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THE ADDITION TO OLEFINS OF ACYLAMINO RADICALS GENERATED BY PHOTOCHEMICAL DECOMPOSITION OF HALOGENATED N-CHLORO- AND N-BROMOACETAMIDES[1]

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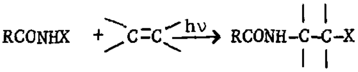
We wish to report that the photochemical decomposition of halogenated N-chloro- and N-bromoacetamides in presence of olefins gives 1,2-adducts in good yields (scheme 1), the α-halogen substituents increasing remarkably the tendency of acetylamino radicals to add to double bonds. These results constitute the first examples of photolytic addition of simple N-halocarboxamides to unsaturated compounds in yields of preparative value (1).



$$\mathrm{RCONHX} + {>}\mathrm{C{=}C}{<} \xrightarrow{h\nu} \mathrm{RCONH{-}}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{{-}}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{{-}X}$$

($R = CH_3$, CH_2Br, CH_2Cl, CH_2F, $CHCl_2$, *or* CCl_3; $X = Cl$ *or* Br)

Scheme 1

We were led to undertake this investigation by the finding that chromous chloride, which was recently shown to be very efficient in promoting the addition of N-chlorocarbamates to unsaturated compounds (2), could initiate efficiently the addition of the acetylamino radical from N-chloro- and N-bromoacetamide[3]. *Since the reactive intermediate in this case could be a metal ion-coordinated* acetylamino radical, it was of interest to study the behaviour of free acylamino radicals[4] and

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[2] Holder of a France-Quebec Studentship 1970-72.

[3] H. Driguez and J. Lessard, unpublished results.

[4] Protonated alkylamino radicals (3) and those produced in metal ion redox systems (4) add efficiently to double bonds whereas the free dimethyl amino radical from thermolysis of tetramethyl tetrazene seems to prefer to abstract allylic hydrogens (5) (see the hypothesis of Neale <u>et al</u>. (6)).

to get more information about factors promoting their addition to double bonds[5].

The irradiations were carried out in dry methylene chloride solutions (0.5 M in N-halocarboxamide and 1 to 1.2 M in olefin) at 10°-20°C, under a nitrogen atmosphere, with Rayonnet 3500 A$^{\circ}$ lamps. The reaction was stopped when the starch-iodide paper test was negative. Table 1 records the yields of the cis and trans adducts 1 from the photolysis of RCONHX in presence of cyclohexene together with the amount of $RCONH_2$ recovered[6]. The main feature of this table is the remarkable increase in the yield of cis adduct (which results in a net increase in the total yield of addition and in a larger cis-trans ratio) by changing R in the following order: $CH_3 < CH_2Br < CH_2Cl \approx CH_2F$

Table 1. Addition of RCONHX to cyclohexene

R	X	Reaction time (h)	1 (cis) yield^a	1 (cis) m.p.(^{o}C)	1 (cis) (Ref.)	1 (trans) yield^a	1 (trans) m.p.(^{o}C)	1 (trans) (Ref.)	$RCONH_2$ yield^a
CH_3	Cl	53	38%	94-96	(11)	18%	128-129	(12)	39%
CH_2Br	Cl	30	60%	109-110		19%	107		24%
CH_2Cl	Cl	44	73%	109		18%	130		10%
CH_2F	Cl	40	75%	93-94		16%	144-145		9%
$CHCl_2$	Cl	37	79%	107-108		15%	119		4%
CCl_3	Cl	21	89%	82		10%	134		
CH_3	Br	5.5	15%	103	(11)	10%	112	(12)	57%
CH_2Cl	Br	4.5	37%	128-129		27%	134-135		34%
CH_2F	Br	4.5	37%	104-105		24%	155-156		30%
CCl_3	Br	4	61%	80-81	(10)	20%	157	(10)	12%

^{a}The yields are based on RCONHX and they represent yields of pure products isolated by preparative layer chromatography on silica gel.

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[5] For instance, it has been shown that upon photo- or azobisisobutyronitrile-initiated decomposition, N-chloro- and N-bromo-N-alkylcarboxamides fail to add to olefins (1,6). On the other hand, the photochemical addition of N-chlorourethane to unsaturated hydrocarbons proceeds in high yields (7) and the thermal reaction of N,N-dichlorourethane to olefins affords 1,2-adducts in moderate to high yields depending on the number of reactive allylic hydrogens (7c,8).

[6] The recovered carboxamide may come from allylic hydrogen abstraction by the acylamino radical or/and from the reaction of RCONHX with the hydrogen halide resulting from allylic hydrogen abstraction by halogen atoms. Among the other products formed, bicyclohexenyl (present in small amounts) and 3-chloro- or 3-bromo-1-cyclohexene (present in variable amounts depending on the extent of addition) were identified by vapor phase chromatographic (vpc) comparison with authentic samples.

< $CHCl_2$ < CCl_3[7]. N-Chloro compounds give better yields, a larger *cis*-*trans* ratio than the corresponding N-bromo derivatives but the reaction time is much longer[8]. The 25% yield of addition with N-bromoacetamide is worth noting since the photolysis in refluxing carbon tetrachloride was reported to give, as the primary product, *trans*-2-bromocyclohexyl-N-bromoacetamidate and only 1% of *trans* adduct 1 (R = CH_3, X = Br) (9).

The photochemical addition of N-chloro- and N-bromo-chloroacetamide was extended to include other olefins with satisfactory results. Some examples are given in table 2. Other examples will be recorded later.

The influence of a N-methyl substituent was also studied. N-chloro-N-methyl-chloroacetamide failed to add to cyclohexene in the conditions used above; the major product was 3-chloro-1-cyclohexene according to vpc analysis and 84% of chloroacetamide were recovered. However both N-chloroacetamide and N-chloro-N-methylacetamide did add to norbornene (no reactive allylic hydrogens) in

Table 2. Addition of $CH_2ClCONHX$ to various olefins

Olefin	X	Reaction time (h)		adduct	yield[a]	m.p. (°C)
1-dodecene	Cl	27	2		95%	64
"	Br	5	2		62%	56-57
1-methyl-1-cyclohexene	Cl	28	3	*cis* *trans*	87% not detected	91-92
"	Br	4.5	3	*cis* *trans*	48% 14%	113-113.5 97-97.5
1-acetyl-1-cyclohexene	Cl	29	4	*cis* or *trans* *cis* or *trans*	16% 54%	78-79 68-69
1-methoxy-1-cyclohexene[b]	Cl	5	5		72%	90-91

[a] Yields of chromatographically pure compounds based on $CH_2ClCONHX$.

[b] The photolysis was carried out at -40° to -30°C (200 watts Havonia lamp, pyrex filter). Under the usual conditions, α-chlorocyclohexanone and the recovered chloroacetamide were the sole products isolated.

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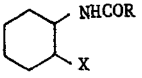
[7] In the dark, other conditions being the same, the reaction of $CH_3CONHCl$ with cyclohexene took 45 days and no addition products were isolated; the reaction of $CCl_3CONHBr$ gave 30% of adducts 1 (R = CCl_3; X = Br) (*cis*/*trans* = 0.5) and was over after 30 h. In neat boiling cyclohexene but not in the dark a 60% yield of addition (*cis*/*trans* = 2) of $CCl_3CONHBr$ has been reported (10).

[8] By using a more energetic radiation (Rayonnet 3000 A° lamps, pyrex filter) the reaction time of $CH_2ClCONHCl$ with cyclohexene was cut down to 7 h and the yields of products were practically unchanged: *cis* 1, 71%; *trans* 1, 18%; $CH_2ClCONH_2$, 9%.

comparable yields upon photolysis in acetonitrile (Rayonnet 2537 A° lamps, 10-20°C, 3h)[9]: the former gave 51% of cis (m.p. 110°) and trans (m.p. 131°) isomers 6 (R=H) (cis/trans = 3.6) and the latter yielded 47% of a liquid mixture of cis and trans isomers 6 (R = CH_3) which we have not yet succeeded in separating.



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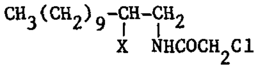
$CH_3(CH_2)_9\text{-}\underset{X}{CH}\text{-}\underset{NHCOCH_2Cl}{CH_2}$

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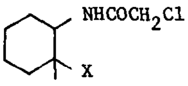

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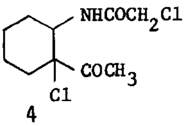

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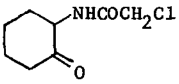

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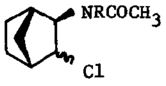

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Further studies are in progress to evaluate the competition between addition to olefins and allylic hydrogen abstraction as a function of the acylamino radical structure.

All compounds had I.R. and N.M.R. spectra consistent with their structures. All new compounds gave satisfactory analytical and/or mass spectral data.

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[9] In these conditions (2.5 h) a 56% yield of cis and trans adducts 1 (R=CH_3; X=Cl) (cis/trans = 0.67) were obtained from N-chloroacetamide and cyclohexene.

REFERENCES

1. R.S. Neale, Synthesis, 1 (1971).
2. J. Lessard and J.M. Paton, Tetrahedron Lett., 4883 (1970); J. Lessard, H. Driguez and J.P. Vermes, Tetrahedron Lett., 4887 (1970).
3. R.S. Neale, J. Org. Chem., 32, 3263 (1967).
4. F. Minisci, R. Galli and M. Cecere, Chem. e Ind. (Milano), 48, 347 (1966).
5. B.R. Cowley and W.A. Waters, J. Chem. Soc., 1228 (1961).
6. R.S. Neale, N.L. Marcus, and R.G. Schepers, J. Am. Chem. Soc., 88, 3051 (1966).
7. a) K. Schrage, Tetrahedron Lett., 5795 (1966); b) Tetrahedron, 23, 3033 (1967); c) Tetrahedron, 23, 3039 (1967).
8. P. Chabrier, Ann. Chim., 17, 353 (1942); T. Foglia and D. Swern, J. Org. Chem., 31, 3625 (1966).
9. S. Wolfe and D.V.C. Awang, Can. J. Chem., 49, 1384 (1971)
10. J.D. Park, H.J. Gerjovich, W.R. Lycan, and J. Lacher, J. Am. Chem. Soc., 74, 2189 (1952).
11. A.E. Osterberg and E.C. Kendall, J. Am. Chem. Soc., 42, 2616 (1920).
12. T.L. Cairns, P.J. Graham, P.L. Barrick, and R.S. Shreiber, J. Org. Chem., 17, 751 (1952).