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## Rearrangement of Cyclopropyl Ketone Oximes to 5,6-Dihydro-4*H*-1,2-oxazines

By *C. N. Rentzea*[*]

*Dedicated to Professor Matthias Seefelder on the occasion of his 60th birthday*

Cyclopropyl 4-methylstyryl ketone oxime *(2a)*, R = *p*-tolyl, was obtained by reaction of the *trans*-ketone *(1a)*[1] with $NH_2OH \cdot HCl$ in ethanol at 40 °C as a *Z/E* mixture[2]; m. p. 118 °C, yield 14% and m. p. 135 °C, yield 57%, respectively. Both the ketone *(1a)* and the oxime *(2a)* led, under more drastic conditions[3] (8 h reflux in ethanol; *(1a)* or *(2a)*: $NH_2OH \cdot HCl = 1:1.5$), to the same *trans*-3-(4-methylstyryl)-5,6-dihydro-4*H*-1,2-oxazine *(5a)*[2] in 41% yield. Further examples are to be found in Table 1.

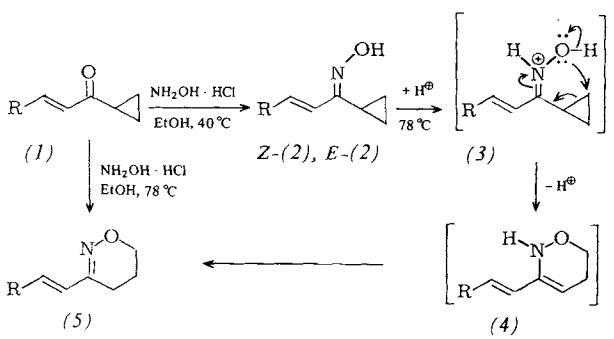



Table 1. Physical data of the compounds *(5a-k)*[2] obtained from the ketones *(1a-k)*[1]. IR in KBr, $^1$H-NMR in $CDCl_3$, TMS as internal standard.

*(5a)*, m. p. 199 °C (from acetone); IR: 1545, 1225, 960, 800 $cm^{-1}$; $^1$H-NMR: $\delta = 2.06-2.2$ (m, 2H), 2.33 (s, 3H), 2.84–2.95 (t, 2H), 4.0–4.11 (t, 2H), 6.77–6.86 (d, 1H), 7.11–7.2 (d, 2H), 7.31–7.42 (d, 1H), 7.37–7.46 (d, 2H); $^{13}$C-NMR ($CDCl_3$): $\delta = 143.63$, 139.42, 136.58, 133.50, 129.63 (×2), 127.36 (×2), 115.07, 62.71, 28.45, 21.28, 16.96

*(5b)*, R = $C_6H_5$; m. p. 164 °C (from acetone); yield 42%; $^1$H-NMR: $\delta = 2.0-2.36$ (m, 2H), 2.83–3.1 (t, 2H), 4.0–4.25 (t, 2H), 6.8–7.02 (d, 1H), 7.3–7.7 (m, 6H)

*(5c)*, R = 4-($C_6H_5$)$C_6H_4$; m. p. 196 °C (from acetonitrile); yield 45%; $^1$H-NMR: $\delta = 1.88-2.33$ (m, 2H), 2.55–2.96 (t, 2H), 3.70–4.10 (t, 2H), 6.52–6.38 (d, 1H), 7.05–7.55 (m, 10H)

*(5d)*, R = 1-$C_{10}H_7$; m. p. 153 °C (from acetic acid); yield 41%; IR: 1540, 1225, 962, 778 $cm^{-1}$; $^1$H-NMR: $\delta = 2.13-2.26$ (m, 2H), 3.0–3.08 (t, 2H), 4.08–4.17 (t, 2H), 7.42–7.57 (m, 4H), 7.62–7.75 (d, 1H), 7.77–7.91 (m, 3H), 8.06–8.15 (d, 1H)

*(5e)*, R = 4-$ClC_6H_4$; m. p. 171 °C (from acetone); yield 30%; IR: 1540, 1232, 960, 805 $cm^{-1}$; $^1$H-NMR: $\delta = 1.95-2.4$ (m, 2H), 2.73–3.1 (t, 2H), 3.88–4.25 (t, 2H), 6.55–6.9 (d, 1H), 7.10–7.50 (m, 5H)

*(5f)*, R = 4-$BrC_6H_4$; m. p. 192 °C (from acetone); yield 40%; IR: 1542, 1230, 963, 802 $cm^{-1}$; $^1$H-NMR: $\delta = 2.0-2.42$ (m, 2H), 2.75–3.1 (t, 2H), 3.84–4.18 (t, 2H), 6.48–6.82 (d, 1H), 7.10–7.45 (m, 5H)

*(5g)*, R = 2,4-$Cl_2C_6H_3$; m. p. 150 °C (from acetone); yield 40%; IR: 1550, 1220, 960, 810 $cm^{-1}$; $^1$H-NMR: $\delta = 1.95-2.5$ (m, 2H), 2.80–3.20 (t, 2H), 3.9–4.35 (t, 2H), 6.9–7.48 (m, 4H), 7.55–7.85 (d, 1H)

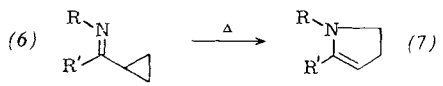
*(5h)*, R = 3,4-$Cl_2C_6H_3$; m. p. 175 °C (from acetonitrile); yield 47%; $^1$H-NMR: $\delta = 2.0-2.58$ (m, 2H), 2.81–3.18 (t, 2H), 3.98–4.38 (t, 2H), 6.62–7.0 (d, 1H), 7.22–7.76 (m, 4H)

*(5i)*, R = 4-($F_3C$)$C_6H_4$; m. p. 196 °C (from acetone); yield 47%; $^1$H-NMR: $\delta = 1.86-2.35$ (m, 2H), 2.54–2.96 (t, 2H), 3.7–4.16 (t, 2H), 6.51–6.9 (d, 1H), 7.12–7.52 (d, 5H)

*(5j)*, R = 4-($O_2N$)$C_6H_4$; m. p. 216 °C (from acetic acid); yield 40%; IR: 1532, 1340, 975, 833 $cm^{-1}$; $^1$H-NMR: $\delta = 2.0-2.48$ (m, 2H), 2.7–3.1 (t, 2H), 3.84–4.2 (t, 2H), 6.52–6.92 (d, 1H), 7.19–7.4 (d, 1H), 7.5–7.6 (d, 2H), 7.88–8.15 (d, 2H)

*(5k)*, R = 4-($CH_3O$)$C_6H_4$; m. p. 169 °C (from acetone) yield 29%; $^1$H-NMR: $\delta = 1.95-2.45$ (m, 2H), 2.7–3.12 (t, 2H), 3.78 (s, 3H), 3.85–4.28 (t, 2H), 6.76–7.64 (m, 6H)

Like the Cloke rearrangement[4] of *(6)* to *(7)*, this novel rearrangement of cyclopropyl ketone oxime *(2)* to oxazines *(5)* appears to involve protonation of the nitrogen atom.




The cyclization of *(3)* to *(4)* is probably an example of 6-*endo-tet* ring closure rarely observed so far.

Received: November 6, 1979 [Z 395 IE]
German version: Angew. Chem. *92*, 195 (1980)

CAS Registry numbers:
*(1a)*, 72881-67-5; *(1b)*, 63261-41-6; *(1c)*, 72881-68-6; *(1d)*, 72881-69-7; *(1e)*, 72881-70-0; *(1f)*, 72881-71-1; *(1g)*, 72881-72-2; *(1h)*, 72881-73-3; *(1i)*, 72881-74-4; *(1j)*, 63261-42-7; *(1k)*, 72881-75-5; (E)-*(2a)*, 72881-76-6; (Z)-*(2a)*, 72881-77-7; (E)-*(2b)*, 72881-78-8; (Z)-*(2b)*, 72881-79-9; (E)-*(2c)*, 72881-80-2; (Z)-*(2c)*, 72881-81-3; (E)-*(2d)*, 72881-82-4; (Z)-*(2d)*, 72881-83-5; (E)-*(2e)*, 72881-84-6; (Z)-*(2e)*, 72881-85-7; (E)-*(2f)*, 72881-86-8; (Z)-*(2f)*, 72881-87-9; (E)-*(2g)*, 72881-88-0; (Z)-*(2g)*, 72881-89-1; (E)-*(2h)*, 72881-90-4; (Z)-*(2h)*, 72881-91-5; (E)-*(2i)*, 72881-92-6; (Z)-*(2i)*, 72881-93-7; (E)-*(2j)*, 72881-94-8; (Z)-*(2j)*, 72881-95-9; (E)-*(2k)*, 72881-96-0; (Z)-*(2k)*, 72881-97-1; *(5a)*, 72881-98-2; *(5b)*, 72881-99-3; *(5c)*, 72882-00-9; *(5d)*, 72882-01-0; *(5e)*, 72882-02-1; *(5f)*, 72882-03-2; *(5g)*, 72882-04-3; *(5h)*, 72882-05-4; *(5i)*, 72882-06-5; *(5j)*, 72882-07-6; *(5k)*, 72882-08-7

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## Synthesis of Carbocyclic and Heterocyclic π-Electron Systems with Pentafulvenoid Chloroformamidinium Chlorides

By *Klaus Hafner* and *Hans-Peter Krimmer*[*]

*Dedicated to Professor Matthias Seefelder on the occasion of his 60th birthday*

In 1960, *Eilingsfeld, Seefelder*, and *Weidinger*[1] first reported the preparation and reactions of "carbamide chlorides" (chloroformamidinium chlorides) which have proved

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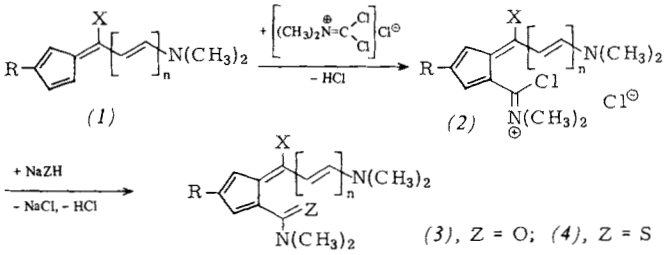
their value as reactive synthons in the past two decades[2]. We have now found a facile method for the preparation of pentafulvenoid chloroformamidinium chlorides, which permit surprisingly easy syntheses of interesting carbo- and heterocyclic $\pi$-electron systems.

By analogy with the formylation of dialkylaminofulvenes of type *(1)*[3], their reaction with dichloromethylene(dimethyl)ammonium chloride[2] gives the cyclically vinylogous chloroformamidinium chlorides *(2)* (yellow hygroscopic crystals; yield 50–70%), which display pronounced reactivity towards numerous nucleophilic partners. Structural proof comes, *inter alia*, from their hydrolysis or reaction with sodium hydrogen sulfide to give amides of carboxylic and thiocarboxylic acids *(3)* and *(4)* (yellow crystals; yield 35–90%).

The 1,4- and 1,6-bifunctional fulvenes *(2)* react with suitable nucleophiles *via* cyclization thus *(2d)* reacts with ammonia to give 5-*tert*-butyl-1,3-bis(dimethylamino)-2-azapentalene *(5)*[4] in 31% yield (blue-violet needles), while 6-*tert*-butyl-1,4-bis(dimethylamino)-2*H*-cyclopenta[*d*]pyridazine *(6)* (dark green needles, yield 51%) is formed with hydrazine. The reaction of *(2d)* with sodium cyclopentadienide and its *tert*-butyl derivative gives the 4,8-bis(dimethylamino)-*s*-indacenes *(7a)* and *(7b)* (green and golden yellow platelets with metallic sheen; 30 and 38% yield, respectively) as heat- and




*(1)* *(2)* *(3)*, Z = O; *(4)*, Z = S

| | R | X | *n* |
|---|---|---|---|
| *a* | H | H | 0 |
| *b* | $(CH_3)_3C$ | H | 0 |
| *c* | H | $(CH_3)_2N$ | 0 |
| *d* | $(CH_3)_3C$ | $(CH_3)_2N$ | 0 |
| *e* | H | H | 1 |

air-stable derivatives of the parent compound so far detected only in solution at low temperature[5].

Like *(2d)*, compound *(2e)* also reacts with ammonia to give the stable 4-(dimethylamino)-5-azaazulene *(8)* (blood red platelets; yield 54%)[6].

Table 1 lists physical data of some new compounds.

Table 1. Selected physical data of compounds *(2a)*, *(3a–d)*, *(4a)*, *(5)*, *(6)*, *(7a)*, *(7b)*, and *(8)*.

| Cpd. | M.p. [°C] | UV (Dioxane) $\lambda$ [nm] (log $\varepsilon$) | $^1$H-NMR($CDCl_3$), $\delta$-values |
|---|---|---|---|
| *(2a)* | 173 | 284 (4.18)<br>386 (4.66) [a] | 3.66 (s, 3H, 6-N $CH_3$), 3.72 (s, 3H, 6-N $CH_3$), 3.87 (s, 6H, CCl $N(CH_3)_2$), 6.90 (m, 2H, H-3,4), 7.73 (m, 1H, H-2), 8.42 (s, 1H, H-6) [d] |
| *(3a)* | 122 | 239 (3.99)<br>340 (4.44) | 3.13 (s, 6H, 6-$N(CH_3)_2$), 3.27 (s, 6H, CO $N(CH_3)_2$), 6.38 (dd, $J_1$ = 4.8 Hz, $J_2$ = 3.2 Hz, 1H, H-3), 6.52 (dd, $J_1$ = 3.2 Hz, $J_2$ = 1.6 Hz, 1H, H-2), 6.71 (dd, $J_1$ = 4.8 Hz, $J_2$ = 1.6 Hz, 1H, H-4), 8.02 (s, 1H, H-6) |
| *(3b)* | 91 | 243 (4.06)<br>342 (4.41) | 1.23 (s, 9H, $C(CH_3)_3$), 3.13 (s, 6H, 6-$N(CH_3)_2$), 3.26 (s, 6H, CO $N(CH_3)_2$), 6.43 (d, $J$ = 1.6 Hz, 1H, H-4), 6.51 (d, $J$ = 1.6 Hz, 1H, H-2), 7.82 (s, 1H, H-6) |
| *(3c)* | 121 | 253 (4.14)<br>356 (4.27) | 3.03 (s, 12H, 6-$N(CH_3)_2$), 3.16 (s, 6H, CO $N(CH_3)_2$), 6.14 (dd, $J_1$ = 4.0 Hz, $J_2$ = 3.1 Hz, 1H, H-3), 6.28 (dd, $J_1$ = 4.0 Hz, $J_2$ = 1.9 Hz, 1H, H-4), 6.52 (dd, $J_1$ = 3.1 Hz, $J_2$ = 1.9 Hz, 1H, H-2) |
| *(3d)* | 236 | 255 (4.18)<br>363 (4.25) | 1.23 (s, 9H, $C(CH_3)_3$), 2.98 (s, 12H, 6-$N(CH_3)_2$), 3.10 (s, 6H, CO $N(CH_3)_2$), 6.03 (d, $J$ = 2.3 Hz, 1H, H-4), 6.43 (d, $J$ = 2.3 Hz, 1H, H-2) |
| *(4a)* | 124 | 265 (4.24)<br>304 (4.38)<br>417 (3.47) | 3.27 (s, 6H, 6-$N(CH_3)_2$), 3.30–3.60 (broad s, 6H, CS $N(CH_3)_2$), 6.26 (dd, $J_1$ = 3.1 Hz, $J_2$ = 1.7 Hz, 1H, H-2), 6.32 (dd, $J_1$ = 4.6 Hz, $J_2$ = 3.1 Hz, 1H, H-3), 6.69 (dd, $J_1$ = 4.6 Hz, $J_2$ = 1.7 Hz, 1H, H-4), 8.04 (s, 1H, H-6) |
| *(5)* | 229 | 225 (4.35)<br>298 (4.32)<br>308 (4.32)<br>388 (3.11)<br>563 (2.71) [b] | 1.29 (s, 9H, $C(CH_3)_3$), 3.17 (s, 6H, 1,3-N $CH_3$), 3.29 (s, 6H, 1,3-N $CH_3$), 5.98 (s, 2H, H-4,6) |
| *(6)* | 152 | 249 (4.49)<br>298sh (3.90)<br>592 (1.08) [b] | 1.31 (s, 9H, $C(CH_3)_3$), 3.11 (s, 12H, 1,4-$N(CH_3)_2$), 6.43 (s, 2H, H-5,7), 11.35 (s, 1H, NH, vanishes with $D_2O$) |
| *(7a)* | 199 | 284 (4.63)<br>410 (4.28)<br>471 (4.21)<br>693 (2.46) | 1.20 (s, 9H, $C(CH_3)_3$), 3.40 (s, 12H, 4,8-$N(CH_3)_2$), 5.93 (t, $J$ = 4.0 Hz, 1H, H-6), 6.36 (s, 2H, H-1,3), 6.45 (d, $J$ = 4.0 Hz, 2H, H-5,7) |
| *(7b)* | 265 | 288 (4.34)<br>412 (4.00)<br>476 (3.91)<br>720 (2.12) | 1.18 (s, 18H, 2,6-$C(CH_3)_3$), 3.36 (s, 12H, 4,8-$N(CH_3)_2$), 6.27 (s, 4H, H-1,3,5,7) |
| *(8)* | 73 | 221 (3.99)<br>267 (4.28)<br>306 (4.29)<br>396 (3.34)<br>410 (3.31)<br>492 (3.16) [c] | 3.42 (s, 6H,$N(CH_3)_2$), 6.30 (dd, $J_1$ = 7.7 Hz, $J_2$ = 6.2 Hz; 1H, H-7), 7.04 (dd, $J_1$ = 3.8 Hz, $J_2$ = 1.7 Hz, 1H, H-3), 7.10 (m, 1H, H-1), 7.27 (dd, $J_1$ = 4.0 Hz, $J_2$ = 3.8 Hz, 1H, H-2), 7.90 (d, $J$ = 7.7 Hz, 1H, H-8), 8.04 (dd, $J_1$ = 6.2 Hz, $J_2$ = 1.7 Hz, 1H, H-6) |

[a] In $CH_3CN$. [b] In $CH_2Cl_2$. [c] In *n*-hexane. [d] In [$D_6$]-acetone.



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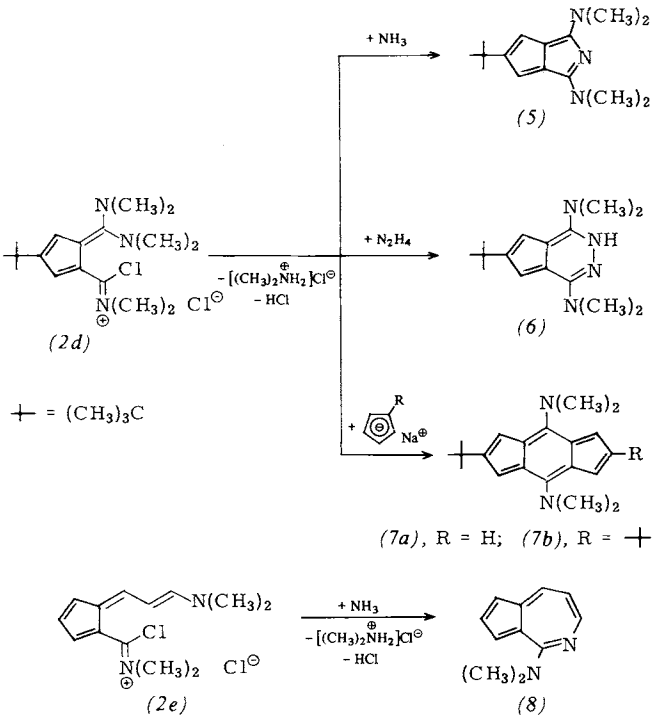





*Procedure*

*(2d):* A suspension of dichloromethylene(dimethyl)ammonium chloride in $CH_2Cl_2$ (20 ml) is added dropwise to a stirred solution of *(1d)*[7] (2.2 g, 20 mmol) and triethylamine (2.0 g, 20 mmol) in $CH_2Cl_2$ (100 ml) at 0 °C. The mixture is then refluxed for 2 h. After cooling to room temperature the solution can be used directly for preparation of *(5)*, *(6)*, and *(7)*. Compound *(2d)* can be isolated as perchlorate.

*(5):* A slow stream of dry ammonia is passed into the solution of *(2d)* at 0 °C for 30 min. After 2 h, saturated aqueous $NH_4Cl$ solution (200 ml) is added and the mixture extracted with $CH_2Cl_2$ (3 × 50 ml). On removal of the solvent the residue is chromatographed on $Al_2O_3$ B IV with ethyl acetate; 770 mg (31%) of *(5)* is isolated from the first violet zone.

*(6):* Anhydrous hydrazine (320 mg, 10 mmol) is added at room temperature to a solution of *(2d)* and the mixture refluxed for 2 h and worked up as *(5)*. The first green zone gives 1.33 g (51%) of *(6)*.

*(7a)* and *(7b):* A 2.69 M solution of sodium cyclopentadienide (3.7 ml, 10 mmol) in tetrahydrofuran is added dropwise to a solution of *(2d)*. After refluxing for 2 h the product is worked up as *(5)*. Yield 880 mg (30%) *(7a)*. Compound *(7b)* is obtained analogously with sodium *tert*-butylcyclopentadienide.

*(8):* A suspension of dichloromethylene(dimethyl)ammonium chloride (1.6 g, 10 mmol) in $CH_2Cl_2$ (20 ml) is added dropwise to a stirred solution of *(1e)*[3] (1.5 g, 10 mmol) and triethylamine (2.0 g, 20 mmol) in $CH_2Cl_2$ (100 ml) at 0 °C under $N_2$. After stirring for 2 h at 0 °C, dry ammonia is passed into the mixture for 30 min and the product is worked up as *(5)*; eluent: hexane/ether (4:1). The first red zone affords 930 mg (54%) of *(8)*.

Received: November 29, 1979 [Z 396 IE]
German version: Angew. Chem. *92*, 202 (1980)

CAS Registry numbers:
*(1a)*, 696-68-4; *(1b)*, 72866-30-9; *(1c)*, 703-24-2; *(1d)*, 72866-31-0; *(1e)*, 2481-72-3; *(2a)*, 72866-32-1; *(2b)*, 72866-33-2; *(2c)*, 72866-34-3; *(2d)*, 72866-36-5; *(2e)*, 72866-37-6; *(3a)*, 72866-38-7; *(3b)*, 72866-39-8; *(3c)*, 72866-40-1; *(3d)*, 72881-43-7; *(4a)*, 72866-41-2; *(5)*, 72866-42-3; *(6)*, 72866-43-4; *(7a)*, 72866-44-5; *(7b)*, 72881-44-8; *(8)*, 72866-45-6; ammonia, 7664-41-7; hydrazine, 302-01-2; sodium-cyclopentadienide, 4984-82-1; sodium *tert*-butylcyclopentadienide, 55562-84-0.

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[2] See *H. G. Viehe, Z. Janousek,* Angew. Chem. *85*, 837 (1973); Angew. Chem. Int. Ed. Engl. *12*, 806 (1973); *Z. Janousek, H. G. Viehe* in *H. Böhme, H. G. Viehe:* Iminium Salts in Organic Chemistry. Part I. Wiley, New York 1976, p. 343.

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[7] *(1d)* is obtained from lithium *tert*-butylcyclopentadienide by analogy with 6,6-bis(dimethylamino)fulvene (*K. Hafner, G. Schulz, K. Wagner,* Justus Liebigs Ann. Chem. *678*, 39 (1964)).

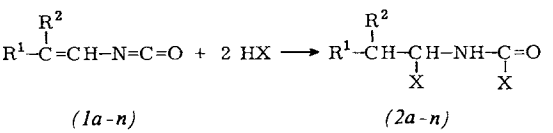
## Synthesis of α-Haloalkylcarbamoyl Halides

By *Karl-Heinz König, Christian Reitel,* and *Karl-Heinz Feuerherd*[*]

*Dedicated to Professor Matthias Seefelder on the occasion of his 60th birthday*

Ever since vinyl isocyanate[1] was first synthesized there have been repeated reports on the polymerizability of α,β-unsaturated isocyanates and their sensitivity to moisture, acids, and bases[2]. Since these compounds are readily accessible on an industrial scale[3] we have been engaged in a detailed examination of their chemical properties.

We have found that α,β-unsaturated isocyanates *(1)* can react with hydrogen halides at low temperature without polymerization to give α-haloalkylcarbamoyl halides in very good yields (Method A; Table 1)[4]. Remarkably, some of these compounds can be stored for several weeks with cooling.



*(1a-n)* *(2a-n)*

Table 1. Overview of the α-haloalkylcarbamoyl halides *(2)*.

| | $R^1$ | $R^2$ | X |
|---|---|---|---|
| *a, b, c* | H | H | Cl, Br, I |
| *d, e, f* | $CH_3$ | H | Cl, Br, I |
| *g, h, i* | $C_2H_5$ | H | Cl, Br, I |
| *j* | $C_2H_5$ | $CH_3$ | Br |
| *k* | $CH(CH_3)_2$ | H | Cl |
| *l* | *n*-$C_6H_{13}$ | H | Br |
| *m* | $(CH_2)_5$ | | Cl |
| *n* | $C_6H_5$ | $CH_3$ | Br |

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