Reactions of α-halo-α,β-unsaturated aldehydes with secondary amines

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Reactions of 2-halo-2-alkenals $R''(R')C=CX-CHO$ with secondary amines R_2NH occur as *ipso*-substitution of the halogen atom, along with fragmentation and condensation, yielding 1,2-diaminoethenes $R_2NCH=CHNR_2$, carbonyl compounds $R''C(O)R'$, 1,3-bis(amino)-2-haloolefins $R''(R')C(NR_2)CX=CHNR_2$, and formamides R_2NCHO. The ratio between the competing reactions depends on the structure of the starting compounds and the experimental conditions.

Key words: 2-halo-2-alkenals, secondary amines, reactions; 2-amino-2-alkenals.

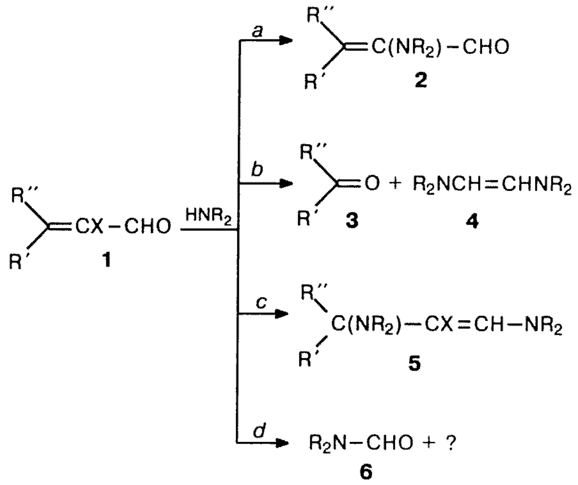
Nucleophilic vinylic substitution ($S_N$vin) has been studied in detail for olefins in which the leaving group is located in the β-position with respect to the activating group.[1–3] $S_N$vin reactions involving olefins in which the leaving and activating groups are attached to the same C atom have been studied less extensively. Available α-halo-α,β-unsaturated carbonyl compounds, mostly ketones, carboxylic acids, and their derivatives, have been used as substrates.[4] In the case of α-halo-α,β-unsaturated aldehydes, which are the most reactive among the compounds under consideration, the process is appreciably complicated due to side reactions involving the aldehyde group. In fact, 2-halo-2-alkenals react with primary amines with participation of both the double bond and the aldehyde group, yielding aldiminoaziridines.[5,6] The complexity and diversity of reactions of α,β-dibromoaldehydes with secondary amines have also been noted.[7]

Previously we suggested a convenient method for preparing α-piperidinocrotonaldehyde by nucleophilic vinylic substitution of the halogen atom in 2-halo-2-butenal.[8] Later this method was extended to a rather wide range of amines and aldehydes.[9–11] However, the synthetic potential of this reaction proved to be much richer. In the present work we have studied interaction of 2-halo-2-alkenals with secondary amines.

It was found that 2-halo-2-alkenals (**1**), unlike β-haloacroleins,[12] react with secondary amines to give a number of fragmentation or condensation products,[10] along with the main product (**2**) resulting from *ipso*-substitution of the halogen atom (Scheme 1). The predominant reaction pathway is determined by the structures of the starting compounds (Table 1).

The reaction of 2-chloropropenal (**1a**) with secondary amines occurs predominantly as 1,4-addition of the amine followed by condensation of the adduct with the second equivalent of the nucleophile to afford 1,3-diamino-2-chloropropene **5a** (Scheme 1, *c*; see Table 1, runs *2* and *3*). The product of replacement of the halogen atom **2a** was obtained in a minor amount in the reaction of aldehyde **1a** with piperidine (run *1*).

Scheme 1



a: R'' = R' = H; X = Cl
b: R'' = Me, R' = H; X = F
c: R'' = Me, R' = H; X = Cl
d: R'' = Me, R' = H; X = Br
e: R'' = Pr^n, R' = H; X = Cl
f: R'' = R' = Me; X = Cl
g: R'' = Ph, R' = H; X = Cl
h: R'' = Ph, R' = H; X = Br
i: R'' = R' = Ph; X = Cl

$NR_2 = NEt_2, NBu_2, N(CH_2)_4, N(CH_2)_5, N(CH_2)_6, N(CH_2CH_2)_2O, N(Me)Ph, NPh_2$

The best yields of 2-amino-2-alkenals **2** were obtained with β-alkyl-substituted α-halo-α,β-unsaturated aldehydes **1c—f** and cyclic amines. In fact, the reaction of 2-chloro-2-hexenal (**1e**) with piperidine in THF gives the substitution product **2e** ($NR_2 = N(CH_2)_5$) with a high selectivity: the ratio between the competing substi-

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Table 1. Reactions of 2-halo-2-alkenals with secondary amines

Run	Aldehyde	NR_2	Reaction conditions			Yield (%)			
			solvent	*T*/°C	duration /h	**2**[a]	**4**[a]	**5**[a]	**6**[b]
1	**1a**	$(CH_2)_5N$	Et_2O	25	48	20	30	30	3
2	**1a**	Et_2N	THF	25	24	0	0	55	4
3	**1a**	$(CH_2)_4N$	Et_2O	25	24	0	0	90	4
4	**1b**	$(CH_2)_5N$	THF	25	24	0	0	80	0
5	**1c**	$(CH_2)_5N$	THF	25	48	85	0	0	2
6	**1c**	$O(CH_2CH_2)_2N$[c]	THF	25	96	75	10	0	2
7	**1c**	Et_2N	Et_2O	25	48	10	45	0	6
8	**1c**	$Bu^n{}_2N$	Et_2O	25	96	15	35	0	8
9	**1c**	$(CH_2)_4N$	Et_2O	25	24	0	0	50	8
10	**1c**	Ph_2N[d]	PhH	60	10	No reaction			
11	**1c**	$Ph(Me)N$[c]	Et_2O	50	16	The same			
12	**1d**	$(CH_2)_5N$	Et_2O	25	24	40	10	0	2
13	**1e**	$(CH_2)_5N$	THF	25	48	90	5	0	3
14	**1f**	$(CH_2)_5N$	THF	25	48	45	20	0	30
15	**1f**	$O(CH_2CH_2)_2N$[c]	THF	55	12	55	5	0	30
16	**1g**	$(CH_2)_5N$	THF	25	48	80	5	0	10
17	**1h**	Et_2N	THF	25	48	50	30	0	10
18	**1i**	$(CH_2)_5N$	THF	25	144	No reaction			

[a] From the ^1H NMR spectra of the reaction mixture after evaporation of the solvent. [b] From GC of the reaction mixture after evaporation of the solvent. [c] In the presence of an equimolar amount of triethylamine. [d] In the presence of an equimolar amount of pyridine.

tution and fragmentation reactions is 9 : 1 (see Table 1, run *13*). The interaction of 2-chloro-2-butenal (**1c**) with piperidine or morpholine in the presence of Et_3N occurs in a similar way (runs *5* and *6*). On going from chlorine derivatives to bromine derivative **1d** the ratio between the competing reactions changes essentially. The process is complicated only by a high degree of resinification, which leads to a decrease in the yield of the expected product (run *12*).

Conversely, the route of the reaction of α-fluorocrotonaldehyde **1b** with piperidine differs dramatically from that observed with isostructural chlorine and bromine derivatives **1c** and **1d**. The ^1H NMR spectrum of the reaction mixture exhibits only signals corresponding to 2-fluoro-1,3-dipiperidino-1-butene **5b** ($NR_2 = N(CH_2)_5$; see Table 1, run *4*).

Such a strong difference in the reactivity of 2-fluoro-2-butenal (**1b**) is apparently caused by the substantial variations of the electron density distribution in the molecule due to the F atom. These variations are clearly manifested in the ^1H and ^{13}C NMR spectra of 2-halo-2-alkenals.[13] The electron density distribution differing from those in the molecules of the chlorine and bromine derivatives and low nucleofugicity of the F atom, which greatly hampers nucleophilic substitution, result in the reaction of compound **1b** with piperidine occurring regiospecifically by pathway *c* (see Scheme 1).

When the second alkyl substituent is present in the β-position of the starting substrate (aldehyde **1f**), the reaction affords, along with aldehydes **2**, the *N*-formyl derivative of the starting amine **6** (see Table 1, runs *14* and *15*). The presence of the latter in the reaction mixtures was confirmed by mass spectrometry and GC. Its formation may be accounted for by cleavage of the C(1)—C(2) bond in the starting substrate or products of its further transformations. The nature of the second component of this fragmentation reaction is unknown.

A dependence of the ratio between the competing reactions on the nature of the amine has also been observed for α-halo-β-phenylacroleins **1g** and **1h** (see Table 1, runs *16* and *17*). Fragmentation reactions involving cleavage of either the C(1)—C(2) or C(2)—C(3) bond in the molecule of the starting substrate or products of its transformations proceeding in parallel with the predominant process, *viz.*, nucleophilic substitution of the halogen atom, give formamide **6** or 1,2-diaminoethene **4** and benzaldehyde (**3g**). It is of interest that the reaction of 2-bromo-3-phenylpropenal (**1h**) with diethylamine, unlike the reaction of β-methyl derivative **1d**, yields mostly the substitution product **2h** (*cf.* runs *7* and *17* in Table 1).

The presence of two phenyl groups in the β-position of 2-halo-2-alkenal causes inertness of this compound with respect to secondary amines. In fact, even after keeping a mixture of 2-chloro-3,3-diphenylpropenal (**1i**) with piperidine at ~20 °C for a long period, only the starting compounds are detected by chromatography (run *18*).

The selectivities of the reactions studied depend substantially on the nature of the nucleophile. For example, reactions of heterocyclic amines, piperidine and morpholine (see Table 1, runs *5* and *6*), with aldehyde **1c** occur as *ipso*-substitution of the halogen atom with high selectivities, whereas in the case of diethylamine and dibutylamine (runs *7* and *8*), fragmentation reactions yielding enediamines **4** predominate. It should be noted that the closest analogs of piperidine, *viz.*, hexamethylenimine and pyrrolidine, give no substitution products **2c** in the reactions with the same substrate **1c**. In the former case, the process is accompanied by considerable resinification, and the reaction of pyrrolidine occurs exclusively as 1,4-anhydro-condensation (run *9*, *cf.* also run *3*). Weakly basic amines, diphenylamine and *N*-methylamine, do not react with 2-halo-2-alkenals under the studied conditions.

The selectivity of interaction of secondary amines with α-halo-α,β-unsaturated aldehydes **1** does not correlate with the basicity of the amine. The reaction is likely to be noticeably affected by the spatial structure of the nucleophile. However, piperidine, pyrrolidine, and diethylamine having similar basicities and steric accessibilities of the N atom react with the same substrate to give absolutely different products. This fact as well as similar deviations observed in the reactions of amines with other reagents,[14,15] are still difficult to explain.

The pathways of the reactions studied depend substantially on the nature of the solvent. An increase in the solvent polarity is favorable for the $S_N$vin reaction.[10]

2-Amino-2-alkenals **2** are usually obtained as mixtures of *Z*- and *E*-isomers, whereas the starting 2-halo-2-alkenals **1** exist as one geometric isomer. A study of the mechanism of the reaction considered will be published in the next communication.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Jeol FX-90Q spectrometer (89.95 and 22.49 MHz) in $CDCl_3$ using HMDS as the internal standard. IR spectra were obtained on a Specord 75-IR instrument in thin films. Mass spectra (EI) were measured on a Varian MAT-212 mass spectrometer (70 eV). GC analysis was carried out using an LKhM-80 chromatograph (heat-conductivity detector, 2000×4 mm column, 5 % Silicone XE-60 on Chromaton N-AW and 5 % SKTFT-50 on Chromaton N-AW-HMDS as sorbents, He as carrier gas).

Commercial propenal, crotonaldehyde, and cinnamaldehyde were used. 3-Methyl-2-butenal was synthesized by a known procedure.[16] 3,3-Diphenylpropenal was obtained by previously described procedures.[17,18]

All the 2-chloro- and 2-bromo-2-alkenals (except for compound **1e**) were obtained by halogenation of the corresponding α,β-unsaturated aldehydes followed by dehydrohalogenation (the general procedure of the synthesis was published previously[19]). The synthesis of 2-chloro-2-hexenal (**1e**) was reported.[13] 2-Fluoro-2-butenal (**1b**) was obtained from propenyl ethyl ether and bromofluorocarbene generated *in situ* from dibromofluoromethane (see Refs. 20—22).

Reactions of 2-halo-2-alkenals 1 with secondary amines (general procedures)

Reaction of 2-chloro-2-hexenal (1e) with piperidine. A solution of compound **1e** (4.2 g, 32 mmol) in 15 mL of anhydrous THF was added dropwise to an intensely stirred solution of piperidine (5.5 g, 64 mmol) in 25 mL of THF. The mixture was allowed to stand at ~20 °C until precipitation of piperidine hydrochloride was over (overall yield 87 %). The precipitate was filtered off; evaporation of the solvent *in vacuo* gave a mixture for which the yields of products and the ratios between them were calculated. Vacuum distillation afforded pure 2-piperidino-2-hexenal (**2e**, $NR_2 = N(CH_2)_5$), yield 3.9 g (66 %), b.p. 65—66 °C (2 Torr), n_D^{20} 1.4970. Found (%): C, 73.04; H, 10.58; N, 8.06. $C_{11}H_{19}NO$. Calculated (%): C, 72.93; H, 10.50; N, 7.74. IR, ν/cm^{-1}: 1610 (C=C); 1682 (C=O). ^1H NMR, δ: *E*-isomer: 0.97 (t, CH_3); 1.54 (m, aliph. CH_2, piperidine ring β-, γ-CH_2); 2.38 (m, $C\underline{H}_2CH=$); 2.96 (m, $N(CH_2)_2$); 5.92 (t, CH=); 9.26 (s, CHO); *Z*-isomer: 0.97 (t, CH_3); 1.54 (m, aliph. CH_2, piperidine ring β-, γ-CH_2); 2.38 (m, $C\underline{H}_2CH=$); 2.70 (m, $N(CH_2)_2$); 5.61 (t, CH=); 9.85 (s, CHO).

Reaction of 2-chloro-2-butenal (1c) with morpholine. A solution of compound **1c** (10.4 g, 0.1 mol) in 15 mL of anhydrous THF was added dropwise to an intensely stirred solution of morpholine (8.7 g, 0.1 mol) and triethylamine (10.1 g, 0.1 mol) in 20 mL of THF. The mixture was allowed to stand at ~20 °C, the precipitated $Et_3N \cdot HCl$ being filtered off at intervals (overall yield 72 %). Evaporation of the solvent and unchanged starting compounds *in vacuo* gave a mixture for which the yields of products and the ratios between them were calculated. Vacuum distillation gave 2-morpholino-2-butenal (**2c**, $NR_2 = N(CH_2CH_2)_2O$), yield 5.4 g (35 %), b.p. 78—80 °C (2 Torr). Spectral characteristics of aldehyde **2c** ($NR_2 = N(CH_2CH_2)_2O$) were reported in Ref. 10.

Reaction of 2-bromo-3-phenylpropenal (1h) with diethylamine. A solution of compound **1h** (10.6 g, 50 mmol) in 25 mL of anhydrous THF was added dropwise to an intensely stirred solution of diethylamine (7.3 g, 100 mmol) in 25 mL of THF. The mixture was allowed to stand at ~20 °C until precipitation of diethylammonium hydrobromide (overall yield 84 %) was over. The precipitate was filtered off. Evaporation of the solvent *in vacuo* gave a mixture for which the yields of products and the ratios between them were calculated. Vacuum distillation gave pure aldehyde **2h** ($NR_2 = NEt_2$), yield 4.4 g (43 %), b.p. 87—89 °C (0.03 Torr), n_D^{20} 1.5150. Found (%): N, 6.79. Calculated (%): N, 6.89. IR, ν/cm^{-1}: 1585 (C=C); 1670 (C=O). ^1H NMR, δ: *E*-isomer: 0.97 (t, CH_3); 3.11 (q, CH_2); 6.72 (s, CH=); 7.22—7.54 (m, C_6H_5); 9.48 (s, CHO); *Z*-isomer: 1.07 (t, CH_3); 3.16 (q, CH_2); 6.60 (s, CH=); 7.22—7.54 (m, C_6H_5); 9.51 (s, CHO). MS, *m/z* (I_{rel} (%)): 203 $[M]^+$ (100), 174 $[M-CHO]^+$ (53).

***N*,*N*-Disubstituted 2-amino-2-alkenals 2c ($NR_2 = N(CH_2CH_2)_2O, N(CH_2)_5$), 2e ($NR_2 = N(CH_2)_5$), 2f ($NR_2 = N(CH_2)_5, N(CH_2CH_2)_2O$), and 2h ($NR_2 = NEt_2$)** were isolated in a pure state by fractional distillation *in vacuo*, and **aldehydes 2c ($NR_2 = NEt_2, NBu_2$)** were purified by preparative-scale GC (SE-30, 75—100 °C). Spectral characteristics and physicochemical characteristics of these compounds were reported in Refs. 10 and 11.

2-Piperidino-3-phenylpropenal (2h, $NR_2 = N(CH_2)_5$) could not be isolated in a pure state. IR, ν/cm^{-1}: 1585 (C=C); 1670 (C=O). ^1H NMR, δ: *E*-isomer: 1.54 (m, piperidine ring β-, γ-CH_2); 2.96 (m, $N(CH_2)_2$); 6.75 (s, CH=); 7.28—7.60 (m, C_6H_5); 9.51 (s, CHO); *Z*-isomer: 1.54 (m, piperidine ring β-, γ-CH_2); 2.96 (m, $N(CH_2)_2$); 6.45 (s, CH=); 7.28—7.60 (m, C_6H_5); 9.41 (s, CHO). MS, *m/z* (I_{rel} (%)): 215 $[M]^+$ (100), 186 $[M-CHO]^+$ (60).

Benzaldehyde (**3h**) was identified by GLC by comparing it with an authentic sample.

The products of the reaction involving 2-chloropropenal were identified in the reaction mixture.

2-Chloro-1,3-dipyrrolidinopropene (5a, NR_2 = $N(CH_2)_4$). IR, ν/cm^{-1}: 1640 (C=C). ^{1}H NMR, δ: 1.78 (m, pyrrolidine ring β-CH_2); 2.55 (m, $-C-N(CH_2)_2$); 3.35 (m, $=C-N(CH_2)_2$); 3.16 (s, NCH_2); 6.20 (s, CH=). ^{13}C NMR, δ: 23.4, 25.3 (pyrrolidine ring β-CH_2); 51.4, 53.3 (pyrrolidine ring α-CH_2); 62.7 (NCH_2); 101.5 (CCl); 133.8 (CH=). MS, *m/z* (I_{rel} (%)): 214 $[M]^+$ (17), 144 $[M-N(CH_2)_4]^+$ (100).

2-Chloro-1,3-bis(diethylamino)propene (5a, NR_2 = NEt_2). IR, ν/cm^{-1}: 1645 (C=C). ^{1}H NMR, δ: 1.01 (t, CH_3); 2.54 (m, $-C-N(CH_2)_2$); 3.14 (m, $=C-N(CH_2)_2$, NCH_2); 5.90 (s, CH=). ^{13}C NMR, δ: 11.2, 13.9 (CH_3); 45.7, 46.6 (aliph. NCH_2); 59.9 (CH_2N); 102.8 (CCl); 133.9 (CH=). MS, *m/z* (I_{rel} (%)): 146 $[M-NEt_2]^+$ (100).

2-Chloro-1,3-dipiperidinopropene (5a, NR_2 = $N(CH_2)_5$). IR, ν/cm^{-1}: 1650 (C=C). ^{1}H NMR, δ: 1.65 (m, piperidine ring β-, γ-CH_2); 2.42 (m, $-C-N(CH_2)_2$); 3.00 (m, $=C-N(CH_2)_2$, NCH_2); 5.86 (s, CH=). ^{13}C NMR, δ: 25.5, 25.6 (piperidine ring β-, γ-CH_2); 51.5, 53.5 (piperidine ring α-CH_2); 65.8 (NCH_2); 113.3 (CCl); 136.3 (CH=). MS, *m/z*: 242 $[M]^+$, 158 $[M-N(CH_2)_5]^+$.

2-Piperidino-2-propenal (2a, NR_2 = $N(CH_2)_5$). ^{1}H NMR, δ: 1.65 (m, piperidine ring β-, γ-CH_2); 2.95 (m, piperidine ring α-CH_2); 4.84 (d, CH_2=); 9.24 (s, CHO).

2-Chloro-1,3-dipyrrolidino-1-butene (5c, NR_2 = $N(CH_2)_4$). IR, ν/cm^{-1}: 1660 (C=C). ^{1}H NMR, δ: 1.31 (d, CH_3); 1.78 (m, pyrrolidine ring β-CH_2); 2.52 (m, $-C-N(CH_2)_2$); 3.30 (m, $=C-N(CH_2)_2$); 6.19 (s, CH=). MS, *m/z* (I_{rel} (%)): 228 $[M]^+$ (10), 158 $[M-N(CH_2)_4]^+$ (100).

2-Fluoro-1,3-dipiperidino-1-butene (5b, NR_2 = $N(CH_2)_5$). IR, ν/cm^{-1}: 1690 (C=C). ^{1}H NMR, δ: 1.23 (d, CH_3); 1.50 (m, β-, γ-CH_2); 2.40 (m, NCH_2); 2.93 (m, $=C-NCH_2$); 2.71 (m, $C\underline{H}-CH_3$); 4.82 (d, CH=, J = 33 Hz). ^{13}C NMR, δ: 15.7 (CH_3); 24.3–24.5 (piperidine ring β-, γ-CH_2); 50.41, 50.86 (piperidine ring α-CH_2); 61.3 (CH—N); 119.9 (CH=); 143.7 (CF, $J_{C,F}$ = 258 Hz).

1,2-Bis(diethylamino)ethene (4, NR_2 = NEt_2) was isolated in the pure state by fractionation *in vacuo*, b.p. 63.5—64.0 °C (5 Torr), n_D^{20} 1.4580 (Ref. 23: b.p. 82—83 °C (17 Torr), n_D^{20} 1.4595). ^{1}H NMR, δ: 1.03 (t, CH_3); 2.70 (q, CH_2); 5.10 (s, CH=). ^{13}C NMR, δ: 12.4 (CH_3); 47.4 (CH_2); 122.9 (CH=).

The other *N,N,N',N'*-tetrasubstituted 1,2-diaminoethenes **4** were identified in the reaction mixtures by ^{1}H NMR spectroscopy.[24]

1,2-Dipiperidinoethene (4, NR_2 = $N(CH_2)_5$). ^{1}H NMR, δ: 1.54 (m, β-, γ-CH_2); 2.69 (m, α-CH_2); 5.15 (s, CH=, *E*-isomer); 5.30 (s, CH=, *Z*-isomer).

1,2-Bis(dibutylamino)ethene (4, NR_2 = NBu_2). ^{1}H NMR, δ: 0.96 (m, CH_3); 1.46 (m, β-, γ-CH_2); 2.68 (m, α-CH_2); 5.14 (s, CH=).

1,2-Dimorpholinoethene (4, NR_2 = $N(CH_2CH_2)_2O$). ^{1}H NMR, δ: 2.66 (m, α-CH_2); 3.73 (m, β-CH_2); 5.18 (s, CH=, *E*-isomer); 5.30 (s, CH=, *Z*-isomer).

N-Formylamines **6** were identified in the reaction mixtures by GC using two phases. Reference samples were synthesized by a previously described procedure.[25,26]

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References

1. Z. Rappoport, *Adv. Phys. Chem.*, 1969, **7**, 1.
2. G. Modena, *Acc. Chem. Res.*, 1971, **4**, 73.
3. B. A. Shainyan, *Usp. Khim.*, 1986, **55**, 942 [*Russ. Chem. Rev.*, 1986, **55** (Engl. Transl.)].
4. N. De Kimpe and R. Verhe, *The Chemistry of α-Haloketones, α-Haloaldehydes, and α-Haloimines*, Wiley-Interscience Publ., New York—London, 1988.
5. Y. Gelas-Miathe, R. Hierle, and R. Vessiere, *J. Heterocycl. Chem.*, 1974, **11**, 347.
6. L. Wartski, *Bull. Soc. Chim. Fr.*, 1975, 1663.
7. J. L. Klein and J. C. Combret, *Bull. Soc. Chim. Fr.*, 1983, 28.
8. USSR Pat. 1204619; *Byull. Izobret.*, 1986, No. 2 (in Russian).
9. N. A. Keiko, A. Yu. Rulev, I. D. Kalikhman, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1801 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1668 (Engl. Transl.)].
10. N. A. Keiko, A. Yu. Rulev, I. D. Kalikhman, and M. G. Voronkov, *Synthesis*, 1989, 446.
11. A. Yu. Rulev, Ph. D. Thesis (Chem.), Irkutsk State University, Irkutsk, 1988 (in Russian).
12. V. T. Klimko, T. V. Protopopova, and A. P. Skoldinov, *Dokl. Akad. Nauk SSSR*, 1962, **146**, 1084 [*Dokl. Chem.*, 1962, **146** (Engl. Transl.)].
13. A. Yu. Rulev, A. S. Mokov, L. B. Krivdin, N. A. Keiko, and M. G. Voronkov, *Zh. Org. Khim.*, 1995, **31** [*J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
14. R. Bartzly, E. Lorz, P. B. Russel, and F. M. Smith, *J. Am. Chem. Soc.*, 1955, **77**, 624.
15. V. A. Zagorevskii, V. L. Savel'ev, N. V. Dudykina, and S. L. Portnova, *Zh. Org. Khim.*, 1967, **3**, 568 [*J. Org. Chem. USSR*, 1967, **3** (Engl. Transl.)].
16. I. N. Nazarov, S. M. Makin, and B. K. Kruptsov, *Zh. Obshch. Khim.*, 1959, **29**, 3683 [*J. Gen. Chem. USSR*, 1959, **29** (Engl. Transl.)].
17. J. Rauss-Godineau, J. Barralis, W. Chodkiewicz, and P. Cadiot, *Bull. Soc. Chim. Fr.*, 1968, 193.
18. I. L. Kotlyarevskii, M. S. Shvartsberg, and L. B. Fisher in *Reaktsii atsetilenovykh soedinenii* [*Reactions of Acetylene Compounds*], Nauka, Novosibirsk, 1967, 59 (in Russian).
19. I. A. Andreeva, M. M. Koton, A. N. Akopova, and N. V. Kukarkina, *Zh. Org. Khim.*, 1975, **11**, 954 [*J. Org. Chem. USSR*, 1975, **11** (Engl. Transl.)].
20. H. Molines, T. Nguyen, and C. Wakselman, *Synthesis*, 1985, 754.
21. Yu. V. Savinykh and V. S. Aksenov, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* [*Bull. Siberian Branch Acad. Sci. USSR, Div. Chem. Sci.*], 1978, 125 (in Russian).
22. Y. Bessiere, D. N. Savary, and M. Schlosser, *Helv. Chim. Acta*, 1977, **60**, 1739.
23. USSR Pat. 368234; *Byull. Izobret.*, 1973, No. 9 (in Russian).
24. L. Duhamel, P. Duhamel, and G. Plé, *Bull. Soc. Chim. Fr.*, 1968, 4423.
25. E. J. Poziomek, *J. Org. Chem.*, 1963, **28**, 243.
26. F. F. Blicke and C.-J. Lu, *J. Am. Chem. Soc.*, 1952, **74**, 3933.

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