

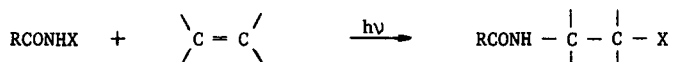
THE INFLUENCE OF TEMPERATURE ON THE COURSE OF THE  
 PHOTODECOMPOSITION OF N-HALOACETAMIDES  
 IN THE PRESENCE OF OLEFINS

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The photochemical decomposition of N-haloamides in the presence of olefins can result in products from two processes, namely 1,2-addition and allylic hydrogen abstraction. Recently we reported (1) that in the case of N-chloro- and N-bromoacetamides in the presence of cyclohexene, the yield of *cis* 1,2-adduct (hence the *cis-trans* ratio) and the total yield of addition products were remarkably increased by  $\alpha$ -halogen substituents<sup>1</sup> whereas the addition was suppressed by a N-methyl group. In continuing our studies to evaluate the factors influencing the competition between the addition and the abstraction, we have studied the effect of temperature on the reaction products and have found that lowering the temperature favours the addition process.



The irradiations were carried out as previously described (1) using Rayonet 3000 Å (pyrex vessel) or 2537 Å (vycor vessel) lamps<sup>2</sup>. At low temperature, the use of

<sup>1</sup> With N-chloro-trifluoroacetamide, only the *cis* 1,2-adduct was isolated in a 97% yield (2).

<sup>2</sup> The shorter wavelength radiation was used mainly for the N-chloroderivatives in order to shorten the reaction time, the wavelength of the radiation having a negligible influence on the yields of the products (1).

more dilute solutions (from 0.07 M to 0.03 M in N-halocarboxamide) together with the addition of methanol was necessary to ensure complete dissolution of the N-halocarboxamide. Table 1 records the total yield of addition products from the photolysis of some N-bromo- and N-chloroacetamides in the presence of cyclohexene at different temperatures together with the yield of the 3-halocyclohexene and that of the recovered carboxamide<sup>3</sup>.

The most interesting aspect of Table 1 is the increase in the yield of the products of addition relative to those resulting from hydrogen abstraction for N-bromoacetamide (experiments 1 to 5) and N-bromo- $\alpha$ -chloroacetamide (experiments 6 and 7) as the temperature is lowered such that at  $-70^{\circ}$  the yield is excellent. In the case of N-chloroacetamide (experiments 9 and 10), lowering the temperature also causes an increase in the yield of the 1,2-adducts but the effect is less dramatic. The influence of temperature on the *cis-trans* ratio is small. The diminution of this ratio at  $-70^{\circ}$  can probably be attributed to the presence of a significant amount of methanol (more than 2%) as in pure methanol the ratio is much smaller (compare experiments 7 and 8).

With N-halo-N-methylacetamides, no addition product on cyclohexene was detectable even at  $-70^{\circ}$  (Table 1, experiments 11 to 14) [*N-bromo-N-methylacetamide is a very efficient allylic brominating agent at  $10^{\circ}$ - $20^{\circ}$  giving a 91% yield of 3-bromocyclohexene (experiment (11))*]. However, on 1-dodecene<sup>4</sup>, the addition of N-chloro-N-methyl-chloroacetamide did occur albeit in low yield and lowering of the temperature had little influence on the yield of addition. At  $15^{\circ}$ , a 17% yield of 1,2-adduct 1 (oil)<sup>5</sup> was obtained together with 77% of recovered amide, at  $-70^{\circ}$ , the yield of 1,2-adduct 1 was 24% and that of recovered amide, 69%.

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<sup>3</sup> The other products formed are dibromo- or dichlorocyclohexane and bicyclohexenyle, and in the case of the N-chloroderivatives, 4-chlorocyclohexene and chlorocyclohexane. When more than 2% of methanol is present, some electrophilic halogenation becomes detectable (formation of 2 to 7% of 2-halo-methoxycyclohexane) and in pure methanol at  $-70^{\circ}$ , it is the main reaction competing with the addition (experiment 8, Table 1).

<sup>4</sup> This olefin has less allylic hydrogens and is probably more reactive than cyclohexene towards the addition of radicals (3).

<sup>5</sup> This compound had IR and NMR spectra and analytical data consistent with its structure.

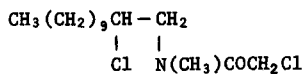
Table 1 Photolysis of N-haloacetamides in the presence of cyclohexene

Experiment	N-halo-carboxamide	Solvent % (V/V) CH <sub>3</sub> OH in CH <sub>2</sub> Cl <sub>2</sub>	Reaction temp	1,2-adducts yield <sup>a</sup> ( <i>cis/trans</i> )	3-halo- cyclohexene yield <sup>b</sup>	carboxamide yield <sup>a</sup>
1	CH <sub>3</sub> CONHBr	0	10° - 20°	25% (1 50)	59%	62%
2		0	-3°	34% (1 43)	51%	59%
3		0.7	-24°	52% (1 47)	38%	38%
4		1.3	-52°	77% (1 50)	10%	17%
5		2.6	-70°	91% (1 27)	4%	5%
6	ClCH <sub>2</sub> CONHBr	0	10° - 20°	61% (1 44)	30%	37%
7		3.8	-70°	97% (1 02)	≈0%	≈0%
8		100	-70°	64% (0 60)	≈0%	31% <sup>c</sup>
9	CH <sub>3</sub> CONHCl	0	10° - 20°	55% (2 66)	7%	39%
10		2.4	-70°	77% (1 65)	1%	17%
11	CH <sub>3</sub> CON(CH <sub>3</sub> )Br	0	10° - 20°	0%	91%	93%
12		1.4	-70°	0%	--	95%
13	ClCH <sub>2</sub> CON(CH <sub>3</sub> )Cl	0	10° - 20°	0%	48%	90%
14		0	-70°	0%	--	93%

<sup>a</sup> Of isolated products (preparative layer chromatography), based on N-halocarboxamide

<sup>b</sup> By precipitating the silver halide upon treatment with alcoholic silver nitrate solution

<sup>c</sup> Other product 2-bromo-methoxycyclohexane (27%)



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These findings extend the synthetic potentiality of the photochemical addition of N-halocarboxamides to olefins since good yields of addition are not necessarily restricted to  $\alpha$ -halogenated carboxamides

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