

The Photodecomposition of Cyclic *N*-Bromo Imides: Evidence for Stereoelectronic Control in Intramolecular Hydrogen Transfer in Imidyl Radicals

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In order to examine the reactivities and configurations of imidyl radicals, several cyclic *N*-bromo imides possessing five- or six-membered imide rings have been photolytically decomposed in the presence of 1,1-dichloroethene in methylene chloride in order to scavenge bromine atoms and bromine. The five-membered *N*-bromo imides and (\pm)-*N*-bromocamphorimide undergo ring opening to afford products derived from *C*-bromo acyl isocyanates. While the corresponding imidyl radicals abstract a hydrogen atom from methylene chloride, none of them undergo intramolecular H-atom abstraction to effect an intramolecular hydrogen-bromine exchange reaction, even when there are suitably located C-H bonds at a fifth (or sixth) position that can overlap the π -orbital of the imidyl radicals. This phenomenon clearly reveals the presence of stereoelectronic controls on the intramolecular H-abstraction of imidyl radicals, and indicates that the reactive state of imidyl radicals does not possess the Π -electronic configuration. We conclude that imidyl radicals possess the Σ -electronic configuration in their reactive state (which is probably the ground state). The intramolecular addition of a *C*-radical centre to an isocyanate group is established; this indicates that the reversibility of the ring-opening reaction of imidyl radicals is controlled by steric strains among other factors. Because of the presence of reactive allylic hydrogens, the *N*-bromo imide (**10**) upon photolysis forms the *C*-bromo compounds (**11**) efficiently by a bromine atom chain process which is retarded by the presence of a better Br \cdot scavenging alkene.

In recent years, the photodecomposition of *N*-bromo imides¹⁻⁵ has attracted considerable attention owing to the mechanistic ambiguities arising from the complex pattern of the reactions. *N*-Bromosuccinimide has been extensively used as a radical brominating agent and/or an oxidizing agent.^{4,5} From 1972, the generation and reactivity of the succinimidyl radical has been investigated again by many groups.^{1-3,6} These groups have agreed that under the ordinary reaction conditions utilized, only one succinimidyl radical exists as a reactive intermediate.^{1,2,7} The proposal of the presence of two succinimidyl radicals⁴ (*i.e.*, those with the Σ - and Π -electronic configuration) has now been withdrawn.¹ The structures of the Σ - and Π -imidyl radical are described in detail in theoretical calculations⁸ and can be visualized by the prototype examples shown in (**35**) and (**36**) (*vide infra*).

The recent calculations show that the ground state succinimidyl radical possesses the Π -electronic configuration and that the lowest excited state has the Σ -electronic configuration with a calculated energy of 14–20 kcal mol⁻¹ higher.^{8b-f} In contrast, a probe of the configuration by competing chemical reactions in an allied succinimidyl radical indicates that such radicals may react with the Σ -electronic configuration under ordinary reaction conditions in solution. A more qualitative theoretical study carried out earlier also suggests that the succinimidyl radical may have the Σ -configuration.^{8a} Experimentally, the investigations by selective excitation have established that the photolysis of an *N*-bromo imide in a mixture with Br₂ affords a bromine radical complex (BRC) in equilibrium with Br \cdot and the imidyl radical.^{7,9,10}

More recently the photodecompositions of other *N*-bromo imides have been reported and the reactivities of the corresponding imidyl radicals clarified.¹¹⁻¹⁴ The imidyl radicals can undergo intermolecular and intramolecular^{14,15} H-abstraction,

addition to alkenic bonds or aromatic rings (*e.g.*, benzene)^{4,13,16} in competition against ring opening reactions.^{4,7,17,18} The kinetic studies of imidyl radical reactions are hampered by the complexity of the reaction patterns and by difficulties in identifying imidyl radicals, except in two cases in which absolute rate constants have been determined; the rate constant of H-abstraction of the 3,3-dimethylglutarimidyl radical from cyclohexane¹⁹ is 3.5×10^3 dm³ mol⁻¹ s⁻¹ and that of the ring opening reaction of the succinimidyl radical³ is about 10⁴ s⁻¹.

Both glutarimidyl and succinimidyl radicals have been shown to undergo the ring-opening reaction to various extents^{3,17,18} depending on structural factors; the latter shows more propensity than the former to ring-open under ordinary conditions.¹¹ It was also established that a precursor of the photolytically generated succinimidyl radical undergoes the ring-opening reaction to afford the same product,^{7,16} β -bromopropionyl isocyanate; the extent of this ring-opening from direct excitation is *ca.* 13% of the total ring-opened product.¹⁶

By analogy with the reactivity of amidyl radicals,²⁰ some acyclic imidyl radicals have been shown to undergo intramolecular H-atom transfer specifically from a fifth position with respect to the nitrogen radical centre;^{14,15} the corresponding H-transfer in the transformation of (**33**) \rightarrow (**34**) (see later) is faster than the intermolecular H-atom transfer in cyclohexane (which also serves as the substrate) by at least an order of magnitude;¹⁴ the rate constant of the intramolecular H-transfer is estimated to be 10⁶ s⁻¹ using a value for the rate constant of 10⁴ dm³ mol⁻¹ s⁻¹ as the approximation of the intermolecular H-transfer from cyclohexane.²¹ In contrast, it is striking that such intramolecular H-atom transfer does not occur in the imidyl radical derived from a tricyclic *N*-bromo imide (**28**) (*vide infra*) though the nitrogen radical centre

has more than one H-atom within a 2.5 Å radius.⁹ It is obvious that intramolecular H-atom transfer in cyclic imidyl radicals is very sensitive to geometrical control. We have studied the photodecomposition of some model cyclic *N*-bromo imides in order to elucidate the structural factors governing the ring opening and intramolecular H-atom transfer reactions. The results allow us to examine the stereoelectronic requirements for intramolecular H-transfer and, in turn, the electronic configuration of these imidyl radicals in their reactive states.

Results

Representative cyclic *N*-bromo imides were prepared from the corresponding imides (Table 1) by a routine method, and were photolysed in methylene chloride in the presence of 1,1-dichloroethene (DCE) to scavenge Br[•] and Br₂ in order to prevent Br[•] initiated chain processes. The conditions were typical of those which generate imidyl radicals as the chain propagatory species.^{4,5} It is known that the ring-opening reaction generally gives β-bromoacyl isocyanates which are decomposed by moisture to β-bromo amides; in the present photolysis, the IR spectra of the photolysate always showed absorptions at 2350 and 2260 cm⁻¹ which are typical of isocyanates and CO₂ whenever the ring-opening reaction occurred; these absorptions decreased gradually during storage. As an imidyl radical also can abstract an H-atom from CH₂Cl₂ to cause bromination such intermolecular brominations served as a reference with which to evaluate the extent of intramolecular processes, e.g., the ring-opening and 1,5-H transfer process. GC-MS and NMR techniques were extensively used to detect the expected product in trace yields.

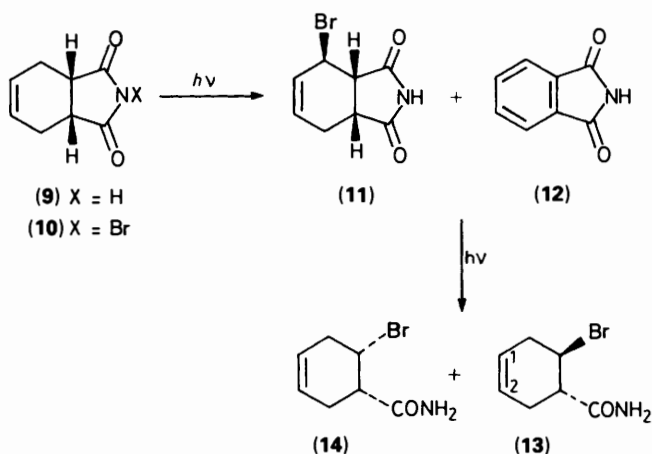
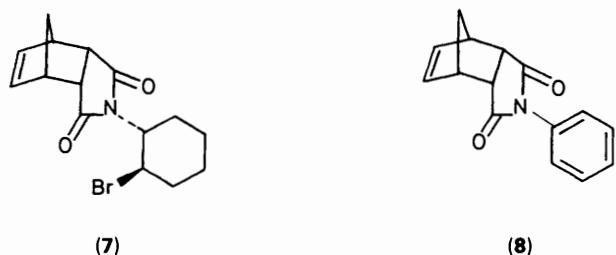
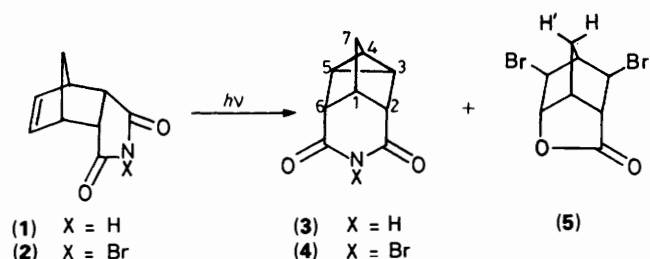
The *N*-bromo imide (2) was purified as a crystalline compound and was photolysed in the presence or absence of DCE with a 300 nm light source to give imide (3) (36–40%) and lactone (5) (9–16%) in addition to the parent imide (1) (34–38%). The lactone fraction was a mixture of the major compound (5) and a small amount of its isomers as shown by GC-MS; the former was isolated pure. The minor compound was assumed to be isomeric with the orientation of the C-Br bonds. The lactones were formed from precursors, such as (6), in the crude product as shown by the increases of the corresponding GC peaks during storage. The photolysis of (2) in a mixture of cyclohexene and CH₂Cl₂ (3:1) gave the *trans*-addition product (7) (36%) and the parent imide (1) (21%). A minor product present in the

mixture gradually decomposed to give more imide (1) during purification and was assumed to be the *cis*-isomer of (7). The photolysis of (2) in a mixture of benzene and CH₂Cl₂ gave *N*-phenylimide (8) in addition to a polybrominated amorphous solid. Similar addition reactions of other imidyl radicals have been described.^{6,11–13} In these two cases compound (3) was detected by GC analysis in trace yields.

The structures of (3) and (5) were determined by spectroscopic and analytical data as shown in Tables 2–5. The presence of a γ-lactone ring in (5) was shown by the IR absorption at 1788 cm⁻¹ and ¹³C NMR signals at 174.98 and 86.62 ppm. The assignments of the proton signals were confirmed by decoupling experiments; in particular, the NOE experiments showed that irradiation of the H₇ protons enhanced the intensities of H₁, H₂, H₄ and H₆ but not on H₃ and H₅. These results indicated the *exo* orientations of the C-Br bonds in (5). The structure of imide (3) possessed a plane of symmetry as shown by only six ¹³C NMR signals and five ¹H NMR signals. The magnetic equivalence of the two H₇ protons confirm the structure as (3).

Other *N*-bromo imides were used for photolysis as crude products without purification, but the disappearance of the N-H bond was monitored by IR and NMR spectroscopy. Photolysis of the *N*-bromo imide (4) in the presence of DCE gave 78–84% of the parent imide (3) and a small amount of the addition product to DCE. Several trace amount peaks detected in the crude product were shown to be something other than (1) by GC co-injection. In the photolysates the lack of IR absorptions at 2260 and 2349 cm⁻¹ indicates that the ring opening reaction does not occur in this case to afford the isocyanate and CO₂.

The photolysis of the *N*-bromo imide (10) in the presence of DCE (0.16 mol dm⁻³) gave the *C*-bromide (11) (48%) in addition to the parent imide (9) (40%); phthalimide (3%) was obtained as a by-product. The ring opened products, amides (13)



and (14), were also formed in trace amounts and their percentages increased significantly when the concentration of DCE was increased to 0.5 mol dm⁻³ or higher; at such high concentrations DCE polymerized to give milky solutions. The photolysis of (10) in the presence of a low concentration of penta-1,3-diene (<0.05 mol dm⁻³) gave amides (13) (40%) and (14) (48%) with a small amount of the parent imide (9); the *C*-bromide (11) was not formed. However, as the concentration of penta-1,3-diene is increased to >0.5 mol dm⁻³, the yields of the amides (13) and (14) decreased, obviously as a result of the reaction of the imidyl radical with the diene becoming significant. The product arising from the intramolecular addition to the double bond was not found in this case as well as in the photolysis of (2); these intramolecular additions were apparently not favourable owing to, among other reasons, severe incipient steric strain.

Table 1. Physical properties of imides and *N*-bromo imides.

Compound (m.p./°C)	IR ^a /cm ⁻¹	δ ^b (ppm)
(1) (184–186) ^c	3 170s, 1 710s, 1 200s	1.65 (m, 2 H), 3.34 (s, 2 H), 3.38 (s, 2 H), 6.22 (s, 2 H), 7.53 (br s, NH)
(2) (133–135)	1 715s, 1 686s, 1 310ms, 1 190ms, 840m, 749m, 700m	1.65 (m, 2 H), 3.47 (s, 4 H), 6.17 (s, 2 H)
(4)	1 695s	1.71 (br s, 3 H), 1.76 (br s, 2 H), 2.52 (br s, 1 H), 2.98 (br s, 2 H)
(9) (137–139) ^{c,d}	3 230s, 1 695s	2.10–2.70 (m, 4 H), 3.12 (m, 2 H), 5.94 (m, 2 H), 8.29 (br s, NH)
(10)	1 700s, 1 300s, 1 200ms, 1 175ms, 695ms	2.17–2.72 (m, 4 H), 3.30 (m, 2 H), 5.95 (m, 2 H)
(15) (134–136) ^e	3 410s, 3 210m, 2 945s, 2 860s, 1 715vs, 1 330s, 1 270s	1.47 (m, 4 H), 1.82 (m, 4 H), 2.92 (m, 2 H), 7.90 (br s, NH)
(16)	2 945s, 2 860s, 1 720s, 1 165s, 815m, 620w	1.49 (m, 4 H), 1.84 (m, 4 H), 3.09 (m, 2 H)
(19) (245–248) ^f	3 210m, 1 695s	1.00 (s, 3 H), 1.06 (s, 3 H), 1.20 (s, 3 H), 1.7–2.5 (m, 4 H), 2.64 (br d, <i>J</i> 6.6 Hz, 1 H), 7.8 (br s, NH)
(20)	2 890m, 1 700s	0.98 (s, 3 H), 1.02 (s, 3 H), 1.31 (s, 3 H), 1.99 (m, 4 H), 2.98 (br d, <i>J</i> 6.2 Hz, 1 H)
(23) (126–127) ^d	3 220m, 1 685s, 1 280s	0.92 (t, <i>J</i> 7.4 Hz, 3 H), 1.07 (s, 3 H), 1.44 (q, <i>J</i> 7.4 Hz, 2 H), 2.44 (s, 4 H), 7.9 (br s, NH)
(24)	1 690s, 1 270m, 1 225s, 1 145m, 1 125ms, 635w	0.92 (t, <i>J</i> 7.3 Hz, 3 H), 1.07 (s, 3 H), 1.44 (q, <i>J</i> 7.3 Hz, 2 H), 2.72 (s, 4 H)

^a The IR spectra were recorded as Nujol mulls except for (4), (19), and (20) which were recorded in CDCl₃ solution and (15) and (16) in CH₂Cl₂ solution. ^b The ¹H NMR spectra were recorded from samples in CDCl₃ solution using a trace of CHCl₃ (δ 7.27 ppm) as an internal standard. ^c Reported m.p. 186–188 °C; A. H. Andrist and M. J. Kovelan, *J. Chem. Soc., Perkin Trans. 1*, 1978, 918. ^d Recrystallized from a commercial sample (Aldrich). ^e Reported m.p. 137 °C; S. S. G. Sircar, *J. Chem. Soc.*, 1927, 1252. ^f Reported m.p. 249 °C; A. H. White and W. S. Bishop, *J. Am. Chem. Soc.*, 1940, 62, 8.

Table 2. ¹H NMR parameters of photolysis products in CDCl₃ solution.

Compound	δ(ppm)	<i>J</i> /Hz
(3)	1.67 (m, 1 H, H ₄), 1.70 (br t, 2 H, H ₃ and H ₅), 1.73 (m, 2 H, H ₇), 2.51 (m, 1 H, H ₁), 2.66 (m, 2 H, H ₂ and H ₆), 7.78 (br s, 1 H, NH)	<i>J</i> _{2,1} = <i>J</i> _{6,1} = 1.7, <i>J</i> _{1,7} = 1.2, <i>J</i> _{4,7} = 1.2, <i>J</i> _{2,4} = <i>J</i> _{6,4} = 1.7, <i>J</i> _{1,3} = <i>J</i> _{1,5} ≈ 0.5, <i>J</i> _{3,4} = <i>J</i> _{5,4} = 5.0
(5)	2.45 (m, 2 H, H ₇ and H ₇ '), 2.95 (m, 1 H, H ₄), 2.98 (d m, 1 H, H ₂), 3.3 (m, 1 H, H ₁), 3.75 (m, 1 H, H ₃), 4.10 (m, 1 H, H ₅), 4.95 (m, 1 H, H ₆)	<i>J</i> _{3,7} ≈ 1.2, <i>J</i> _{2,1} = 4.8, <i>J</i> _{6,1} ≈ 5.0
(11)	2.15 (ddd, 1 H, H _{6e}), 2.52 (ddd, 1 H, H ₆), 3.45 (ddd, 1 H), 3.63 (dddd, 1 H), 4.68 (m or dddd, 1 H, H ₃), 6.03 (ddd, 1 H, H ₃), 6.24 (dddd, 1 H, H ₄)	<i>J</i> _{6',1} = 10.3, <i>J</i> _{6',6} = 14.5, <i>J</i> _{6',3} = 4.0, <i>J</i> _{6,1} = 6.0, <i>J</i> _{6,3} = 4.5, <i>J</i> _{6,4} ≈ 0.6, <i>J</i> _{1,2} = 8.5, <i>J</i> _{1,3} ≈ 0.5, <i>J</i> _{2,4} = 2.6, <i>J</i> _{2,5} = 4.0, <i>J</i> _{2,3} = 1.0, <i>J</i> _{3,4} = 5.0, <i>J</i> _{5,4} = 9.8, <i>J</i> _{5,3} ≈ 0.7
(13)	2.41 (m, 1 H, H _{3a}), 2.48 (m, 1 H, H _{3a} '), 2.61 (m, 1 H, H _{6a}), 2.73 (m, 1 H, H _{4a}), 2.81 (m, 1 H, H _{6e}), 4.38 (ddd, 1 H, H _{5a}), 5.53 (m, 1 H, H ₁ or H ₂), 5.71 (m, 1 H, H ₂ or H ₁), 5.64 (br s, 2 H, NH ₂)	<i>J</i> _{3e,3a} = 17, <i>J</i> _{3a,4a} = 10, <i>J</i> _{3e,4a} = 5.5, <i>J</i> _{6a,6e} = 18, <i>J</i> _{6a,5a} = 10, <i>J</i> _{4a,5a} = 10, <i>J</i> _{6e,5a} = 5.5, <i>J</i> _{1,2} = 9.0, <i>J</i> _{3a,x} = 2.5, <i>J</i> _{3a,y} = 4.0, <i>J</i> _{6a,u} = 2.5, <i>J</i> _{6a,v} = 3.5, <i>J</i> _{6e,z} = 5.4, <i>J</i> _{6e,w} = 5.5
(14)	2.35 (m, 1 H, H _{6e}), 2.55 (m, 1 H, H _{3a}), 2.66 (m, 1 H, H _{6a}), 2.88 (m, 2 H, H _{3e} , H _{4a}), 4.84 (m, 1 H, H _{5e}), 5.67 (m, 1 H, H ₁ or H ₂), 5.57 (m, 1 H, H ₂ or H ₁), 5.71 (br s, 2 H, NH ₂)	<i>J</i> _{6a,6e} = 17, <i>J</i> _{6e,5e} = 2, <i>J</i> _{3a,4a} = 10, <i>J</i> _{3e,4e} = 15, <i>J</i> _{1,2} = 10, <i>J</i> _{3a,x} = 2.0, <i>J</i> _{3a,y} = 4.0, <i>J</i> _{6a,z} = 5.0, <i>J</i> _{6a,w} = 10, <i>J</i> _{3e,u} = 2.5, <i>J</i> _{3e,v} = 4.5, <i>J</i> _{5e,q} = 5.0, <i>J</i> _{5e,r} = 1.5
(17)	1.30 (m, 1 H, H ₅), 1.35 (m, 1 H, H _{6a}), 1.62 (m, 1 H, H ₄), 1.80 (m, 3 H, H ₃ , H ₄ , and H ₅), 1.97 (m, 1 H, H _{6e}), 2.42 (m, 1 H, H ₃), 2.42 (m, 1 H, H ₃ '), 2.50 (m, 1 H, H _{1a}), 4.24 (ddd, 1 H, H _{2a})	<i>J</i> _{1a,6e} = 3.5, <i>J</i> _{1a,6a} = 12.0, <i>J</i> _{1a,2a} = 11.0, <i>J</i> _{2a,3e} = 3.5, <i>J</i> _{2a,3a} = 12.0, <i>J</i> _{6e,6a} = 13.0, <i>J</i> _{3e,4e} = 4.5, <i>J</i> _{3e,4a} = 3.0, <i>J</i> _{6e,5a} = 5.0, <i>J</i> _{6e,5e} = 3.0, <i>J</i> _{3a,3e} = 12.0
(22)	1.00 (s, 3 H, H ₇ or H ₈), 1.19 (s, 3 H, H ₈ or H ₇ '), 1.65 (m, 3 H, H ₆), 2.38 (m, 1 H, H _{5e}), 2.62 (m, 1 H, H _{5e} '), 2.66 (t, 1 H, H ₄), 5.27 (m, 1 H, H ₁), 5.43 (br s, 2 H, NH ₂)	<i>J</i> _{1,5} = 2.5 and 2.0, <i>J</i> _{4,5} = 7.5 and 10.0, <i>J</i> _{5,5} = 15.0, <i>J</i> _{6,5} = 1.2 and 2.0
(27)	1.75 (m, 3 H), 1.97 (m, 2 H), 2.22 (m, 1 H), 3.50 (dt, H ₅), 3.92 (dt, H ₁)	<i>J</i> _{1,5} = <i>J</i> _{1,2x} = <i>J</i> _{5,4x} = 8.6, <i>J</i> _{1,2n} = 1.4, <i>J</i> _{5,4n} = 2.9
(7) ^a	6.14 (m, 2 H), 4.82 (dt, 1 H, <i>J</i> 11 and 4.5 Hz) 4.00 (dt, 1 H, <i>J</i> 11 and 4.5 Hz), 3.35 (m, 4 H), 1.6 (m, 10 H)	
(8) ^a	7.0–7.5 (m, 5 H), 6.23 (m, 2 H), 3.40 (m, 4 H), 1.6 (AB system, δ 14.0 Hz, <i>J</i> 9 Hz)	

^a Recorded on a Varian EM360 instrument; spectra for all other compounds were recorded on a Bruker WH400 instrument.

The orientation of the C–Br bond in (11) was obtained from the proton coupling constant of H₁ and H₂ (geminal to Br) at 1 Hz; these two protons must be *trans* oriented with a nearly 90°

arrangement. The stereochemistry of the amides (13) and (14) was readily decided from the coupling pattern of H₅ (that geminal to the bromine); *trans*-amide (13) showed the signal at

Table 3. ^{13}C NMR parameters of photolysis products in CDCl_3 solution.

Compound (m.p./°C)	δ (ppm)
(3) (164–166)	17.17, 17.26, 34.03, 37.10, 48.49, 175.14
(5) (79–80)	33.90, 45.67, 46.81, 49.53, 50.02, 54.74, 86.62, 174.98
(11) (105–108)	31.96, 37.71, 40.69, 41.30, 123.45, 131.78, 175.82, 178.36
(13) (136–138)	29.70, 36.06, 47.94, 49.81, 124.83, 174.99
(14) (127–129)	25.14, 35.61, 45.62, 49.19, 123.36, 124.89, 173.67
(17) (183–184)	24.50, 26.85, 31.24, 37.25, 51.95, 54.71, 175.40
(22) (97–98)	12.344, 20.87, 27.16, 32.45, 48.39, 56.72, 121.02, 146.66, 175.8
(27) —	26.84, 30.62, 31.73, 42.86, 59.06, 169.11

Table 4. Mass spectral data of the photolysis product.

Compound	Mode	m/z (rel. intensity)
(3)	EI	163 (M^+ , 52), 91 (100), 65 (28)
(5)	EI	298 (M^+ , 1), 296 (M^+ , 2), 294 (M^+ , 1) 217 (M^+ - Br, 30), 215 (M^+ - Br, 30) 107 (M^+ - 2Br, 40), 91 (40), 79 (80), 65 (25), 51 (20)
(7)	EI	325 (M^+ , 31), 323 (30), 260 (10), 258 (10), 244 (8), 178 (22), 165 (23), 164 (100), 98 (62), 91 (37), 81 (52), 67 (65), 66 (85)
(8)	EI	239 (M^+ , 82), 174 (88), 173 (100), 129 (41), 91 (50), 66 (71)
(11)	EI	150 (M^+ - Br, 75), 105 (55), 79 (M^+ - Br - CONHCO)
(13)	EI	205 (M^+ , 1.6), 203 (M^+ , 0.5), 124 (M^+ - Br, 95) 81 (100), 79 (80), 44 (CONH_2^+ , 22)
(14)	EI	205 (M^+ , 1.6), 203 (M^+ , 1.8), 124 (M^+ - Br, 90) 81 (86), 79 (100), 44 (CONH_2^+ , 20)
(17)	EI	207 (M^+ , 2), 205 (M^+ , 2), 126 (M^+ - Br, 78), 81 (53), 67 (48), 55 (65), 44 (100)
	CI	208 (M^+ + 1, 96), 206 (M^+ + 1, 100), 126 (M^+ - Br, 23)
(22)	EI	153 (M^+ , 60), 138 (20), 110 (100), 95 (90) 79 (35), 67 (75), 55 (30), 41 (40)
	CI	154 (M^+ + 1, 100)
(27)	EI	208 (6), 206 (10), 170 (21), 134 (18), 132 (14), 121 (85), 119 (100), 91 (8)
	CI	290 (20, M^+ + 1), 288 (45, M^+ + 1), 286 (28, M^+ + 1), 174 (35), 172 (18)

Table 5. IR parameters of the photolysis products.^a

Compound	ν/cm^{-1}
(3)	3 450m, 3 180br s, 3 080m, 1 685s, 1 260s, 1 005m
(5) ^b	2 998w, 2 985w, 1 788vs, 1 402w, 1 345m, 1 170m, 1 014m, 942m, 903m, 860w, 700w
(7)	1 765m, 1 695s, 1 181s, 971w, 885w, 870w, 859w, 815m, 750w, 689m, 665w
(8)	1 770w, 1 700s, 1 597w, 1 499m, 1 182s, 845m, 740m, 721m, 690m
(11)	3 257br s, 1 775s, 1 704br vs, 1 640m, 1 343s, 1 187s, 1 175s, 1 004s, 771s
(13)	3 410m, 3 220w, 1 665s, 1 620w
(14)	3 405m, 3 200m, 1 663s, 1 650s
(17)	3 350s, 3 160s, 1 665vs, 1 620s, 1 186w, 1 010w
(22) ^c	3 527m, 3 410m, 2 963s, 1 682vs, 1 589s
(27)	3 510m, 3 400m, 1 705s, 1 580m, 1 345m

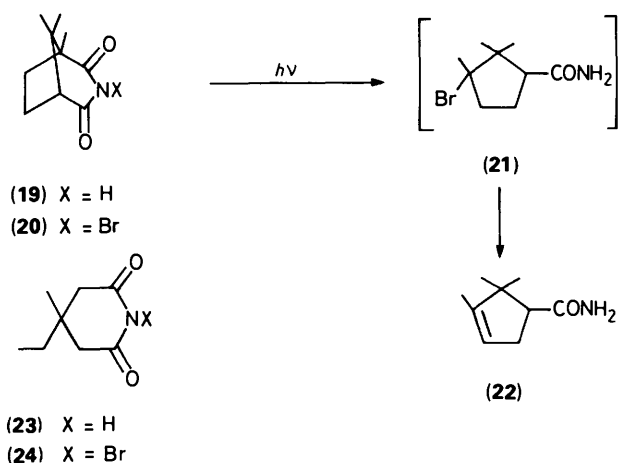
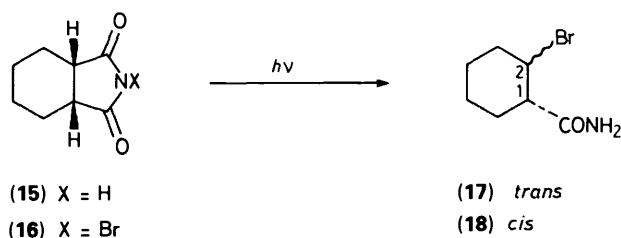
^a Unless specified otherwise, the spectra were taken in Nujol mulls.^b Neat. ^c CH_2Cl_2 solution

4.38 ppm (J 10.2, 10.1 and 5.5 Hz) for the axial C–H bond, and *cis*-amide (14) at 4.85 ppm ($J_{1,2}$ 8 Hz) for the equatorial C–H bond.

Table 6. Microanalysis data.

		C	H	N
(2)	Calc.	44.82	3.32	5.81
$\text{C}_9\text{H}_8\text{BrNO}_2$	(Found)	44.89	3.51	5.75)
(3)	Calc.	66.26	5.52	8.59
$\text{C}_9\text{H}_9\text{NO}_2$	(Found)	66.04	5.40	8.31)
(5)	Calc.	32.43	2.70	
$\text{C}_8\text{H}_8\text{Br}_2\text{O}_2$	(Found)	32.29	2.55)	
(7)	Calc.	55.73	5.57	4.33
$\text{C}_{15}\text{H}_{18}\text{BrNO}_2$	(Found)	55.85	5.59	4.11)
(8)	Calc.	75.31	5.44	5.90
$\text{C}_{15}\text{H}_{13}\text{NO}_2$	(Found)	75.10	5.53	5.73)
(11)	Calc.	41.74	3.48	6.09
$\text{C}_8\text{H}_8\text{BrNO}_2$	(Found)	41.84	3.54	6.00)
(14)	Calc.	41.28	4.90	6.86
$\text{C}_7\text{H}_{10}\text{BrNO}_2$	(Found)	41.55	4.90	6.91)
(17)	Calc.	40.80	5.83	6.80
$\text{C}_7\text{H}_{12}\text{BrNO}_2$	(Found)	40.80	5.97	6.67)
(22)	Calc.	70.59	9.80	9.15
$\text{C}_9\text{H}_{15}\text{NO}$	(Found)	70.40	9.92	8.99)

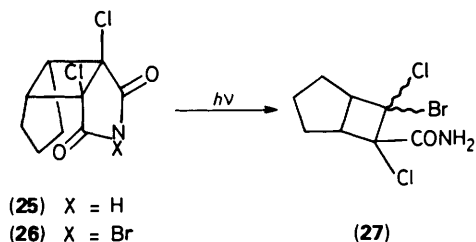
The photolysis of the *N*-bromo imide (16) in the presence of DCE gave the *trans* and *cis*-amides (17) (75%) and (18) (7%) in addition to the parent imide (15) (15%); no other product could be detected by GC analysis. Amide (17) showed the typical coupling pattern of the axial orientation for H_1 and H_2 with $J_{1,2}$ 12.0 Hz. Amide (18) was not isolated but showed a similar mass spectrum to that of (17). The photolysis of *N*-bromocamphorimide (20), in the presence of DCE gave amide (22) (60%) in addition to the parent imide (19) (35%); amide (22) was most likely derived from an intermediate such as the *C*-bromo amide (21). The presence of the double bond in (22) was clearly shown by NMR data at 121.0 and 146.7 ppm for the ^{13}C signals and the multiplet at 5.27 ppm for the alkenic hydrogen.



The photolysis of *N*-bromo imide (24) and *N*-bromo-3,3-dimethylglutarimide (NBDMG) under similar conditions gave only the parent imide (23) and 3,3-dimethylglutarimide in

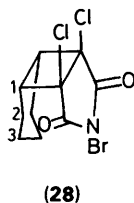
>90% yields and trace amounts (<3%) of the addition product to DCE. In spite of extensive search by GC-MS, the corresponding side-chain brominated compounds were not obtained. The photodecomposition of NBDMG has also been reported previously.^{16-13,17}

Imide (25) was synthesized²² and its *N*-bromo imide (26) was photolysed in the presence of DCE (Scheme 1) to give the *trans*-



Scheme 1.

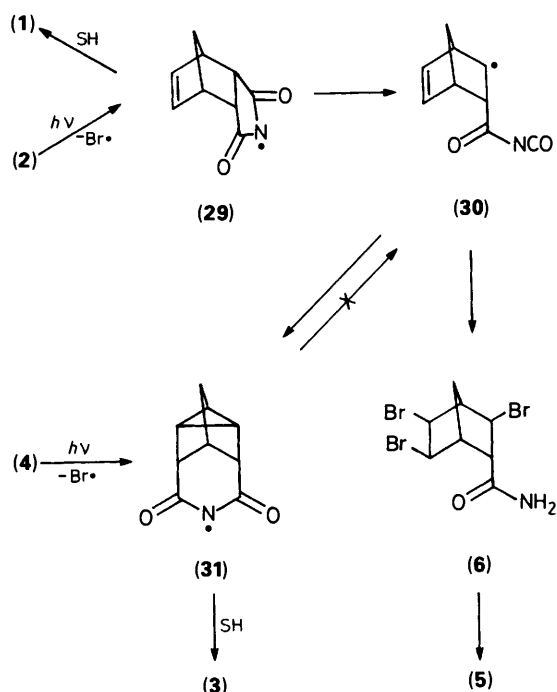
and *cis*-amides (27) (23%) and imide (25) (68%); the imide with bromination at the cyclopentane ring was not detected by careful GC-MS analysis; such *C*-bromo compounds were prepared from imide (25) and described in the thesis presented by one of us (Y.M.A.N.). Two amides showed closely placed GC peaks and showed similar GC-MS patterns; one amide was isolated but its structure was not confirmed. This decomposition pattern is the same as that of (28) reported previously.



Discussion

The photolysis of these *N*-bromo imides is characterized by the ring-opening reaction except those of (4), (24) and NBDMG; the mechanism is illustrated in Scheme 1 in analogy to the photodecomposition of NBS^{7,13} using the *N*-bromo imide (2) as the model compound. Under the photodecomposition conditions, a cyclic imidyl radical undergoes competing reactions of H-abstraction from CH₂Cl₂ against the ring opening reaction (as well as other radical reactions); the intermolecular H-abstraction, being a pseudo-first order reaction, can serve as a reference in the comparison of reactivities.

In the tricyclic ring system, while the imidyl radical (29) ring-opens, the imidyl radical (31) does not do so sufficiently efficiently to compete with intermolecular H-abstraction from CH₂Cl₂. It is probable that the direct photolysis of (4) also causes ring opening^{7,9} to give (30) which efficiently cyclizes to afford (31), since reversibility of the ring-opening reaction has been established previously.¹⁷ It appears that the cyclization of (30) to (29) is much less efficient than that of (30) to (31) owing to the steric strain in (29). The amide (5) isolated in the photolysis of (2) is no doubt derived from the tribromo precursor (6) which should be obtained by ring opening and the addition of bromine. Under the reaction conditions, it is difficult to judge the timing of the bromination step. The hydrolysis and decarboxylation of acylisocyanates to give amides is well established.^{4,5} The intramolecular nucleophilic substitution of amides and subsequent hydrolysis to give lactones such as (5) have been previously demonstrated in open chain systems.²⁰ In the presence of high concentrations of cyclohexene or benzene,



the imidyl radical (29) is trapped by addition¹³ or intermolecular H-abstraction reactions to give (7) and (8) as the major products. The photolysis of (10), (16) and (20) follows the prototype reaction pattern as reviewed above to give the expected products except that the last one involves dehydrobromination [*e.g.* (21) → (22)] most likely arising from steric crowding. Only the *N*-bromo imide (20), among the three, is a derivative of *N*-bromoglutarimide; the facile ring opening of (20), as compared with (4), (24) and NBDMG, undoubtedly arises from the release of bicyclic ring strain and the formation of the more stable tertiary radical. The sluggish ring opening of (10) at a moderate concentration of DCE indicates that *C*-bromide (11) is formed by allylic bromination with a Br• chain process and the corresponding imidyl radical is not generated. The allylic hydrogens of cyclohexenes and cyclopentenes are fairly reactive, even toward mildly reactive^{6,7} Br• H-abstraction. The allylic bromination in the photolysis of tricyclic *N*-bromo imide (32) (*n* = 1, 2) most likely involves a similar Br• chain process but not intramolecular imidyl radical H-abstraction; this will be discussed later. This is essentially the Bloomfield mechanism which can occur in the presence of reactive C-H bonds^{4,5} and involves the reaction of HBr with *N*-bromo imide to generate Br₂. When Br• and Br₂ are efficiently scavenged by penta-1,3-diene, the imidyl radical process dominates the reaction as shown by the formation of (13) and (14).

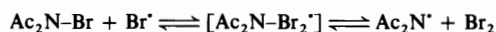
While the failure of the intramolecular addition to occur in the photolysis of (2) and (10) may be convincingly rationalized by the retardation arising from steric strain in the addition reaction, it is at first sight indeed puzzling to observe the complete failure of intramolecular hydrogen-bromine exchange reactions in the photolysis of (24) and (26). In both cases, the intermolecular H-abstraction from CH₂Cl₂ can occur extensively and the competition from the ring-opening reaction in the latter case is not serious. Certainly, the corresponding imidyl radicals possess readily abstractable C-H bonds within the 2.5–2.7 Å radius (the C to N distance) from the nitrogen radical centre; this range of interatomic distances has been estimated to be the probable distance for intramolecular H-atom transfer to alkoxy²²⁻²⁵ or aminium radical centres.^{20,26} From a kinetic point of view, an imidyl radical¹⁹ is just as reactive in H-abstraction as aminium radicals²⁶ or amidyl radicals²¹ since

their rate constants in intermolecular H-abstraction from a range of substrates are comparable and in the same order in the range 10^3 – 10^4 dm³ mol⁻¹ s⁻¹. Aminium radicals are known to possess the Π -configuration and can abstract a suitably placed hydrogen atom efficiently by an intramolecular process.²⁶ For example, 4-ethyl- and 4-propyl-*N*-chloropiperidine readily undergo a photolytic hydrogen–chlorine exchange reaction at the side chain *via* the corresponding aminium radicals.²⁷

If we assume that imidyl radicals possess the Π -radical configuration, we would expect a similar intramolecular hydrogen–bromine exchange reaction to occur at the ethyl group in (24) and the cyclopentane ring in (26); in both cases, since extensive intermolecular H-abstraction from CH₂Cl₂ occurs, intramolecular H-abstraction of the imidyl radical should also occur unless another factor, namely stereoelectronic influences, operates to frustrate the H-abstraction. Therefore, the total absence of such hydrogen–bromine exchange products in the photolysis of (24) and (26) unambiguously indicates that the corresponding imidyl radicals do not possess the Π -electronic configuration at all times along the reaction coordinate. In analogy to the previous finding⁹ in the photolysis of (28), we have concluded that imidyl radicals must possess the Σ -electronic configuration under the reaction conditions and must react from this state without the possibility of tunnelling to a Π -radical state. Using the imidyl radical derived from (26) as the model, Π and Σ -electronic configurations (35) and (36) are shown below; undoubtedly in the Σ -radical (35) the sp² orbital (σ -orbital) containing the unpaired electron is oriented coplanar to the imide group and cannot overlap with the H-atoms in the cyclopentane ring opposite to the nitrogen atom.⁵ Similar lack of overlap can be visualized for the Σ -imidyl radical derived from (24); an H-atom of the CH₃ group can orient itself very close to the nitrogen centre but cannot overlap with the half-occupied σ -orbital. Similar arguments can be made with the imidyl radical derived from *N*-bromocamphorimide (20); this case is not as compelling as the above cases since ring-opening may compete and the CH₃ group is not as close to the imide group as above. Acyclic *N*-bromo imide (33) undergoes the intramolecular hydrogen–bromine exchange reaction extremely efficiently either upon photolysis or on Br[•] initiated decomposition; obviously in the corresponding imidyl radical, a C₄-H atom can orient itself to overlap with the half occupied

σ -orbital.¹⁴ Stereoelectronic controls in the allied intramolecular H-abstraction of triplet excited state cyclic ketones have been studied and show a different kind of preference, probably depending on the orientation of the half-filled orbital.^{28,29}

The unusual conclusions that the reactive state of the imidyl radical possesses the Σ -radical configuration leads us to consider whether this is the ground state or, as claimed by the theoretical calculations,^{8c–f} the lowest excited state. Noting that the imidyl radical reactions can be induced to occur by the photolysis of Br₂ (to generate Br[•]) on a mixture with an *N*-bromo imide, we have proposed the following thermal reaction for the generation of the corresponding imidyl radical.^{7,9,10,14} Given that the imidyl radicals generated by this method (Scheme 2) and by the photolysis of *N*-bromo imides show the



Scheme 2.

same type of chemical reaction, we are inclined to believe that so far we have seen one type of imidyl radical that possesses the Σ electronic configuration and exists in the ground state. The results from the photolysis of (20), (24), and (26) also indicate that during the reaction lifetime of the Σ -imidyl radicals, they have not been promoted to the lowest excited state Π -radical.

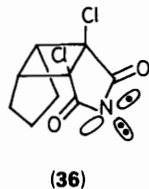
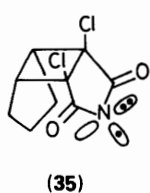
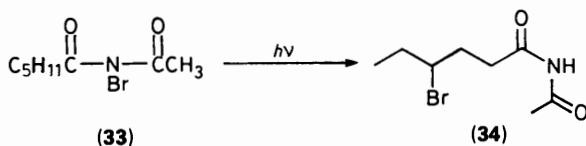
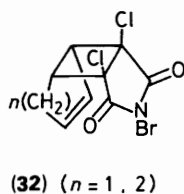
Imidyl radicals have been shown to have vigorous and indiscriminate intermolecular H-atom abstraction reactivity;^{1,4} we wish to rationalize this reactivity on the basis of the Σ -imidyl radical configuration occupying the ground state. As shown in the Salem state correlation diagram³⁰ (Figure 1), the succinimidyl radical H-abstraction from methane can occur from the Σ - and Π -electronic configurations that correlate with the ground state (N) and excited state zwitterionic (Z) products, respectively. The matching of energy surfaces indicates that such H-abstraction is facile with little or no energy barrier. It should be noted that a similar state correlation diagram with matching energy surfaces can be drawn to show the facile and reversible ring-opening of the Σ -succinimidyl radical to the propionyl-isocyanato- β -yl radical. This scheme will certainly have a lower energy barrier than that advocated previously.^{8b,c}

Finally we wish to use the Salem state correlation method to examine the recent reports that the ground state succinimidyl radical possesses the Π -electronic configuration (from theoretical calculations)⁸ and to compare this finding with the present results. As shown in Figure 2, the Σ - Π radical energy levels are reversed with respect to Figure 1. For this case, the Π -radical must be promoted to the Σ -radical and follow the forbidden surface crossing to give the ground state products. Alternatively, the Π -electronic state may follow the avoided crossing (broken line) to lead directly to the ground state products. In both cases, there should be energy barriers to H-abstraction that are related to the Σ - Π energy split. These analyses hint that the Π -imidyl radical intermolecular H-abstraction may not be as facile as those experimentally observed.

In conclusion, the present results indicate that ground state imidyl radicals have the Σ -radical configuration.

Experimental

General Conditions.—Instruments and their recording conditions, ordinary chemicals and solvents were the same as those described before. In general imides were prepared by heating the anhydrides of the corresponding dicarboxylic acids in concentrated ammonia solution (Table 1). Camphorimide (19) and glutarimides (23) were purchased from the Aldrich Chemical Co.; imide (25) was secured from a [2 + 2] photocycloaddition followed by extensive purification.⁹



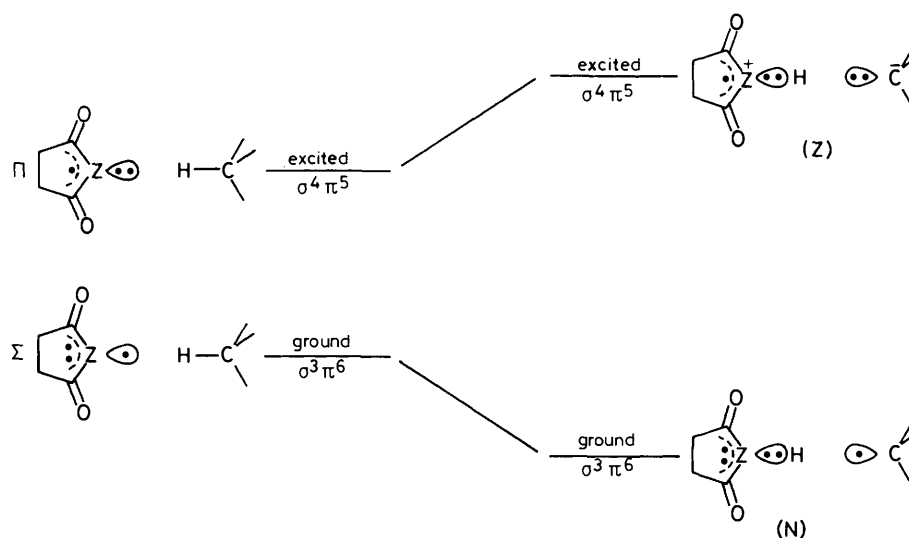


Figure 1. The state correlation diagram for intermolecular H-abstraction of the succinimidyl radicals from CH_4 .

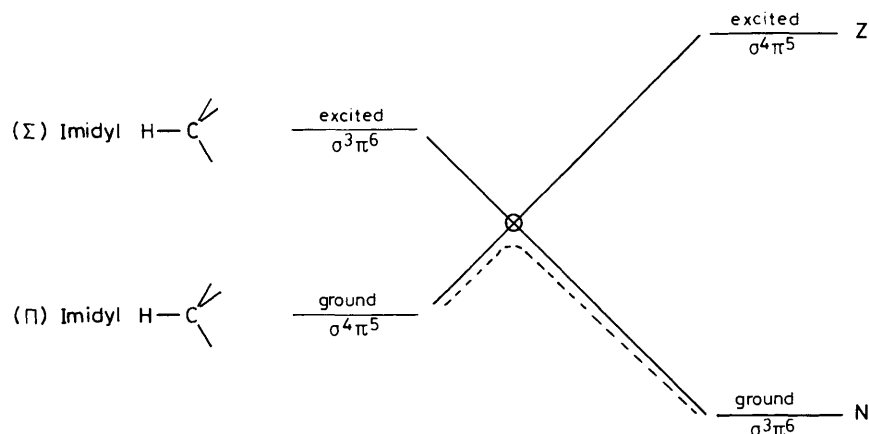


Figure 2. An alternative state correlation diagram for the H-abstraction reaction shown in Figure 1.

These imides were treated with *t*-butyl hypobromite in a mixture of CH_2Cl_2 – CCl_4 at an ice–salt temperature to afford *N*-bromo imides.^{9,14} These crude products were examined by IR and NMR spectroscopy until no signal due to the NH bond was observed (Table 1) and were used directly in the photolysis experiments. The *N*-bromo imide (2) was recrystallized from CCl_4 –light petroleum–ether in the dark to afford a crystalline compound, m.p. 133–135 °C; (Found: C, 44.9; H, 3.5; N, 5.75%. Calc. for $\text{C}_9\text{H}_8\text{BrNO}_2$: C, 44.82; H, 3.82; N, 5.81%).

Photolysis of *N*-Bromo Imides.—The *N*-bromo imide (0.1–0.01 mol dm^{-3}) and an appropriate quantity of DCE (usually *ca.* 0.5 of the *N*-bromo imide concentration) in CH_2Cl_2 were placed in a flat photocell (50–30 cm^3) under nitrogen and irradiated with a Rayonette RPR 3 000 Å light source. The details of the purging with nitrogen and irradiation have been described in the previous report.⁷ The photolyses were carried out until the disappearance of the *N*-bromo imides was shown by testing with KI–starch paper; this required *ca.* 1 h or less for small scale reactions. The crude products were analysed by GC which was used to follow the course of the isolation and purification by column chromatography. The details of these procedures were described in ref. 31. The technique of GC–MS was extensively utilized to examine the nature of minor peaks, particularly those of trace amounts; none of these were shown to be *C*-brominated parent imides. The spectroscopic data of isolated products were shown in Table 2–6.

Photolysis of (2).—A solution of (2) (0.7 g) in a mixture of cyclohexene (260 cm^3) and methylene chloride (40 cm^3) were photolysed under nitrogen in a Hanovia Pyrex reactor at *ca.* –10° for 3 h. The crude product was treated with CCl_4 – CH_2Cl_2 to give several fractions of precipitates of imide (1). The recovered crude product was chromatographed on silicic acid to afford several fractions of *trans*-amide (7) (230 mg, 30%). The combined solid was recrystallized from a mixture of light petroleum–ether and CH_2Cl_2 to give colourless crystals m.p. 139–141 °C.

A solution of (2) (1.5 g) in benzene (700 cm^3) and CH_2Cl_2 (100 cm^3) was photolysed as above at room temperature for 1.5 h. The photolysate was evaporated to 35 cm^3 to afford precipitates (500 mg) that were shown to be polybrominated products and were not investigated further. The mother liquor was further evaporated to afford a precipitate of imide (1) (300 mg). The remaining solid was chromatographed to give *N*-phenyl derivative (8) (660 mg) which was recrystallized from CCl_4 to give colourless crystals; m.p. 142–144 °C (lit., 144 °C).³²

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