethylbut-1-ene.[20,21,25] The bromine-transfer step (**11**)→(**3**) is also known to occur at almost a diffusion-controlled rate if the donor is bromine or a *N*-bromo imide.[26] The photolysis of (**2**) must involve a chain process, judging from the much faster and cleaner reaction than that of the *N*-chloro imides reported previously.[2] This type of intramolecular functionalization has many analogous examples in alkoxy radical chemistry.[24] Though a bromine atom is also generated from the photolysis of (**2**) as in Scheme 2, it probably enters into reaction pathways (*e.g.*, Scheme 1)[20] other than intermolecular H-atom abstractions.



(**2**) (**10**)

Scheme 2.

In the bromine-atom-initiated decompositions of *N*-bromoimide (**2**) in experiments 5–10, the persistent formation of high percentages of C_4-bromide (**3**) implies that a high concentration of the imidyl radical (**10**) is generated during photolysis of bromine although *N*-bromo imide is not photoexcited. This clearly shows that a bromine atom reacts with (**2**) to give the imidyl radical (**10**) as proposed in Scheme 1 and that the reverse reaction of imidyl radical (**10**) with bromine, also occurs to establish an equilibrium. The latter assertion is supported by two observations: first, the percentage of C_4-bromide (**3**) derived solely from imidyl radical (**10**) decreases and those of other *C*-bromides (**4**)–(**6**) and imide (**1**) increase as the concentration of bromine is increased as shown by the two series experiments 5–10; a high bromine concentration undoubtedly shifts the equilibrium to the right. Second, in experiments 3 and 4 imidyl radical (**10**) generated in the photolysis of (2) is rapidly and competitively scavenged by bromine to give yields of C_4-bromide (3) much lower than those obtained in the absence of bromine (see experiments 1 and 2). It is significant that the product distribution of experiment 4 is very similar to that of the $Br^{\cdot}$-initiated reaction of experiment 6. This indicates that the equilibrium of Scheme 1 is rapidly established regardless of whether it is approached from the imidyl radical or the bromine atom.

In the photolysis of a mixture of an *N*-bromo imide and bromine a similar equilibrium between the corresponding imidyl radical and a bromine atom has been proposed[20–23] and supporting evidence for such an equilibrium has been described. In these equilibria, a bromine radical complex, such as (12), is shown to be a distinctive intermediate which can behave as an independent reactive species in intramolecular[23] and intermolecular[22] reactions. The bromine radical complex derived from the photolysis of an NBS and Br_2 system has been shown to exhibit an intermolecular H-abstraction reactivity very similar to that of a bromine atom at room temperature.[20,22] This conclusion is again confirmed here in the intermolecular photobromination of imide (1) with Br_2–K_2CO_3 and NBS–Br_2 to give approximately the same 3:1 ratio of C_2-bromide (4) to C_5-bromide (5), although the rates of bromination for the two systems are quite different. The C–H bond reactivities of imide (1) toward intermolecular H abstraction are such that C_2-H and C_5-H are more reactive than others; their reactivity ratio of *ca* 3:1 is probably common to the imide analogues of (1) as supported by the similar reactivity in the intermolecular photobromination of (7) by the three types of reagents mentioned above. The preferential intermolecular H abstraction by radicals from the C_2-position probably arises from the effect of the carbonyl group and that from the C_5-position most likely arises from the ω-1 effects in intermolecular H abstraction.[28]

Assuming that in the photolysis of a mixture of *N*-bromo imide (2) and bromine in experiments 3–11, intermolecular H abstraction by a bromine atom or (12) from the hexanoyl chain also afford the same 3:1 ratio for (4) to (5), the results in Table 1 clearly show that the extra amounts of C_5-bromide, (Δ5), are produced and can be defined as

$$\Delta(5) = [\%\,(5)] - 1/3[\%\,(4)]$$

in those experiments. This assumption is reasonable in view of the various comparative photobrominations carried out with either imides (1) or (7) under various conditions as shown above. We propose that the extra C_5-bromide Δ(5) is formed from an intramolecular bromine–hydrogen exchange reaction of bromine radical complex (12). An analogous complex has been suggested to explain anomalous results obtained in the photobromination with an NBS–Br_2 mixture.[12] The mechanism of bromination by such complexes as the chain carrier might resemble those described in a regioselective intramolecular chlorination[29] with $ArICl^{\cdot}$ and in a selective chlorination directed by chlorine atom complexed with a pyridine ring.[30] While the structure of (12) and the detailed mechanism of its intramolecular bromination process are intimately interrelated, they can not be defined clearly until more relevant data are available. In this respect, laser flash photolysis at nanosecond domain is deemed to be a suitable tool for the detection of the intermediate (12) and to monitor its decay kinetics.

These discussions lead us to note that the percentage yields of C_4-bromide (3) are overwhelmingly higher than those of extra C_5-bromide Δ(5) even in the presence of $[Br_2]$ as high as 0.2 mol dm^{-3}. Indeed the significance of the yields of (3) in these experiment becomes apparent when these figures are compared with the low percentage yields (< 10%) of the ring-opening products BPI from the decomposition of NBS under a set of similar conditions.[20] These observations indicate that the imidyl radical (10) is very efficiently generated from the reaction of a bromine atom with *N*-bromo imide (2), and suggest that the lifetime of (12) is relatively short so that C_5-bromide Δ(5) is not formed in significant amounts. The instability of (12) is readily rationalized by the fact that (12) is subject to steric crowding because of the unconstrained acyl chains that can force out Br_2 easily to give the imidyl radical (10). It is obvious that the stability of (12) does not change significantly in the region of the room temperature to −20 °C as shown by the similar percentage yields of Δ(5) in experiments 9 and 11.

The discussion presented here assumes that the photolysis of *N*-bromoimide (2) and/or bromine in their mixtures leads directly to homolytic dissociation promptly on photoexcitation; that is, their excited states are pre-dissociative states and do not have lifetimes long enough to sensitize the other component. A similar discussion has been presented in the photodecomposition[20] of NBS in the presence of bromine. We have studied the photolysis of various *N*-bromo imides in mixtures with bromine;[20–23] the results of all these cases are in agreement with the existence of the equilibrium between imidyl radicals, bromine atoms, and the bromine radical complexes, regardless of cyclic or acyclic *N*-bromo imides or of type of imidyl radical reactions.

Experimental

General Conditions.—The instruments and their operating conditions, and the purification of solvents and common reagents were the same as those reported in our previous papers.[20,21,23] The treatment of photolysate for product analysis by n.m.r. and g.c. were discussed in detail in the previous paper[20,21] and are briefly reported here.

Preparations of Imide (1) *and* (7).—A solution of hexanoyl chloride (22.4 cm^3, 0.138 mmol), acetamide (10.2 g, 0.155 mmol) and pyridine (16 cm^3, 0.20 mol) in dichloromethane (400 cm^3) was stirred at room temperature for 48 h. A white precipitate of pyridine hydrochloride was separated off by filtration. After the solvent was removed from the filtrate under reduced pressure, the residue was treated with acetone (100 cm^3) and a saturated aqueous $NaHCO_3$ solution (100 cm^3). Acetone was removed under reduced pressure. The aqueous solution was extracted with dichloromethane (5 × 10 cm^3). The combined extracts were washed with water (100 cm^3) and dried over anhydrous magnesium sulphate. Removal of the solvent under reduced pressure left a yellow solid (11.4 g). The crude product (7 g) was flash chromatographed using 30% ethyl acetate–hexane as the eluant to afford imide (1) (2.45 g) as white crystals: m.p. 64—65 °C (lit.,[31] m.p. 66 °C); $\delta_H(CDCl_3)$ 0.90 (3 H, t, *J* 6.7 Hz), 1.35 (4 H, m), 1.66 (2 H, m), 2.37 (3 H, s), 2.52 (2 H, t, *J* 9.3 Hz), 9.07 (1 H, br s, NH); $\delta_C(CDCl_3)$ 13.78, 22.30, 24.08, 24.98, 31.19, 37.27, 172.39, and 174.05; i.r.(Nujol) 3 260m, 3 170m, 1 736vs, 1 456s, 1 379m, 1 256s, 1 205m, and 1 165m cm^{-1}; *m/z* 114(22), 101(68), 73(25), 59(40), and 43(100); (CI), 158 (M^+ + 1, 100).

N-methylacetamide (5.9 g, 81 mmol), hexanoyl chloride (6.0 cm^3, 37 mmol) and pyridine (10 cm^3, 125 mmol) in dichloromethane (100 cm^3) was stirred for 25 h at room temperature. The brown solution was worked up in a similar manner to that described above to afford a yellow oil (6 g). Chromatography of part of the crude product (elution with 20% ethyl acetate–light petroleum) afforded imide (7) as a yellowish oil: $\delta_H(CDCl_3)$ 0.91 (3 H, t, *J* 7.0 Hz), 1.18—1.20 (4 H, m), 1.66 (2 H, m), 2.43 (3 H, s), 2.66 (2 H, t, *J* 7.5 Hz), 3.21 (3 H, s); δ_C 13.85, 22.43, 24.38, 26.68, 31.34, 31.47, 37.86, 173.34, 176.20; i.r. (CH_2Cl_2) 1 695s, 1 460w, 1 415w, 1 370s, 1 305m, 1 270m, 1 140m, and 980m cm^{-1}; *m/z* 171 (M^+, 2), 156 (M^+ − CH_3, 10), 128(35), 115(100), 99(40), 86(30), 73(70), 58(20), and 43(65)

(Found: C, 63.30; H, 10.16; N, 7.93. Calc. for $C_9H_{17}NO_2$: C, 63.16; H, 9.94; N, 7.93%).

Preparation of C-*Bromides* (**4**) *and* (**6**).—Hexanoyl chloride (2.86 g, 21.3 mmol) and bromine (1.0 cm^3, 20 mmol) were heated to 80 °C gradually with stirring. After evolution of hydrogen bromide ceased (*ca.* 1 h), the mixture was heated for an additional 2 h. To the yellowish liquid was added acetamide (1.24 g, 21 mmol). The solution was heated to 90 °C for 5 h with stirring. The oily residue was washed with acetone–water (100 cm^3 v/v 1:1) solution of $NaHCO_3$. The extraction and usual work-up afforded a syrup (730 mg). Recrystallization from acetone gave crystalline C_2-bromide (**4**) (300 mg); m.p. 103—105 °C. The injection of (**4**) in g.c. analysis always gave a peak at 3.09 min and, also, a small peak at 2.59 min which was shown by g.c.–m.s. to arise from the dehydrobromination of (**4**); this peak was too small to be integrated.

A solution of α-bromoacetyl bromide (0.46 cm^3, 5.2 mmol), hexanamide (0.566 g, 4.35 mmol), and pyridine (0.4 cm^3, 5 mmol) in CCl_4 (100 cm^3) was refluxed for 2 h. The residue was dissolved in acetone–water (100 cm^3 v/v 3:1) solution of $NaHCO_3$ (0.3 g). The solution was concentrated on a hot water bath under reduced pressure. The residue was extracted with dichloromethane (3 × 50 cm^3), and the combined extracts were dried over anhydrous magnesium sulphate to afford a brownish solid (0.6 g). A peak at 4.25 min was observed when the solid was analysed by g.c. (160 °C, isothermal, 10 psi*). Chromatography of the crude product (elution with 2% ethyl acetate–hexane) followed by recrystallization from CH_2Cl_2 gave (**6**) as crystals: m.p. 117–119 °C.

Preparation of C_5-*Bromide* (**5**).—A heterogeneous mixture of (**1**) (314 mg, 2.0 mmol), bromine (0.6 cm^3, 11.6 mmol), and K_2CO_3 (724 mg, 5.2 mmol) in CH_2Cl_2 (25 cm^3) was placed in a 25 cm^3 Pyrex cell, stirred vigorously and irradiated through a GWV filter under N_2 for 17 h. G.c. analysis (column temperature 160 °C isothermal, column pressure 10 psi*) of the photolysate indicated the presence of three major peaks of t_R 3.06 min (9%), 4.79 min (4.5%), and 5.21 min (4.8%) in addition to the peak due to the parent imide (**1**) [t_R 1.96 min (76%)], and three minor peaks. Chromatography of the crude product (elution with 25% ethyl acetate–light petroleum) gave fifty fractions of 15 cm^3 each. Fractions 12–19 contained C_2-bromide (**4**) and fractions 20–24 contained mixtures of (**1**) and (**4**). Elution with acetone (100 cm^3) afforded a yellowish gum (11 mg); this was purified by preparative t.l.c. on silica gel (R_F 0.4) with 25% ethyl acetate–hexane and followed by recrystallization from CH_2Cl_2 to afford C_5-bromide (**5**) (5 mg) as white crystals: m.p. 99–101 °C.

Preparation of the C-*Bromides* (**8**) *and* (**9**).—A solution of (**7**) (670 mg, 3.9 mmol), NBS (810 mg, 4.5 mmol), and bromine (100 mm^3, 2 mmol) in CH_2Cl_2 (20 cm^3) in a 25-cm^3 Pyrex photocell was irradiated through a GWV filter for 1 h. The residue was extracted with CCl_4 (3 × 100 cm^3). G.c. analysis of the CCl_4 solution (160 °C isothermal, 10 psi) afforded (t_R, peak area) (**8**) (3.87 min, 25%), (**9**) (6.10 min, 10%), the parent imide (**7**) and several minor peaks. Chromatography of the mixture (elution with 10% ethyl acetate–light petroleum) gave thirty fractions of 15 cm^3 each. Fractions 20 and 21 contained (**8**) (60 mg) as a yellowish oil. The column was then eluted with 20% ethyl acetate–light petroleum to give 20 fractions of 15 cm^3 each. Fractions 9, 10, and 11 contained (**9**) contaminated by (**7**). Removal of the solvent from fraction 10 gave a yellowish oil (20 mg). It was further purified with h.p.l.c. [Water Associates, Bondapak C_{18} column, 5% isopropylalcohol–hexane as the eluant (2 cm^3 min^{-1})]. Under these conditions, (**9**) was eluted at t_R 4.48 min. Removal of the solvent afforded (**9**) (13 mg). An injection of (**8**) in g.c. analysis showed a small peak (*ca.* 1%) at *ca.* 1.80 min which was shown by g.c.–m.s. to arise from dehydrobromination. The percentage yield of (**8**) was calculated from the sum of these two peaks.

Preparation of the N-*Bromo Imide* (**2**).—The reaction was carried out in the dark. A solution of imide (**1**) (157 mg, 1.00 mmol) in CH_2Cl_2 (10 cm^3) was placed in a 50-cm^3 flask equipped with a drying tube and cooled to −20 °C with an ice–salt bath. One drop of cyclohexene was added to scavenge fortuitous bromine. A Freon solution of t-butyl hypobromite (8 cm^3, 5 mmol) was added in one portion. The solution was stirred at −20 °C for 2.5 h. Removal of the solvent under reduced pressure at 13–15 °C left (**2**) as a colourless oil (240 mg): δ_H($CDCl_3$) 0.92 (3 H, t, *J* 6.7 Hz), 1.35 (4 H, m), 1.67 (2 H, m), 2.63 (3 H, s), and 2.90 (2 H, t, *J* 7.5 Hz); i.r. (CCl_4) 3 010m, 1 720s, 1 370w, 1 230m, 1 190w, 1 160ms, 1 025w, and 640w cm^{-1}; no $\nu_{max.}$(NH) was observed in 3 300–3 600 cm^{-1} region.

Photodecomposition of the N-*Bromo Imide* (**2**) *in the Presence of an Alkene*.—A solution of (**2**) (236 mg, 1.0 mmol) and 3,3-dimethylbutene (0.10 cm^3, 2.5 mmol) in CH_2Cl_2 (25 cm^3) was placed under nitrogen in a 30 cm^3 Pyrex photocell which was kept in an ice–water bath at about 0 °C and irradiated with a 200 W mercury lamp for 1 h. The solution (0.5 cm^3) before and after photolysis was analysed by n.m.r. spectroscopy (Bruker SY100), and the intensity of the signal at 2.63 ppm was measured to estimate the conversion of *N*-bromo imide (**2**).

The photolysate was washed with 5% aqueous $NaHSO_3$ solution, dried over anhydrous magnesium sulphate, and filtered. G.c. analysis of the filtrate (160 °C, isothermal, 10 psi) afforded the peaks due to (**1**) (retention time 1.94 min, 8%), (**3**) (4.74 min, 80%), and an unidentified monobrominated product (**X**) (7.45 min, 6%). Chromatography of the crude product (eluted with 20% ethyl acetate–hexane) gave 50 fractions of 10 cm^3 each. Removal of the solvent from fraction 10 gave (**X**) (6 mg) as a gum: *m/z* (relative intensity) 279.2 (M^+, 25), 277.1 (M^+, 27), 117.1 (40); δ_H($CDCl_3$) 0.90 (3 H, t, *J ca.* 6 Hz), 1.33 (6 H, m), 1.65 (1 H, m), 1.75 (1 H, m), 1.88 (1 H, m), 2.13 (1 H, m), 2.33 (2 H, m), 3.98 (1 H, ddd, *J* 5, 9, and 10 Hz), 4.92 (m, *J* 5, 9, and 1 Hz); i.r. (Nujol) 1 730s, 1 450br m, 1 380br m), 1 100w; δ_C($CDCl_3$) 172.80, 75.57, 52.86d, 35.69, 34.49, 31.28, 25.55, 24.69, 23.33, 22.38, and 13.85q. Fractions 39–48 contained pure C_4-bromide (**3**) and fractions 34–38 mixtures of (**1**) and (**3**) as shown by g.c. analysis. The recrystallization of the solid from fractions 39–48 from acetone afforded (**3**) as crystals (10 mg): m.p. 88–90 °C. The experiment described above was repeated. After the photolysis the photolysate was combined with benzophenone (200 mg) as an internal standard, and the solution was analysed by g.c. to afford (**3**) (207 mg, 0.88 mmol), (**1**) (14 mg, 0.088 mmol), and the unidentified compound (**X**) (0.065 mmol).

Bromine-atom Initiated Decomposition of (**2**).—A solution of (**2**) (9.4 mg, 0.040 mmol) and bromine (1 mm^3, 0.02 mmol) in CCl_4 (1 cm^3) was placed in an n.m.r. tube, sealed, and purged with Argon for 5 min. The tube was placed in an ice–water bath and irradiated for 10 min with a $\geq$400 nm light source [200 W Hanovia lamp filtered through a solution containing sodium nitrite (3 mol dm^{-3}) and sodium hydrogen phthalate (0.027 mol dm^{-3})].[32] The conversion of (**2**) was determined by n.m.r. analysis. The photolysate was washed with sodium bisulphite solution (10%). The organic layer was dried over magnesium sulphate and filtered. To the filtrate was added a CH_2Cl_2 solution of benzophenone (25 mm^3, 0.0220 mol dm^{-3}) as an internal standard. The mixture was analysed by g.c. (160 °C

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* 1 psi = 6.894 757 × 10^3 Pa.

isothermal, 10 psi) to afford (**1**) (retention time 1.97 min; 0.008 mmol), (**4**) (3.08 min, 0.0029 mmol), (**6**) (4.19 min, 0.000 28 mmol), (**3**) (4.82 min, 0.021 mmol), (**5**) (5.32 min, 0.0036 mmol), an unidentified compound (**X**) (7.45 min, 0.0014 mmol) and a few small peaks. The results are listed in Table 1.

A similar sample was immersed in an ice–salt bath (*ca.* −20 °C) and irradiated with the ≥400 nm light source. The conversion of (**2**) was monitored by n.m.r. spectroscopy to be 81% after 55 min of irradiation. The photolysate was treated and analysed by g.c. as above (Table 1, experiment 11).

Photobromination of the Imides (**1**) *and* (**7**).—A solution of (**1**) (6.3 mg, 0.040 mmol), bromine (1.0 mm^3, 0.02 mmol), and NBS (15 mg, 0.084 mmol) in CCl_4 (1.0 cm^3) placed in an n.m.r. tube was photolysed in a similar method as described above. The treatment and analysis of the photolysate were carried out by the same method. The results are shown in Table 2. The photobromination of (**7**) with Br_2 and NBS or Br_2 and *N*-acetyl-*N*-bromoacetamide follow the same processes.

Bromine (1.0 mm^3, 0.020 mmol), (**1**) (6.3 mg, 0.040 mmol), K_2CO_3 (0.12 mmol), and CCl_4 (2 cm^3) together with a magnetic bar were placed in a 1 cm fluorescence cuvette. After the cuvette was capped, the heterogeneous mixture was purged with nitrogen and irradiated and stirred for 160 min. The photolysate was filtered and mixed with acetone (0.4 cm^3) and g.c. analysis to afford (**1**) (retention time 1.97 min, 96.0%), (**4**) (3.13 min, 2.5%), (**5**) (5.41 nin, 1.0%). The peaks due to (**3**) and (**6**) were detected, but were too small to be integrated by g.c. (Table 2). Imide (**7**) was also photobrominated and analysed similarly.

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