Photolytic and Chromium(II)-Promoted Addition Reactions of *N*-Halogenoformamides with Alkenes

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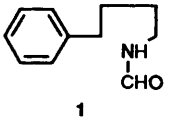
Formamidyl radicals (HCONR) do not intramolecularly abstract hydrogen or cyclise onto aromatic rings, but do add intermolecularly to alkenes. The photolytic addition of *N*-halogenoformamides to alkenes is inhibited by *N*-alkylation. However, *N*-alkyl-*N*-halogenoformamides add to alkenes in the presence of chromium(II) species. The addition of *N*-halogenoformamides to alkenes occurs regiospecifically with formamidyl bonding to the less substituted terminus of the alkene. The adducts obtained from *N*-alkylformamidyls exist as mixtures of rotameric isomers whose configurations have been assigned. The reactivity of the formamidyl radical has been discussed in terms of its conformation and electronic state.

Continuing our investigations[1,2] into the chemistry of amidyls, we have explored some reactions of *N*-alkylformamidyls (HCONR) in order to assess the influence acyl substituents could have on the reactivity of amidyl radicals. Amidyl (RCONR) and carbamyl (ROCONR) radicals, generated by photolysis of *N*-halogeno amides[1,3-5] and *N*-halogeno carbamates,[6] respectively, readily abstract hydrogen *via* six-membered transition states. Chow and co-workers[7] have shown that the abstraction occurs through nitrogen, and preferentially from the δ-position of the *N*-alkyl side-chain.

Results and Discussion

(i) *Photolysis Reactions.*—Irradiation of either *N*-(4-phenylbutyl)formamide **1** in the presence of *tert*-butyl hypochlorite and iodine, or of its *N*-iodo derivative, failed to give any products resulting from hydrogen abstraction of a benzylic hydrogen. Furthermore, in contrast to the photolysis reactions of *N*-methylbiphenyl-2-carboxamide in the presence of *tert*-butyl hypoiodite[8] and benzyl *N*-bromo-*N*-methylcarbamate,[2] both of which produced products resulting from intramolecular cyclisation, *N*-(*o*-phenylbenzyl)formamide underwent no cyclisation when irradiated after treatment with *tert*-butyl hypochlorite and iodine. These observations indicate a clear difference in reactivity between formamidyl and amidyl radicals.



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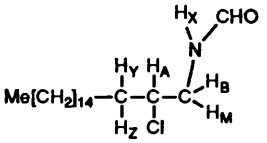
Formamidyl radicals were, however, found to add intermolecularly to alkenes. These reactions were accomplished by irradiation of *N*-chloro- and *N*-bromo-formamides in the presence of a series of alkenes. The adducts obtained and their yields are given in Table 1. The *N*-chloroformamides were only sparingly soluble in dichloromethane and displayed UV absorptions at shorter wavelengths than 280 nm. Hence their irradiations were carried out on dilute solutions contained in quartz flasks. The results demonstrate that *N*-substituents impede the photochemical addition reaction of *N*-chloroformamide with alkenes. Addition could not be effected with electron-deficient alkenes. The photodecomposition of *N*-chloroformamide was severely retarded in the presence of benzylideneacetone, with the former displaying a half-life of *ca.* one week. This is presumably due to strong absorption of the radiation by benzylideneacetone, thereby screening the *N*-chloroformamide. The photochemical reaction of *N*-chloroformamide with dihydropyran gave a complex mixture which could not be satisfactorily resolved.



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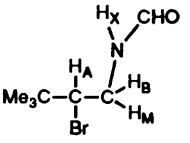

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The regiospecificity of addition of *N*-halogenoformamides to monosubstituted alkenes has been established by NMR analysis of the adducts **2** and **3** obtained from photolysis reactions. The ^{1}H NMR spectrum of adduct **2** is characterised by an ABMXYZ spin system in which H_A is assigned to the methine proton and H_B and H_M, and H_Y and H_Z, the respective adjacent diastereotopic proton pairs. The large chemical shift between the diastereotopic methylene protons H_B and H_M is similar to that reported by Lessard and Tuaillon[9] in the spectrum of *N*-(2-bromo-3,3-dimethylbutyl)trichloroacetamide. Both H_B and H_M display coupling with the amino proton (H_X) which disappears when D_2O is added. Since the nitrogen atom must therefore be bonded to a methylene and not a methine carbon, the structure of adduct **2** and consequently the regioselectivity of addition of *N*-chloroformamide to octadec-1-ene, are clearly established. This conclusion is further supported by off-resonance ^{13}C data for adduct **2**. The most deshielded side-chain carbon is expected to be the one bonded to chlorine. This carbon resonates as a doublet at δ_C 62.66 while the NCH_2 carbon appears as a triplet at δ_C 44.18.

The ^{1}H NMR spectrum of adduct **3** displays an ABMX spin system in which the splittings of both H_B and H_M are simplified after shaking with D_2O, while H_A remains unaffected. As in the case of adduct **2**, H_B and H_M are assigned to the methylene protons which couple with NH_X. Hence the orientation of addition in adduct **3** is the same as in adduct **2**.

An off-resonance ^{13}C NMR spectrum reveals that the methine carbon resonates as a doublet at δ_C 70.17 and the methylene carbon as a triplet at δ_C 41.43, which confirms the above assignment. The observed ^{13}C–^{1}H coupling constants for the methine and methylene carbons are similar to those reported[10] for the adduct obtained from methyl *N*-bromo-*N*-methylcarbamate and 3,3-dimethylbutane.

Table 1 Photolysis of *N*-halogeno formamides (R·NX·CHO) in the presence of Alkenes

Formamide				
R	X	Alkene	Adduct	Yield (%)
Bu	Cl	Cyclohexene	*N*-Butyl-*N*-(2-chlorohexyl)formamide	6
$PhCH_2$	Cl	Cyclohexene		0
H	Cl	Cyclohexene	*N*-(2-chlorocyclohexyl)formamide	35
H	Cl	Norbornene	*N*-(3-Chloro[2.2.1]bicyclohexan-2-yl)formamide	33
H	Cl	Octadec-1-ene	*N*-(2-Chlorooctadec-1-yl)formamide **2**	51
H	Cl	3,3-Dimethylbut-1-ene	*N*-(2-Chloro-3,3-dimethylbutyl)formamide	61
H	Cl	1-Acetylcyclohexene		0
H	Cl	Dihydropyran		0
H	Cl	Benzylideneacetone		0
Bu	Br	Cyclohexene		0
H	Br	3,3-Dimethylbut-1-ene	*N*-(2-Bromo-3,3-dimethylbutyl)formamide **3**	18

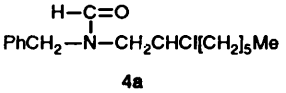
Table 2 Chromium(II)-promoted addition of *N*-halogenoformamides (RN(X)CHO) to Alkenes

Formamide				
R	X	Alkene	Adduct	Yield (%)
$PhCH_2$	Cl	Cyclohexene	*N*-Benzyl-*N*-(2-chlorocyclohexyl)formamide	38
$PhCH_2$	Cl	Pent-1-ene	*N*-Benzyl-*N*-(2-chloropentyl)formamide	42
$PhCH_2$	Cl	Oct-1-ene	*N*-Benzyl-*N*-(2-chlorooctyl)formamide **4**	17
Bu	Cl	Cyclohexene	*N*-Butyl-*N*-(2-chlorocyclohexyl)formamide	28
Bu	Cl	Oct-1-ene	*N*-Butyl-*N*-(2-chlorooctyl)formamide **5**	7
H	Cl	Cyclohexene	*N*-(2-Chlorocyclohexyl)formamide	23
H	Cl	3,3-Dimethylbut-1-ene	*N*-(2-Chloro-3,3-dimethylbutyl)formamide	33
H	Cl	Benzylideneacetone		0
H	Cl	1-Acetylcyclohexene		0
$PhCH_2$	Br	Cyclohexene	*N*-Benzyl-*N*-(2-bromocyclohexyl)formamide	24
H	Br	Cyclohexene	*N*-(2-Bromocyclohexyl)formamide	14
H	Br	3,3-Dimethylbut-1-ene	*N*-(2-Bromo-3,3-dimethylbutyl)formamide	21
H	Br	1-Acetylcyclohexene		0

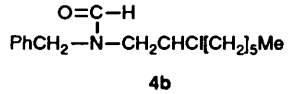
(ii) *Chromium*(II) *Reactions.*—Lessard and co-workers[11] have shown that chromium(II) salts are effective reducing agents for generating amidyl radicals from *N*-halogeno amides. This procedure was applied during our investigation of the reactions of *N*-halogenoformamides with olefins. The adducts obtained are given in Table 2. In contrast to the photochemical additions to alkenes which were strongly impeded by *N*-substituents on the formamide, *N*-alkyl-*N*-halogenoformamides underwent addition reactions with alkenes in the presence of chromium(II) salts. These results therefore demonstrate that the failure of *N*-alkyl-substituted formyl radicals to add to olefins in the photolysis reactions cannot be solely attributed to steric effects. However, as in the photolysis reactions, no reaction occurred with electron-deficient alkenes. We attribute the greater reactivity of *N*-halogenoformamides in the redox reactions to the acidic conditions under which these reactions were conducted. It is possible that the formamidyl radical is protonated prior to it attacking the alkene. Protonation is likely to increase the electrophilicity of the formamidyl radical and hence its reactivity towards alkenes, analogously to that observed for protonated alkoxyl radicals.[12]

Similarly to the photochemical reactions, the chromium(II)-initiated addition of *N*-halogenoformamides was regiospecific with the addition reaction being initiated by formamidyl attack at the less hindered terminus of the double bond.

The ^{1}H NMR spectrum of the adduct **4** obtained from the chromium(II)-catalysed addition of *N*-benzyl-*N*-chloroformamide to oct-1-ene is characterised by duplication of its formyl, *N*-methylene and methine signals. This arises from restricted rotation about the N–CHO bond as a result of its well developed π-character. The adduct consequently exists as a pair of rotamers (**4a** and **4b**) whose rate of interconversion is slow with respect to the NMR time-scale. The spectrum is further



4a



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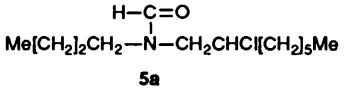

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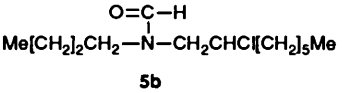


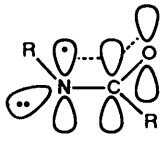
5b

complicated by the chiral centre (–CHCl–)which renders methylene proton pairs diastereotopic. However, the chemical shifts of the –CHO, $-CH_2Ph$ and $-NCH_2CHCl-$ protons were correlated for the two rotamers with the aid of a COSY 2D-spectrum. Proton–carbon connectivities were established with a HETCOR spectrum. These spectra are consistent only with the structures **4a** and **4b**, in which the *N*-benzylformamidyl radical has added regioselectively to the 1-position of oct-1-ene.

The ^{1}H NMR spectrum of the rotameric adducts **5a** and **5b** obtained from the chromium(II)-catalysed addition of *N*-butyl-*N*-chloroformamide to oct-1-ene shows similarities to that of the rotamers **4a** and **4b**.

The failure of formamidyl radicals to undergo intramolecular hydrogen abstraction can be due to neither unfavourable steric nor electrophilicity factors since nitrogen-centred formamidyl radicals would be expected to be less hindered and more electrophilic than amidyl radicals, whose abstraction reactions have been shown to be promoted by electron-donating groups attached to the abstraction site.[13] It has been established that

amidyls have a π-electronic ground state[14] **6** and it has been suggested[7] that intramolecular 1,6-hydrogen abstraction by amidyls in the Σ-electronic state is not energetically feasible since this electronic state precludes a collinear arrangement of the orbital containing the unpaired electron and the orbitals of the C–H bond in the transition state. Ar_1-5 Cyclisation of biphenyl-2-carboxamides has been proposed[8] to occur from the radical in the higher energy Σ-electronic state. Hence the failure of *N*-alkylformamidyls to react similarly could be due to differences in their electronic ground states. For steric and electronic reasons that arrangement in which the carbonyl oxygen atom and nitrogen non-bonding orbital are *anti* is preferred for acyclic amidyls.[12] The π-electronic state for the amidyl **2** is favoured since interaction of the p-orbital on nitrogen with the carbonyl leads to a greater reduction in energy when the p-orbital is singly occupied. One possible explantion for the difference in reactivity of formamidyls is that their favoured conformation contains the carbonyl group and the nitrogen non-bonding orbital in a *syn*-arrangement **7**. Dipolar interaction would then be minimised if the non-bonding orbital were to be singly occupied. Hence we suggest that a greater contribution of the Σ-electronic state to the ground state of formamidyls **7** relative to amidyls could reduce their reactivity in intramolecular hydrogen abstraction.



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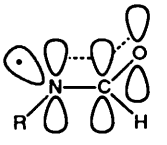

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Experimental

M.p.s were determined in a tube with a Gallenkamp melting point apparatus and are uncorrected. IR spectra were run on a Perkin-Elmer infrared spectrophotometer, Model 297. 60 MHz ^{1}H NMR spectra were recorded on a Perkin-Elmer R12 A spectrometer and 200 MHz ^{1}H and 50 MHz ^{13}C spectra on a Varian Gemini spectrometer. 300 MHz ^{1}H and 75 MHz ^{13}C spectra and 500 MHz ^{1}H and 125 MHz ^{13}C NMR spectra were recorded on a Bruker AM300 and a Bruker WM500 spectrometer, respectively, at the NCRL/CSIR laboratories in Pretoria. *J*-values are given in Hz. UV spectra were recorded on a Varian Techtron spectrophotometer, Series 634. Light petroleum refers to the fraction boiling in the range 40–60 °C.

N-(4-*Phenylbutyl*)*formamide* **1**.—A solution of 4-phenylbutylamine (3.2 g, 21 mmol) and formic acid (9.66 g, 210 mmol) in toluene (50 cm^3) was heated under reflux in a Dean–Stark apparatus for 24 h. The reaction solution was concentrated under reduced pressure to give an oil which, after distillation, afforded *N*-(4-phenylbutyl)formamide **1** (1.03 g, 27.8%), b.p. 250 °C/0.75 mmHg, $\nu_{max}(CHCl_3)$/cm^{-1} 3450 and 1690; δ_H (CCl_4) 1.15–1.86 (4 H, m), 2.25–2.70 (2 H, m), 2.30–3.38 (2 H, m), 7.05 (5 H, s), 7.46–7.83 (1 H, br s) and 7.93 (1 H, s) (Found: C, 74.6; H, 8.7; N, 8.3. Calc. for $C_{11}H_{15}NO$: C, 74.6; H, 8.5; N, 7.9%).

N-(2-*Phenylbenzyl*)*formamide*.—A solution of (2-phenyl)-benzylamine (4.6 g, 25 mmol) and formic acid (11.5 g, 250 mmol) in toluene (50 cm^3) was heated under reflux in a Dean–Stark apparatus for 24 h. The solution was concentrated under reduced pressure to give a solid, which was recrystallised from diethyl ether to afford *N*-(2-phenylbenzyl)formamide, m.p. 82–88 °C; $\nu_{max}(CHCl_3)$/cm^{-1} 3450, 3010, 2875 and 1690; $\delta_H(CDCl_3)$ 4.20–4.50 (2 H, d), 5.40–6.10 (1 H, br s), 7.25 (9 H, s) and 7.99 (1 H, s) (Found: C, 79.9; H, 5.9; N, 6.2. Calc. for $C_{14}H_{13}NO$: C, 79.6; H, 6.2; N, 6.6%).

N-*Benzyl*-N-*butylformamide*.—Benzaldehyde (5 g, 47 mmol) and butylamine (3.44 g, 47 mmol) were heated in benzene (100 cm^3) in a Dean–Stark apparatus until liberation of water ceased. The reaction mixture after work-up afforded benzylidenebutylamine, which was reduced with excess of sodium borohydride to *N*-benzyl-*N*-butylamine and then condensed with formic acid to afford *N*-benzyl-*N*-butylformamide, b.p. 220 °C/8 mmHg; $\delta_H(CDCl_3)$ 8.27 ($\frac{1}{2}$ H, s), 8.18 ($\frac{1}{2}$ H, s), 7.27 (5 H, m), 4.52 (1 H, s), 4.38 (1 H, s). 3.21 (1 H, t), 3.12 (1 H, t) 1.37 (4 H, dm) and 0.9 (3 H, t).

N-*Bromoformamide*.—Potassium *tert*-butoxide (14.9 g, 133 mmol) was added to a stirred, cooled solution of bromine (21.3 g, 7.1 cm^3, 133 mmol) in dichloromethane (150 cm^3) and the mixture was stirred for 1 h in the dark. Formamide (1.49 g, 33 mmol) was added to the reaction mixture, which was then stirred for a further 1 h. After filtration under suction, the mother liquor was concentrated (<40 °C) in the dark under reduced pressure to afford a brown oil. Lixiviation with light petroleum yielded *N*-bromoformamide as an unstable yellow solid, m.p. 60–66 °C; λ_{max} 268 nm (Found: Br, 51. Calc. for CH_2BrNO: Br, 64.5%).

N-*Alkyl*-N-*bromoformamides*.[15]—Bromine (1.73 cm^3, 30 mmol) was added to a mixture containing the formamide (20 mmol), dichloromethane (150 cm^3), and saturated aq. sodium hydrogen carbonate (100 cm^3). The resultant mixture was stirred vigorously at 20 °C in the dark for 24 h. After this period a further amount of bromine (1.73 cm^3, 30 mmol) was added and the mixture was stirred for a further 24 h. After being cooled to 0 °C, the organic layer was separated, washed with cold, saturated aq. sodium hydrogen carbonate and dried (Na_2SO_4). The solvent was evaporated off under reduced pressure and the residue was analysed for positive halogen by iodometry.

(a) *N*-Bromo-*N*-butylformamide was an oil, ν_{max}/cm^{-1} 1670 (Found: Br, 35.3. Calc. for $C_5H_{10}BrNO$: Br, 44%).

(b) *N*-Benzyl-*N*-bromoformamide was an oil (Found: Br, 33.8. Calc. for C_8H_8BrNO: Br, 37%).

General Procedure for the Synthesis of N-*Chloroformamides*.[11]—The formamide (20 mmol), suspended in chloroform (40 cm^3) containing *tert*-butyl hypochlorite (24 mmol), was treated with bromine (2 drops) and the mixture was stirred at ambient temperature until the solution became clear (*ca.* 10 min). After being stirred for a further 20 min the mixture was evaporated under reduced pressure and the residue was analysed for positive halogen by iodometry.

(a) *N*-Chloroformamide had m.p. 51–55 °C (decomp.), $\nu_{max}(CHCl_3)$/cm^{-1} 3160br and 1690; λ_{max} 215 nm. (Found: Cl, 44.6. Calc. for CH_2ClNO: Cl, 44.65%).

(b) *N*-Butyl-*N*-chloroformamide was an oil, $\nu_{max}(CHCl_3)$/cm^{-1} 1680; $\delta_H(CDCl_3)$ 0.75–1.96 (7 H, m), 3.41–3.78 (2 H, t) and 8.09 (1 H, s) (Found: Cl, 21.5. Calc. for $C_5H_{10}ClNO$: Cl, 26.2%).

(c) *N*-Benzyl-*N*-chloroformamide was an oil, $\nu_{max}(CHCl_3)$/cm^{-1} 1680; $\delta_H(CDCl_3)$ 4.51 (2 H, s), 7.13 (5 H, s) and 8.45 (1 H, s) (Found: Cl, 18.8. Calc. for C_8H_8ClNO: Cl, 20.9%).

N-*Iodo*-N-(4-*phenylbutyl*)*formamide*.[3]—A mixture of *N*-(4-phenylbutyl)formamide (1.0 g, 5.6 mmol) and iodine (4.63 g, 18.1 mmol) in benzene (65 cm^3) was treated with *tert*-butyl hypochlorite (1.5 cm^3, 13.1 mmol) and stirred for 30 min in the dark. Addition of light petroleum deposited a gum, and the mother liquor was poured off. The gum was washed with light petroleum to give *N*-iodo-*N*-(4-phenylbutyl)formamide, $\nu_{max}(CHCl_3)$/cm^{-1} 1660 (Found: I, 36.9. Calc. for $C_{11}H_{14}INO$: I, 41.9%).

General Procedure for Irradiation of N-*Chloroformamides in the Presence of Olefins.*—The previously reported[16] method was followed. The results are summarised in Table 1.

(a) *N*-Butyl-*N*-chloroformamide (2.75 g, 20 mmol) and cyclohexene (3.70 g, 45 mmol) in dry dichloromethane irradiated for 1 week afforded an oil, which was separated by chromatography on silica gel plates ($CHCl_3$) into five fractions. The fraction with the third highest R_f-value was an oil (0.21 g), which was distilled (130–133 °C/0.6 mmHg) to afford *N*-butyl-*N*-(2-chlorocyclohexyl)formamide, ν_{max}(film)/cm^{-1} 1670; δ_H($CDCl_3$) 0.70–2.60 (15 H, m), 2.95–4.10 (4 H, m) and 8.05 (1 H, s) (Found: C, 60.2; H, 9.4; N, 6.6. Calc. for $C_{11}H_{20}ClNO$: C, 60.7; H, 9.2; N, 6.4%).

(b) *N*-Benzyl-*N*-chloroformamide (5.60 g, 33 mmol) and cyclohexene (8.20 g, 100 mmol) in dry dichloromethane (100 cm^3) irradiated for 68 h afforded an intractable oil (9.50 g).

(c) *N*-Chloroformamide (3.30 g, 42 mmol) and cyclohexene (7.00 g, 85 mmol) in dichloromethane (100 cm^3) irradiated for 15 h afforded an oil (6.51 g), of which a portion (3.00 g) was separated by chromatography on silica gel plates [MeOH–$CHCl_3$ (4:96)] into three fractions. The fraction with the second highest R_f-value was a solid (1.08 g), which was recrystallised from benzene–light petroleum to afford *N*-(2-chlorocyclohexyl)formamide, m.p. 67.5–70 °C; ν_{max}($CHCl_3$)/cm^{-1} 3420 and 1680; δ_H(CCl_4) 0.90–2.25 (8 H, m), 3.60–4.60 (2 H, m), 7.55 (1 H, br d) and 8.00 (1 H, s) (Found: C, 52.0; H, 7.1; N, 8.5. Calc. for $C_7H_{12}ClNO$: C, 52.0; H, 7.4; N, 8.7%).

(d) *N*-Chloroformamide (3.20 g, 41 mmol) and norbornene (7.70 g, 82 mmol) in dichloromethane (100 cm^3) irradiated for 19 h afforded an oil (14.00 g), of which a portion (3.00 g) was separated by chromatography on silica gel plates [MeOH–$CHCl_3$ (4:96)] into four fractions. The fraction with the third highest R_f-value was a solid (0.50 g), which was recrystallised from tetrachloromethane to afford *N*-(2-chloronorbornyl)-formamide, m.p. 133.5–135.5 °C; ν_{max}($CHCl_3$)/cm^{-3} 3420, 2960, 2870 and 1680; δ_H($CDCl_3$) 0.90–2.60 (8 H, m), 3.95–4.20 (2 H, m), 5.70–6.70 (1 H, br s) and 8.15 (1 H, s) (Found: C, 55.0; H, 6.9; N, 8.3. Calc. for $C_8H_{12}ClNO$: C, 55.3; H, 6.9; N, 8.1%).

(e) *N*-Chloroformamide (3.00 g, 38 mmol) and octadec-1-ene (19.20 g, 76 mmol) in dichloromethane (150 cm^3) irradiated for 19 h afforded a solid (21.90 g), of which a portion (3.00 g) was separated by chromatography on silica gel plates ($CHCl_3$) into four fractions. The fraction with the second highest R_f-value was a solid (0.88 g), which was recrystallised from light petroleum to afford *N*-(2-chlorooctadecyl)formamide **2**, m.p. 52–53 °C; ν_{max}($CHCl_3$)/cm^{-1} 3450 and 1690; δ_H(300 MHz) 8.19 (d, *J* 1.49, CHO), 6.09 (br, NH_X), 3.98 (dddd, J_{AB} 3.56, J_{AM} 8.18, J_{AY} 8.43, J_{AZ} 4.35, CH_ACl), 3.80 (dddd, J_{BA} 3.56, J_{BM} 14.06, J_{BX} 7.04, *J* 0.65,* NCH_B), 3.29 (ddd, J_{MA} 8.18, J_{MB} 14.06, J_{MX} 5.51, NCH_M), 1.75–1.65 (m, $CH_YH_Z[CH_2]_{14}Me$), 1.50–1.35 (m, $CH_2[CH_2]_{13}Me$), 1.23 (s, $[CH_2]_{13}Me$) and 0.85 (t, Me); δ_C (75 MHz) 161.09 (d), 62.66 (d), 44.18 (t), 35.71 (t), 31.87 (t), 29.63–28.99 (m), 26.21 (t), 22.63 (t) and 14.04 (q). (Found: C, 68.6; H, 11.6; N, 4.3. Calc. for $C_{19}H_{38}ClNO$: C, 68.8; H, 11.5; N, 4.2%).

(f) *N*-Chloroformamide (4.00 g, 50 mmol) and 3,3-dimethylbut-1-ene (8.40 g, 100 mmol) in dichloromethane (150 cm^3) irradiated for 14 h afforded an oil (7 g), of which a portion (3.0 g) was separated by chromatography on silica gel plates [MeOH–$CHCl_3$ (4:96)] into three fractions. The fraction with the second highest R_f-value was an oil (2.20 g), which was distilled (125 °C/0.75 mmHg) to afford *N*-(2-chloro-3,3-dimethylbutyl)formamide, ν_{max}($CHCl_3$)/cm^{-1} 3430 and 1680; δ_H(CCl_4) 1.05 (9 H, m), 2.60–4.20 (3 H, m), 7.10–7.90 (1 H, br s) and 8.08 (1 H, s). (Found: C, 51.3; H, 8.4; N, 8.4. Calc. for $C_7H_{14}ClNO$: C, 51.4; H, 8.6; N, 8.6%).

(g) *N*-Chloroformamide (4.40 g, 56 mmol) and 1-acetylcyclohexene (13.9 g, 112 mmol) in dichloromethane (150 cm^3) irradiated for 42 h afforded an oil (17.0 g), of which a portion (1.8 g) was separated by chromatography on silica gel plates [MeOH–$CHCl_3$ (4:96)]. The only significant fraction was recovered 1-acetylcyclohexene (1.056 g, 72% recovery), identical (NMR, IR and TLC) with an authentic sample.

(h) *N*-Chloroformamide (4.00 g, 50 mmol) and dihydropyran (8.40 g, 100 mmol) in dichloromethane (150 cm^3) irradiated for *ca.* 72 h afforded an oil, shown by TLC to be a complex mixture which could not be separated by chromatography on silica gel plates.

(i) A mixture of *N*-chloroformamide (3.04 g, 38 mmol) and benzylideneacetone (11.1 g, 76 mmol) in dichloromethane (150 cm^3) was irradiated for 1 week, after which time 48% positive chlorine was shown to be present by iodometry.

Dark Reaction of N-*Bromoformamide and Cyclohexene.*—*N*-Bromoformamide (1.50 g, 121 mmol) and cyclohexene (2.00 g, 24 mmol) in acetonitrile (75 cm^3) kept in the dark at ambient temperature for 6 days afforded an oil, shown by TLC [MeOH–$CHCl_3$ (4:96)] to be a complex mixture which could not be separated. Repetition of this experiment with dichloromethane as solvent gave identical results.

General Procedure for Irradiation of N-*Bromoformamides in the Presence of Olefins.*—The irradiation of *N*-bromoformamides was carried out as for *N*-chloroformamides except that the reaction vessel was Pyrex and the lamp was placed under the Pyrex cooling bath. The results are summarised in Table 1.

(a) *N*-Bromo-*N*-butylformamide (2.55 g, 14.2 mmol) and cyclohexene (2.33 g, 28.4 mmol) in dichloromethane (150 cm^3) irradiated for 36 h afforded an oil (3.40 g) which was shown by TLC to be a complex mixture. Separation of a portion (3.00 g) by chromatography on silica gel plates [MeOH–$CHCl_3$ (3:97)] afforded *N*-butylformamide (0.125 g, 10%) as the major component, identical (NMR, IR and TLC) with an authentic sample.

(b) *N*-Bromoformamide (2.40 g, 19.0 mol) and 3,3-dimethylbut-1-ene (3.2 g, 38 mmol) in dichloromethane (80 cm^3) irradiated for 13 h afforded an oil, which was separated by chromatography on silica gel plates [MeOH–$CHCl_3$ (4:96)] into six fractions. The fraction with the fourth highest R_f-value was a solid (0.431 g), which was recrystallised from light petroleum to afford *N*-(2-bromo-3,3-dimethylbutyl)-*N*-butylformamide, identical (NMR, IR, TLC and m.p.) with a sample prepared by chromium(II) reduction (Found: C, 40.6; H, 6.7; N, 7.1. Calc. for $C_7H_{14}BrNO$: C, 40.4; H, 6.7; N, 6.7%).

Irradiation of N-*Iodoformamides.*—(a) (i) *N*-(4-Phenylbutyl)-formamide (1.60 g, 9 mmol) and iodine (7.40 g, 29 mmol) in stirred benzene (50 cm^3) were treated with *tert*-butyl hypochlorite (2.40 cm^3, 21 mmol) for 15 min at ambient temperature. The stirred reaction mixture was photolysed with a medium-pressure mercury lamp at <30 °C for 5 h, more *tert*-butyl hypochlorite (3 × 0.8 cm^3) being added after the first three successive hours. The reaction mixture was washed in turn with aq. sodium thiosulfate solution and water, then dried (Na_2SO_4), and concentrated under reduced pressure to yield an oil. The oil was identical (NMR, IR) with an authentic sample of *N*-(4-phenylbutyl)formamide.

(ii) *N*-iodo-*N*-(4-phenylbutyl)formamide (0.348 g containing 70% N–I, 8 × 10^{-4} mol) in benzene (50 cm^3) was irradiated with a medium-pressure mercury lamp at <30 °C for 16 h. Analysis of an aliquot (4 cm^3) indicated that 36.4% of the *N*-iodo derivative was still present. The solution was heated under

* This coupling is attributed to the formyl proton. Although it is not evident in the formyl signal, the lines are broadened.

reflux and irradiated for a further 3 h after which time the reaction solution contained 13.4% of the *N*-iodo derivative.

(b) *N*-(2-Phenylbenzyl)formamide (0.9 g, 4.3 mmol) and iodine (3.50 g, 14 mmol) in stirred benzene (50 cm^3) were treated with *tert*-butyl hypochlorite (2.40 cm^3, 21 mmol) for 15 min and photolysed with a medium-pressure mercury lamp at < 30 °C for 4 h with *tert*-butyl hypochlorite (3 × 0.8 cm^3) being added after the first 3 successive hours. The stirred reaction mixture was then photolysed for a further 3.75 h under reflux. Work-up as before afforded a solid, identical (NMR, IR) with an authentic sample of *N*-(2-phenylbenzyl)formamide.

General Procedure for Chromium(II) *Chloride-promoted Additions of* N-*Halogenoformamides to Olefins.*—The reactions were carried out according to a published procedure.[11] Yields indicated are of isolated products based on the *N*-halogenoformamides and products other than adducts were not investigated. The results are summarised in Table 2.

(a) A solution of cyclohexene (2 cm^3, 20 mmol) in chloroform (4 cm^3) was added to a solution of *N*-benzyl-*N*-chloroformamide (1.70 g, 10 mmol) in a mixture of chloroform (6 cm^3) and absolute methanol (2 cm^3). The resulting solution, after treatment with the chromium(II) solution, afforded a light yellow oil, which was separated by chromatography on silica gel plates ($CHCl_3$) into three fractions. The fraction with the second highest R_f-value was an oil (0.954 g) which was crude *N*-benzyl-*N*-(2-chlorocyclohexyl)formamide, $\nu_{max}(CHCl_3)/cm^{-1}$ 1662; $\delta_H(CCl_4)$ 0.50–2.45 (11 H, m), 2.80–4.85 (4 H, m), 7.15 (5 H, d) and 8.12 (1 H, s), which decomposed on distillation (190 °C/0.7 mmHg).

(b) The product obtained from reaction of pent-1-ene (1.70 g, 24 mmol), *N*-benzyl-*N*-chloroformamide (2 g, 12 mmol) and the chromium(II) solution was separated by chromatography into three fractions. The fraction with the second highest R_f-value was an oil (1.39 g), which was distilled (110 °C/1.0 mmHg) to afford *N*-benzyl-*N*-(2-chloropentyl)formamide, $\nu_{max}(CHCl_3)/cm^{-1}$ 2950, 2870 and 1660; $\delta_H(CCl_4)$ 0.50–2.16 (7 H, m), 2.75–4.90 (5 H, m), 6.60–7.65 (5 H, s) and 8.1 (1 H, d) (Found: C, 64.5; H, 7.5; N, 6.4. Calc. for $C_{13}H_{18}ClNO$: C, 65.2; H, 7.6; N, 5.85%).

(c) The product obtained from reaction of cyclohexene (2 cm^3, 20 mmol), *N*-butyl-*N*-chloroformamide (1.01 g, 7.5 mmol) and the chromium(II) solution gave, after chromatography, an oil (0.450 g), which was distilled (115 °C/0.06 mmHg) to afford *N*-butyl-*N*-(2-chlorocyclohexyl)formamide, ν_{max} 1660 cm^{-1}; $\delta_H(CDCl_3)$ 0.60–2.65 (15 H, m), 2.80–4.20 (4 H, m) and 7.93 (1 H, s) (Found: C, 61.2; H, 10.0; N, 6.4. Calc. for $C_{11}H_{20}ClNO$: C, 60.7; H, 9.3; H, 6.4%).

(d) Reaction of cyclohexene (2.0 cm^3, 20 mmol), *N*-chloroformamide (0.83 g, 10 mmol) and the chromium(II) solution and then chromatography gave a solid (0.372 g), which recrystallised from benzene–light petroleum to afford *N*-(2-chlorocyclohexyl)formamide, m.p. 74–76 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3425 and 1680; $\delta_H(CDCl_3)$ 0.80–2.50 (8 H, m), 2.80–4.25 (2 H, m), 6.00–7.10 (1 H, br s) and 8.03 (1 H, m) (Found: C, 52.3; H, 7.5; N, 9.0. Calc. for $C_7H_{12}ClNO$: C, 52.0; H, 7.4; N, 8.7%).

(e) 3,3-Dimethylbut-1-ene (1.70 g, 20 mmol), *N*-chloroformamide (0.8 g, 10 mmol) and the chromium(II) solution gave, after chromatography, an oil (0.524 g), which was distilled (85 °C/0.7 mmHg) to afford *N*-(2-chloro-3,3-dimethylbutyl)-formamide, $\nu_{max}(CHCl_3)/cm^{-1}$ 3430 and 1682; $\delta_H(CDCl_3)$ 1.05 (9 H, s), 2.40–4.40 (3 H, m), 6.30–7.45 (1 H, br s) and 8.10 (1 H, s) (Found: C, 51.4; H, 8.8; N, 8.4. Calc. for $C_7H_{14}ClNO$: C, 51.4; H, 8.6; N, 8.6%).

(f) Benzylideneacetone was recovered unchanged after reaction with *N*-chloroformamide.

(g) 1-Acetylcyclohexene was recovered unchanged after reaction with *N*-chloroformamide.

(h) Cyclohexene (3.5 g, 42 mmol), *N*-benzyl-*N*-bromoformamide (4.5 g, 21 mmol) and the chromium(II) solution gave, after chromatography, crude *N*-benzyl-*N*-(2-bromocyclohexyl)formamide (1.4 g), $\nu_{max}(CHCl_3)/cm^{-1}$ 3340 and 1655; $\delta_H(CDCl_3)$ 0.75–2.70 (8 H, m), 4.00–5.10 (4 H, m) 7.20 (5 H, s) and 8.10–8.40 (1 H, m) (Found: C, 57.6; H, 6.35; N, 4.8. Calc. for $C_{14}H_{18}BrNO$: C, 56.8; H, 6.1; N, 4.7%).

(i) Cyclohexene (1.60 g, 19 mmol), *N*-bromoformamide (1.20 g, 9.8 mmol) and the chromium(II) solution gave, after chromatography, a solid (0.283 g), which was recrystallised from benzene–light petroleum to afford *N*-(2-bromocyclohexyl)formamide, m.p. 83.5–85 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3410 and 1680; $\delta_H(CDCl_3)$ 1.00–2.50 (8 H, m), 3.60–4.80 (2 H, m), 5.70–6.67 (1 H, br s) and 8.07 (1 H, s) (Found: C, 40.8; H, 5.9; N, 6.8. Calc. for $C_7H_{12}BrNO$: C, 40.8; H, 5.8; N, 6.8%) and a solid (0.286 g), which was recrystallised from benzene–light petroleum to afford a second isomer of *N*-(2-bromocyclohexyl)-formamide, m.p. 93–95 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 3425, 2940, 2860 and 1685; $\delta_H(CDCl_3)$ 0.70–2.77 (8 H, m), 3.00–4.30 (2 H, m), 6.50–7.50 (1 H, br s) and 8.10 (1 H, s) (Found: C, 40.8; H, 5.9; N, 6.8. Calc. for $C_7H_{12}BrNO$: C, 40.8; H, 5.8; N, 6.8%).

(j) 3,3-Dimethylbut-1-ene (1.64 g, 19.4 mmol), *N*-bromoformamide and the chromium(II) solution gave, after chromatography, a solid (0.423 g), which was recrystallised from benzene–light petroleum to afford *N*-(2-bromo-3,3-dimethyl butyl) formamide **3**, m.p. 62.5–64.5 °C; δ_H(500 MHz) 8.19 (s, CHO), 5.99 (br, NH_X), 3.96 (dd, J_{AB} 2.37, J_{AM} 10.78, CH_ABr), 4.25 (dddd, J_{BA} 2.37, J_{BM} 14.55, J_{BX} 8.16, J 0.79,* NCH_B), 3.09 (ddd, J_{MA} 10.78, J_{MB} 14.55, J_{MX} 3.82, NCH_M) and 1.09 (s, Me); δ_C (125 MH_Z) 168.89 (d), 70.17 (d), 41.43 (t), 35.36 (s) and 27.44 (q) (Found: C, 40.3; H, 6.3; N, 7.1. Calc. for $C_7H_{14}BrNO$: C, 40.4; H, 6.7; N, 6.7%).

(k) 1-Acetylcyclohexene was recovered unchanged after reaction with *N*-bromoformamide.

(l) Oct-1-ene (6.77 g, 0.06 mmol), *N*-benzyl-*N*-chloroformamide (3.4 g, 20 mmol) and the chromium(II) solution gave, after chromatography, *N*-benzyl-*N*-(2-chlorooctyl)formamide **4** (0.98 g) as an oil; δ_H (200 MHz) 8.35 (s, CHO, **4a**), 8.23 (s, CHO, **4b**), 7.16–7.48 (m, Ph, **4a** and **4b**), 4.85 (d, $J_{A'B'}$ 14.95, $PhC_{A'}$, **4b**), 4.61 (s, $PhCH_{A'}H_{B'}$, **4a**) 4.34 (d, $J_{B'A'}$ 14.95, $PhCH_{B'}$, **4b**), 4.20 (septet, J_{AB} 4.11, J_{AM} 9.04, J_{AY} 8.0, J_{AZ} 4.5, CH_ACl, **4a**),† 3.87 (quintet, J_{AB} 6.78, J_{AM} 5.95, J_{AY} 8.3, J_{AZ} 5.2, CH_ACl, **4b**),† 3.66 (dd, J_{BA} 4.11, J_{BM} 14.28, NCH_BCHCl, **4a**), 3.36 (d, J_{BA} 6.78, NCH_BCHCl, **4b**), 3.35 (d, J_{MA} 5.95, NCH_MCHCl, **4b**), 3.21 (dd, J_{MA} 9.04, J_{MB} 14.28, NCH_MCHCl, **4a**), 1.5–1.8 (m, CH_YH_Z-$[CH_2]_4Me$, **4a** and **4b**), 1.3 (s, $[CH_2]_4Me_3$, **4a** and **4b**) and 0.9 (m, Me, **4a** and **4b**); δ_C(50 MHz) 165.66, 165.59, 130.99, 130.84, 130.26, 129.90, 129.64, 62.6, 61.54, 55.67, 54.86, 51.21, 48.1, 37.99, 37.48, 33.59, 33.53, 30.67, 30.57, 28.09, 24.51 and 16.01.

(m) Oct-1-ene (3.37 g, 30 mmol), *N*-butyl-*N*-chloroformamide (1.97 g, 15 mmol) and the chromium(II) solution gave, after chromatography, *N*-butyl-*N*-(2-chlorooctyl)formamide **5** (0.27 g); δ_H(200 MHz) 8.1 (s, CHO, **5a**), 8.07 (s, CHO, **5b**), 4.20 (septet, J_{AB} 4.48, J_{AM} 8.70, J_{AY} 8.50, J_{AZ} 4.05, CH_ACl, **5a**), 3.95 (distorted quintet, CH_ACl, **5b**), 3.72 (dd, J_{BA} 4.48, J_{BM} 14.12, NCH_BCHCl, **5a**), 3.5–3.1 (m, NCH_BH_MCHCl, **5b** and NCH_2-C_3H_7, **5a** and **5b**), 3.28 (dd, J_{MA} 8.70, J_{MB} 14.12, NCH_MCHCl, **5a**), 1.9–1.4 (m, $CHClCH_2[CH_2]_4Me$ and NCH_2CH_2Et, **5a** and **5b**), 1.3 (br, $[CH_2]_4$, **5a** and **5b**) and 0.9 (m, Me, **5a** and **5b**); δ_C (50 MHz) 165.28, 62.48, 61.85, 56.13, 51.51, 50.67, 44.69, 37.96, 37.48, 33.6, 32.81, 31.40–21.63, 16.01, 15.75 and 15.61.

* See footnote on preceding page.

† J_{AY} and J_{AZ} were obtained by simulation of the ABMYZ system.

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