Succinimidation by *N*-Bromosuccinimide of *N,N*-Dimethylamido and *N,N*-Dimethylamino Groups

Corrado Caristi,* Alida Ferlazzo, and Mario Gattuso
Dipartimento di Chimica Organica e Biologica, Università Piazza S. Pugliatti, 98100 Messina, Italy

N,N-Dimethylamides (1)—(6) and *N,N*-dimethylamines (7)—(10) are converted by the action of *N*-bromosuccinimide (NBS) in carbon tetrachloride and in the presence of a catalytic amount of benzoyl peroxide into the corresponding succinimido derivatives (11)—(23). The reaction involves two steps: (i) a radical bromination of the *N*-methyl moiety; and (ii) subsequent reaction of the resulting *N*-bromomethyl derivatives (24) with NBS. The latter step occurs *via* electrophilic substitution of the bromine atom of NBS by stabilized azacarbonium ions of which the *N*-bromomethyl derivatives (24) are effective sources. Proof of the suggested ionic mechanism is obtained from the conversion of independently synthesized *N*-bromomethylamides (25) and (26) and *N*-bromomethyl-*N,N*-dimethylamine (27) into the succinimido derivatives (11), (15), and (28) respectively by reaction with NBS in carbon tetrachloride. Bromomethylphthalimide (29), in which the two carbonyl groups destabilize the charge in the corresponding imidocarbonium ion, reacts only when a more solvolytic solvent such as nitrobenzene is used.

N-Bromosuccinimide (NBS) may be considered one of the most important reagents in organic synthesis.[1] Its versatility is increased by the high selectivity and by the variety of experimental conditions under which it can be used in different types of reactions such as bromination, addition, and oxidation.

Although bromination with NBS has been extensively studied because of the intrinsic interest in the mechanism [2] and the wide synthetic applicability, some aspects of the reactivity of NBS in this field still remain unexplored.

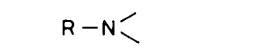
The literature contains a few examples of reactions of NBS leading to an unexpected succinimidation of the substrates instead of the usual bromination; it was previously reported that *N*-(α-methoxy-*p*-nitrobenzyl)succinimide, *N*-[α-(*p*-bromophenoxy)benzyl]succinimide, *N*-(cyclohepta-2,4,6-trienyl)succinimide, and elusive 2-succinimido-1,3-dioxolanes were formed by reaction of *p*-nitrobenzylmethyl [3] and *p*-bromophenylbenzyl [4] ethers, cycloheptatriene,[5] and bicyclic 2-aryl-1,3-dioxolanes [6] with NBS.

The formation of these succinimidyl derivatives has been explained by either a radical chain path [4] or the reaction of an intermediate bromo derivative with succinimide [5] or NBS.[6]

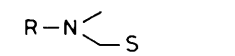
In all these cases no direct evidence for the suggested mechanism was advanced, and the driving force for the formation of the succinimido derivatives still remains obscure.

During our studies on the reaction of NBS with *N*-alkylamides [7] bearing *N*-α-allyl hydrogens, some succinimido derivatives were found in the reaction products. This prompted us to determine whether the formation of succinimido derivatives in the reactions of NBS could be considered as an occasional event or as a new and more general succinimidation reaction.

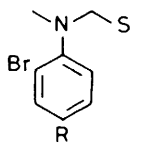
We report here the results of the reaction of NBS with the *N,N*-dimethylamides [8] (1)—(6) and *N,N*-dimethylamines (7)—(10) which leads to the succinimido derivatives (11)—(21) in high yields.



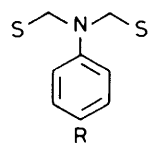
(1) R = PhCO
(2) R = *p*-$MeOC_6H_4CO$
(3) R = *m*-$NO_2C_6H_4CO$
(4) R = $PhSO_2$
(5) R = EtOCO
(6) R = MeCO
(7) R = *p*-$NO_2C_6H_4$
(8) R = *p*-CNC_6H_4
(9) R = *p*-ClC_6H_4
(10) R = *p*-$MeOCOC_6H_4$



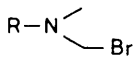
(11) R = PhCO
(12) R = *p*-$MeOC_6H_4CO$
(13) R = *m*-$NO_2C_6H_4CO$
(14) R = $PhSO_2$
(15) R = EtOCO
(16) R = MeCO
(17) R = *p*-$NO_2C_6H_4$
(18) R = *p*-CNC_6H_4



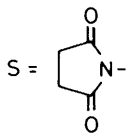
(19) R = CN
(20) R = Cl
(21) R = CO_2Me



(22) R = NO_2
(23) R = CN



(24)
(25) R = PhCO
(26) R = EtOCO



Results and Discussion

The reactions of the amides (1)—(6) were carried out in boiling carbon tetrachloride in the presence of benzoyl peroxide and required a 2 : 1 molar ratio of NBS to amide. The free bromine, which was liberated during the course of the reaction, was continually distilled off. At the end of the reaction the resulting mixture was treated with concentrated Na_2SO_3–$NaHCO_3$ solution to give the succinimido derivatives (11), and (13)—(15) in almost quantitative yield, while the derivatives (12) and (16) were both recovered in 70% yield.

The reactions of the amines (7)—(10) with NBS, carried out under the same conditions but with additional bubbling of ethylene to remove the bromine produced, gave the succinimido derivatives (17) (almost quantitative yield), (18) (80%), (20) (51%), and (21) (52%), respectively. Moreover, from the reaction of (7) traces of the aniline (22) were also obtained, while (19) (14%) and a trace of (23) were formed from the cyanoaniline (8).

The structures of the succinimido derivatives (11)—(23) are

Table. ^{1}H N.m.r. parameters. Chemical shifts (δ) in $CDCl_3$; *J* in Hz

Compd.	Succinimido moiety	NMe	CH_2	Aromatics	Others
(11)	2.70 (s)	2.97 (s)	5.15 (s)	7.47 (br s)	
(12)	2.63 (s)	2.90 (s)	5.07 (s)	6.7—7.4 (A_2B_2)	3.73 (s, OMe)
(13)	2.80 (s)	3.03 (s)	5.17 (s)	7.3—8.5 (m)	
(14)	2.66 (s)	2.98 (s)	4.90 (s)	7.4—8.0 (m)	
(15)	2.77 (s)	3.00 (s)	5.08 (s)		1.28 (t, *J* 7.4, Me)
					4.20 (q, *J* 7.4, OCH_2)
(16) [a]	2.77 (s, 1.8 H)	2.93 (s, 1.65 H)	5.08 (s, 1.1 H)		2.12 (s, 1.35 H)
	2.82 (s, 2.2 H)	3.12 (s, 1.35 H)	5.13 (s, 0.9 H)		2.42 (s, 1.65 H)
(17)	2.67 (s)	3.17 (s)	5.02 (s)	6.8—8.0 (A_2B_2)	
(18)	2.68 (s)	3.15 (s)	5.03 (s)	6.9—7.5 (A_2B_2)	
(19)	2.63 (s)	2.83 (s)	5.03 (s)	6.90 (d, *J* 9.0)	
				7.42 (dd, *J* 9.0, *J* 1.5)	
				7.77 (d, *J* 1.5)	
(20)	2.68 (s)	2.87 (s)	4.97 (s)	6.92 (d, *J* 9.0)	
				7.22 (dd, *J* 9.0, *J* 2)	
				7.60 (d, *J* 2)	
(21)	2.58 (s)	2.83 (s)	5.02 (s)	6.88 (d, *J* 8.0)	3.78 (s, OMe)
				7.80 (dd, *J* 8.0, *J* 2)	
				8.18 (d, *J* 2)	
(22) [b]	2.65 (s)		5.35 (s)	7.18—8.18 (A_2B_2)	
(23) [b]	2.63 (s)		5.33 (s)	7.15—7.73 (A_2B_2)	
(25) [c]		3.05	5.33 (s)	7.4 (br s)	
(26) [c]		2.88	5.33		1.40 (t, *J* 7.0, Me)
					4.08 (q, *J* 7.0, OCH_2)
(28)	2.67 (s)	2.27 (s)	4.27 (s)		
(30)	2.70 (s)		5.32 (s)	7.7 (br s)	

[a] The spectrum shows a doubling up of signals owing to the restricted rotation around the C–N bond of the amide group. [b] In $(CD_3)_2SO$. [c] In CCl_4.

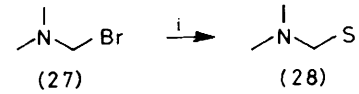
based on analytical and spectroscopic data. The ^{1}H n.m.r. spectra (see Table) clearly indicate the presence of a succinimido moiety (δ 2.58—2.80) attached to an amidomethyl (δ 4.90—5.17) or aminomethyl (δ 4.97—5.33) group. In addition the i.r. spectra (see Experimental section) all show a peak near 1 770 cm^{-1} which accords well with an imidic carbonyl absorption.

The substitution of the aromatic nucleus in compounds (19)—(21) is based on the first-order analysis of the aromatic pattern in their ^{1}H n.m.r. spectra. The higher field portion of the aromatic region shows two pairs of lines (each one proton) with a coupling constant consistent with an *ortho* arrangement. The pair of lines at lowest field is further split by a *meta*-coupling with a downfield resonating proton which appears as a doublet. The observed chemical shift of the remaining proton and the coupling constants clearly indicate a 1,2,4-ring substitution with the bromine atom *ortho* to the amino group.

It is likely that the *N*-bromomethyl derivatives (24) are intermediates in the succinimidation of the *N*,*N*-dimethyl derivatives (1)—(10). Indeed our previous study [7] has demonstrated that *N*-alkylamides, on reaction with NBS, give products which are derived from very reactive *N*-bromoalkyl derivative intermediates.

To establish the intermediacy of *N*-bromomethyl derivatives, the progress of the reactions of the amides (1) and (5) with NBS in CCl_4 was monitored by ^{1}H n.m.r. The analysis of the spectra of quenched samples showed for both the amides (1) and (5) the appearance of singlets centred at δ 5.33 which we assigned to the bromomethylene resonance of compounds (25) and (26) respectively, by comparison with the spectra of authentic samples.

On standing, free bromine was liberated while the resonances of the bromomethylene groups of (25) and (26) partially disappeared and were replaced by a new set of signals at



(27) (28)

Scheme 1. S = succinimido. *Reagents:* i, NBS

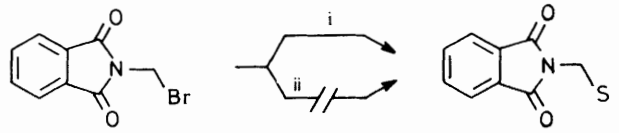
δ 5.15 and 2.70 in the former case, and at δ 5.08 and 2.77 in the latter, which clearly indicate conversion into the corresponding succinimido derivatives (11) and (15).

The bromomethylamides (25) and (26) were also detected by ^{1}H n.m.r. in the reaction of the amides (1) and (5) with NBS, in cooled (10 °C) carbon tetrachloride, with irradiation at 254—366 nm.

To confirm that the intermediate *N*-bromomethyl derivatives were directly involved in the succinimidation of the *N*,*N*-dimethyl derivatives (1)—(10) we allowed the independently synthesized *N*-bromomethyl derivatives (25)—(27) to react with NBS in carbon tetrachloride at room temperature. Immediately, free bromine was liberated and the succinimido derivatives (11) and (15) were quantitatively recovered from the reaction mixture of (25) and (26) respectively, while the succininimido derivative (28) was recovered from (27) as an unstable colourless oil which decomposed on standing.

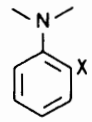
In addition, although *N*-bromomethylphthalimide (29) was unreactive towards NBS in carbon tetrachloride, it quantitatively gave the succinimido derivative (30) in nitrobenzene solution.

The evidence thus far presented shows that the succinimidation of *N*,*N*-dimethyl-amides (1)—(6) and -amines (7)—(10) occurs through two consecutive reactions: (i) a radical bromination by NBS of the *N*,*N*-dimethyl derivatives (1)—(10) which leads to the bromomethyl derivatives (24); and (ii) subsequent reaction of these intermediates with excess of NBS to give the succinimido derivatives (11)—(21).



(29) (30)

Scheme 2. S = succinimido. *Reagents:* i, NBS in $PhNO_2$; ii, NBS in CCl_4



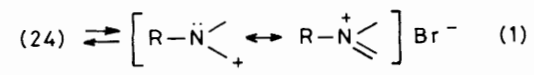
(31) X = Cl
(32) X = NO_2

The mechanism of the radical bromination will be discussed elsewhere. Here we wish to focus our attention on the reaction of NBS towards the *N*-bromomethyl derivatives (24).

It is well known that the presence of an α-nitrogen can stabilize carbonium ions derived from a variety of precursors, usually in strongly acidic media. Such azacarbonium ions [9] have been postulated to be involved in many reactions as transient species, or are detected as short-lived species under equilibrium conditions. Moreover, it has been shown that halogenomethylamines (24; R = alkyl) exist, even in the solid state, as crystalline aminocarbonium salts.[10]

In the case of halogenomethylamides (24; R = acyl), the extent of ionization of the carbon–halogen bond would be lower because the amido function is less basic than the amino function; however, the amidocarbonium ion may be expected to be more electrophilic.[9]

In view of the above described features of *N*-halogenomethyl derivatives it appears that the reaction of the intermediate *N*-bromomethyl derivatives (24) with NBS is an ionic reaction promoted by attack of an azacarbonium ion at the imidic nitrogen of NBS [equation (1)].



(24) (1)

Additional proof for the electrophilic character of the reaction arises from the observed lack of reactivity of *N*-bromomethylphthalimide (29) towards NBS in carbon tetrachloride compared to the ease with which it reacts in nitrobenzene. This drastic change in reactivity may be explained by taking into account both the 'mobility' of the halogen due to structural factors and the solvolytic power of the solvents. The presence of the two carbonyl groups in the phthalimide (29) would destabilize an intermediate imidocarbonium ion, thus making its concentration in CCl_4 extremely low. On the other hand, nitrobenzene, a solvent of high dielectric constant,[11] may solvate any ion (or ion pair) derived from breaking of the carbon–bromine bond thus enhancing the reactivity of the bromomethylimide (29) towards NBS.

The formation of the bromoaniline products (19)—(21) deserves a brief comment. Although the reactions of the anilines (7)—(10) were carried out in the presence of bubbled ethylene as scavenger of the bromine produced in the succinimidation step, competitive electrophilic bromination may occur depending on the nature of the *para* substituent. The position taken up by the bromine in the anilines (19)—(21) accords well with the rules of orientation [12] for the bromination of disubstituted benzenes. We found that the *ortho* substituted *N*,*N*-dimethylanilines (31) and (32) do not give succinimido derivatives on reaction with NBS. This may indicate that the ring-bromination at the 2-position of the aromatic nucleus in the cases of compounds (7)—(10) occurs after the succinimidation step.

The formation of some of the monosubstituted derivatives (22) and (23) in the reaction of the anilines (7) and (8) could be explained by radical bromination of the *N*-methyl of the succinimido derivatives (17) and (18) followed by a direct reaction of the resulting *N*-bromomethyl intermediates with NBS.

We believe that the evidence presented in this paper supports the mechanism proposed for the formation of succinimido derivatives (11)—(23) in the reaction of the amides (1)—(6) and arylamines (7)—(10) with NBS.

The most important point is the reaction of the intermediate bromomethyl derivatives with NBS itself which gives the final products.

Other succinimido derivatives have been found in the reaction of NBS with various substrates.[3-6] It is reasonable to assume that in these cases the reaction also occurs with the same ionic mechanism. Indeed, the intermediate bromo derivatives have similar structural features since in all cases the halogen shows some 'mobility' due to the resonance stabilization of the positive charge in the resulting cation. This behaviour could suggest a more general reactivity of NBS with any substrate able to give a stabilized carbonium ion upon dissociation.

Finally, the solvent effect is also remarkable, as shown by the behaviour of the phthalimide (29) in solvents of different polarity. As expected this trend seems to be quite general; in fact preliminary results [13] from our laboratory showed that although α-bromobenzyl benzoate does not react with NBS in carbon tetrachloride, substitution of the bromine atom by the succinimido residue occurs at room temperature in more polar media such as acetonitrile or nitrobenzene.

Experimental

M.p.s were determined on a Kofler apparatus and are uncorrected. I.r. spectra were taken on a Perkin-Elmer 225 instrument. ^1H N.m.r. spectra were recorded on a Varian EM-360A spectrometer. Alkylamides (1)—(6), arylamines (7)—(10), and the bromomethylphthalimide (29) are commercial products or were prepared by standard methods. Authentic samples of the *N*-bromomethylamides (25) and (26) were prepared analogously to the reported synthesis of *S*-ethyl *N*-bromomethyl-*N*-methylthiocarbonamide.[14] They are very reactive oils and are difficult to purify. The yields (n.m.r. based) were *ca.* 70 and 90% for (25) and (26) respectively. *N*-Bromomethyl-*N*,*N*-dimethylamine (27) was prepared by the literature method.[15]

Reaction of Amides (1)—(6) *with NBS. General Procedure.*—The amides (10 mmol) were treated with NBS (20 mmol) in refluxing carbon tetrachloride (200 ml) in the presence of a catalytic amount of benzoyl peroxide. When the liberation of the bromine began the reflux condenser was replaced by a distillation set and the mixture was distilled, keeping the volume of the carbon tetrachloride constant, until no more bromine distilled off. Chloroform (100 ml) was added and the cooled mixture was treated with aqueous Na_2SO_3–$NaHCO_3$ (30 ml). After evaporation of the dried (Na_2SO_4) organic layer the following products were obtained: N-*methyl*-N-*succinimidomethylbenzamide* (11) (98%), m.p. 116—118 °C (from

EtOH–H_2O) (Found: C, 63.6; H, 5.9; N, 11.3. $C_{13}H_{14}N_2O_3$ requires C, 63.4; H, 5.7; N, 11.4%); $\nu_{max.}$ 1 779w, 1 718, 1 647, 1 330, 1 167, 1 080, 925, 822, 797, 742, 728, and 703 cm^{-1}.

N-*Methyl*-N-*succinimidomethyl*-p-*methoxybenzamide* (12) * (70% yield after chromatography on a Merck silica gel 60 column, eluant $CHCl_3$–Me_2CO, 9 : 1), as a viscous oil (Found: C, 60.7; H, 5.7; N, 10.0. $C_{14}H_{16}N_2O_4$ requires C, 60.9; H, 5.8; N, 10.1%); $\nu_{max.}$ 1 780w, 1 710, 1 635, 1 608, 1 325, 1 248, 1 165, 1 070, 1 025, 837, 760, and 745 cm^{-1}.

N-*Methyl*-N-*succinimidomethyl*-m-*nitrobenzamide* (13) (92% yield after chromatography on a Merck silica gel 60 column, eluant $CHCl_3$–Me_2CO, 3 : 1), as a viscous oil (Found: C, 53.7; H, 4.5; N, 14.3. $C_{13}H_{13}N_3O_5$ requires C, 53.6; H, 4.5; N, 14.4%); $\nu_{max.}$ (in $CHCl_3$) 1 780w, 1 705, and 1 635 cm^{-1}.

N-*Methyl*-N-*succinimidomethylbenzenesulphonamide* (14) (96%), m.p. 134 °C (from EtOH) (Found: C, 51.3; H, 5.1; N, 10.1. $C_{12}H_{14}N_2O_4S$ requires C, 51.1; H, 5.0; 9.9%); $\nu_{max.}$ 1 763sh, 1 715, 1 346, 1 258, 1 169, 1 086, 952, 892, 822, 738, and 694 cm^{-1}.

Ethyl N-*methyl*-N-*succinimidomethylcarbamate* (15) (94%), as an oil (Found: C, 50.3; H, 6.7; N, 13.1. $C_9H_{14}N_2O_4$ requires C, 50.5; H, 6.6; N, 13.1%); $\nu_{max.}$ 1 778w, 1 695, 1 308, 1 195, and 1 140 cm^{-1}.

N-*Methyl*-N-*succinimidomethylacetamide* (16) (70% yield after chromatography on a Merck silica gel 60 column, eluant EtOAc–Et_2O) as a viscous oil (Found: C, 51.9; H, 6.8; N, 15.1. $C_8H_{12}N_2O_3$ requires C, 52.2; H, 6.6; N, 15.2%); $\nu_{max.}$ 1 775w, 1 695, 1 638, 1 390, 1 310, 1 193, 1 125, 1 005, 892, and 812 cm^{-1}.

Reaction of Amines (7)—(10) *with NBS. General Procedure.*—The amines (10 mmol) were treated with NBS (20 mmol) in refluxing carbon tetrachloride (200 ml), in the presence of a catalytic amount of benzoyl peroxide and under a fast-flowing stream of ethylene. The mixture changed colour to yellow/pale orange. Within 30 min the colour disappeared, and chloroform (100 ml) was then added and the cooled mixture was treated with aqueous Na_2SO_3–$NaHCO_3$ (50 ml). After evaporation of the dried (Na_2SO_4) organic layer the following products were obtained: N-*methyl*-N-*succinimidomethyl*-p-*nitroaniline* (17) (98%), m.p. 162 °C (from EtOH) (Found: C, 54.4; H, 4.7; N, 15.8. $C_{12}H_{13}N_3O_4$ requires C, 54.7; H, 5.0; N, 16.0%); $\nu_{max.}$ 1 748w, 1 704, 1 595, 1 302, 1 107, 898, 824, and 754 cm^{-1}, together with traces of sparingly soluble N,N-*bis*(*succinimidomethyl*)-p-*nitroaniline* (22), m.p. 299 °C (from Me_2SO) (Found: C, 53.1; H, 4.6; N, 15.6. $C_{16}H_{16}N_4O_6$ requires C, 53.3; H, 4.5; N, 15.6%); $\nu_{max.}$ 1 775w, 1 700, 1 323, 1 278, 1 220, 1 208, 1 113, 1 100, 915, 897, and 842 cm^{-1}.

N-*Methyl*-N-*succinimidomethyl*-p-*cyanoaniline* (18) (80% yield after fractional crystallization), m.p. 109—110 °C (from EtOH) (Found: C, 64.2; H, 5.2; N, 17.2. $C_{13}H_{13}N_3O_2$ requires C, 64.2; H, 5.4; N, 17.3%) $\nu_{max.}$ 2 217, 1 779w, 1 715, 1 613, 1 321, 1 127, 903, and 826 cm^{-1}, together with N-*methyl*-N-*succinimidomethyl*-o-*bromo*-p-*cyanoaniline* (19) (14%), m.p. 160—162 °C (from EtOH) (Found: C, 48.6; H, 3.9; N, 13.3. $C_{13}H_{12}BrN_3O_2$ requires C, 48.5; H, 3.7; N, 13.0%); $\nu_{max.}$ 2 218, 1 765w, 1 695, 1 105, 1 198, 1 122, 893, and 823 cm^{-1}, and traces of sparingly soluble N,N-*bis*(*succinimidomethyl*)-p-*cyanoaniline* (23), m.p. 280 °C (from Me_2SO) (Found: C, 59.9; H, 4.7; N, 16.6. $C_{17}H_{16}N_4O_4$ requires C, 60.0; H, 4.7; N, 16.5%); $\nu_{max.}$ 2 225, 1 770w, 1 690, 1 285, 1 228, 1 065, 900, and 832 cm^{-1}.

N-*Methyl*-N-*succinimidomethyl*-o-*bromo*-p-*chloroaniline* (20) (51%), m.p. 134—136 °C (from CCl_4) (Found: C, 43.3; H, 3.7; N, 8.4. $C_{12}H_{12}BrClN_2O_2$ requires C, 43.4; H, 3.6; N, 8.4%); $\nu_{max.}$ 1 770sh, 1 712, 1 198, 1 127, 1 062, 1 038, 962, 898, 820, and 802 cm^{-1}.

N-*Methyl*-N-*succinimidomethyl*-o-*bromo*-p-*methoxycarbonylaniline* (21) (52%), m.p. 106—107 °C (from CCl_4–light petroleum) (Found: C, 47.2; H, 4.4; N, 7.8. $C_{14}H_{15}N_2BrO_4$ requires C, 47.3; H, 4.2; N, 7.9%); $\nu_{max.}$ 1 775w, 1 690, 1 285, 1 245, 1 195, 1 116, 1 054, 1 035, 955, 893, 838, 770, and 766 cm^{-1}.

Reaction of N-*Bromomethyl*-N-*methylbenzamide* (25) *and Ethyl* N-*Bromomethyl*-N-*methylcarbamate* (26) *with NBS.*—The bromomethylamides (25) and (26) (10 mmol) were allowed to react with NBS (10 mmol) in CCl_4 (100 ml) at room temperature, with stirring. Free bromine was liberated immediately and the mixtures were treated with aqueous Na_2SO_3–$NaHCO_3$ to give, after evaporation of the solvent, the succinimido derivatives (11) and (15) in almost quantitative yield respectively.

Reaction of N-*Bromomethyl*-N,N-*dimethylamine* (27) *with NBS.*—The bromomethylamine (1 g, 7 mmol) was treated with NBS (1.3 g, 7 mmol) in boiling carbon tetrachloride (50 ml). After 10 min an insoluble reddish oil was separated. The oil was treated with a mixture of $CHCl_3$ (50 ml) and saturated aqueous Na_2SO_3–$NaHCO_3$ (5 ml). The yellowish organic layer was dried (Na_2SO_4) and evaporated to dryness. The yellow oil was then extracted with light petroleum, from which, after evaporation, N,N-*dimethyl*-N-*succinimidomethylamine* (28) was recovered as an unstable colourless oil which on standing turned pale yellow (60%) (Found: C, 53.8; H, 7.9; N, 17.9. $C_7H_{12}N_2O_2$ requires C, 53.9; H, 7.7; N, 18.0%); $\nu_{max.}$ 2 926, 2 820, 2 800, 1 773w, 1 700, 1 325, 1 270, 1 146, 1 052, 902, and 820 cm^{-1}.

Reaction of Bromomethylphthalimide (29) *with NBS.*—Bromomethylphthalimide (1 g, 4 mmol) was treated with NBS (0.5 g, 4 mmol) in nitrobenzene (10 ml) at 80 °C. Free bromine was liberated immediately. After 10 min chloroform (50 ml) was added and the solution was treated with aqueous Na_2SO_3–$NaHCO_3$. The solvent was dried (Na_2SO_4) and removed under reduced pressure (5 mmHg). The residue was crystallized from EtOH to give *succinimidomethylphthalimide* (30) (96%), m.p. 202—204 °C (Found: C, 60.4; H, 3.9; N, 10.8. $C_{13}H_{10}N_2O_4$ requires C, 60.5; H, 3.9; N, 10.9%); $\nu_{max.}$ 1 795, 1 748, 1 721, 1 477, 1 439, 1 339, 1 255, 1 239, 925, 721, and 712 cm^{-1}.

* To prevent ring bromination occurring a dry nitrogen stream was used to accelerate the bromine distillation.

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