Journal of Organometallic Chemistry, 206 (1981) 257—264
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ORGANOSILVER(I) CHEMISTRY: ON THE REACTION OF RAg AND R_2AgMgCl COMPOUNDS WITH CONJUGATED ENYNENITRILES

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(Received August 27th, 1980)

Summary

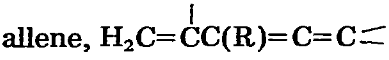
The addition of RAg and $R_2AgMgCl$ to enynenitriles $H\overset{|}{C}=\overset{|}{C}C\equiv CCN$ is described. RAg reagents prefer to transfer their R group to the double bond of these nitriles, so that after protolysis 2,3-alkadienenitriles are obtained, while the homoargentates generally give 2,4-alkadienenitriles. The regio- and stereochemical course of the reactions are compared with those in additions of RCu and $R_2CuMgCl$ to the enynenitriles.

Introduction

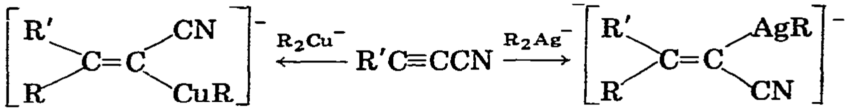
While organocopper(I) compounds have been used successfully in many synthetic investigations during the last decade, the synthetic applicability of the corresponding silver(I) compounds was only recently noted [1—4]. It appears that silver(I) reagents very often behave in complementary way to copper(I) reagents with respect to stereo- and regio-chemical features. For example, conjugated enynes, $H_2C=\overset{|}{C}C\equiv CH$, undergo 1,4-addition with organosilver(I) compounds to give allenylsilver(I) reagents, $RCH_2\overset{|}{C}=C=CHAg$ [1], while organocopper(I) reagents prefer to attack the triple bond to form $H_2C=\overset{|}{C}C(R)=CHCu$ [5,6]. The allenylsilver(I) compounds formed react selectively with a large variety of electrophiles to give the corresponding allenes in excellent yields [4].

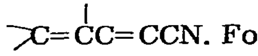
Another interesting synthetic application of alkylsilver(I) compounds is based on the ready formation of butatriene $RCH_2\overset{|}{C}=C=C=C<$, from $H_2C=\overset{|}{C}C\equiv C\underset{|}{\overset{|}{C}}OS(O)Me$ [3]. The enynyl esters undergo 1,3-substitution when

0022—328X/81/0000—0000/$02.50, © 1981, Elsevier Sequoia S.A.

copper(I) reagents are used and the product is an allene,  $H_2C{=}\overset{|}{C}C(R){=}C{=}C\lessgtr$ [3].

In a preliminary communication we have further shown that silver(I) reagents can also show different stereochemical features from copper(I) compounds; thus 2-alkynenitriles undergo *trans* addition with alkylargentates [2] and *cis* addition with cuprates [7]:

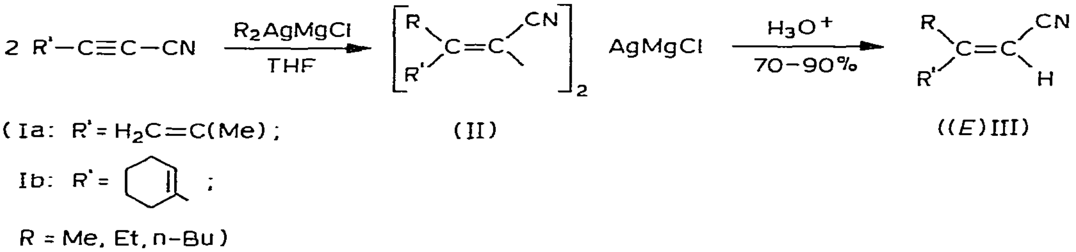


The present study concerns the reaction of $R_2AgMgCl$ and RAg compounds with some enynenitriles,  $>C{=}\overset{|}{C}C{\equiv}CCN$. For purposes of comparison we have also examined the reaction of two enynenitriles with copper(I) compounds.

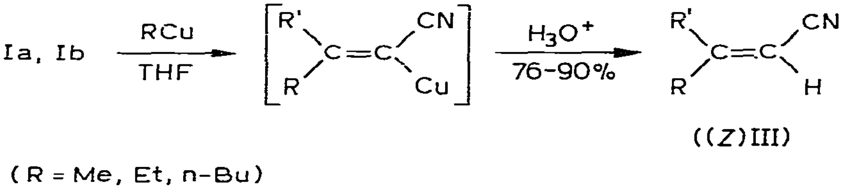
Results and discussion

(a) Addition of dialkylargentates to enynenitriles

Dialkylargentates, $R_2AgMgCl$*, readily react with the enynyl nitriles Ia and Ib ($R'C{\equiv}CCN$; Ia: $R' = H_2C{=}C(Me)$, Ib: R' = 1-cyclohexenyl) in tetrahydrofuran (THF). The regiochemistry of the reaction appears to depend on the group R′ in I, and on the nature of R in the argentate. A smooth transfer to both R groups of $R_2AgMgCl$ to the C—C triple bond of Ia and Ib took place when R was a primary alkyl group. Protolysis of the intermediary adducts II gave (*E*)-2,4-alkadienenitriles in high yield (70—90%):


(II) ((*E*)III)

The stereochemistry of this reaction is *trans*. We proved this by comparing the spectroscopic data for III with those for their *Z*-isomers; the latter were prepared as described in ref. 7, by a *cis* addition of RCu reagents ** to Ia and Ib:


((*Z*)III)

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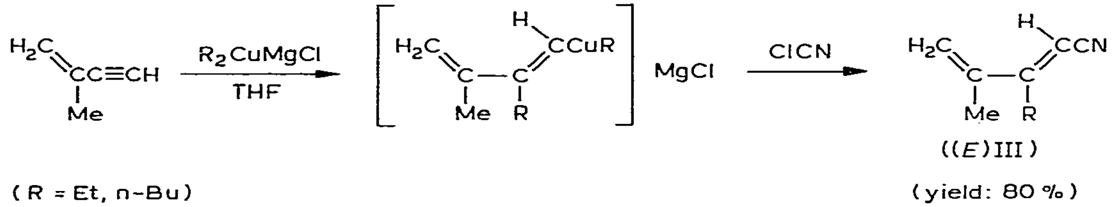
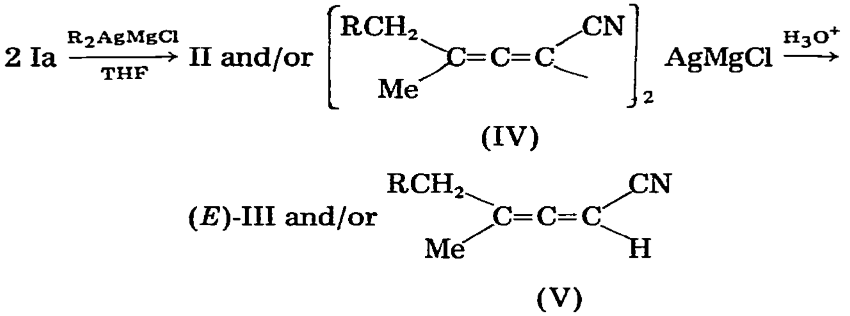
* The argentates were prepared from RMgCl and the THF-soluble complex $AgBr \cdot 3\,LiBr$. Reactions of I with $Ph_2AgMgCl$ did not give identifiable products.

** The copper(I) reagents mentioned in this paper were prepared from RMgCl and the complex $CuBr \cdot LiBr$.

In two cases we obtained additional proof for the *E*-geometry of the α,β-double bond of III. As indicated in the equation below we prepared two *E*-2,4-alkadienenitriles, III, by converting isopropenylacetylene stereospecifically into a dienylcuprate and treating this with cyanogen chloride. This procedure, which we described some time ago [8], gives (*E*)-III in excellent yield (80%). The two 2,4-alkadienenitriles III (R = Et and n-Bu) obtained in this manner were identical to those isolated from the reaction of Ia with $Et_2AgMgCl$ and $n\text{-}Bu_2AgMgCl$, respectively:



A more complex reaction is observed when enynenitriles (I) are treated with dialkylargentates in which the alkyl groups are branched. For example, the reaction of nitrile Ia with $i\text{-}Pr_2AgMgCl$ led, after protolysis, to a mixture of (*E*)-III (R = i-Pr) * and another compound, viz. allene V (R = i-Pr), in a ratio 80/20. The corresponding reaction of Ia with $t\text{-}Bu_2AgMgCl$ give, exclusively, V (R = t-Bu; yield: 90%). It is noteworthy that the reaction of Ia with $t\text{-}Bu_2CuMgCl$ or with t-BuCu produces a mixture of III (R = t-Bu) and V (R = t-Bu) in a 75/25 ratio. Thus the copper(I) reagents prefer to attack the C—C triple bond of Ia.



(IV)

(V)

(R = i-Pr: III/V = 80/20;
R = t-Bu: III/V = 0/100; yield of III + V: 90%)

The cyclohexenyl compound Ib, on the other hand, only undergoes addition to the C—C triple bond when treated with $i\text{-}Pr_2AgMgCl$; the product in this case is *E*-III (R = i-Pr, R′ = 1-cyclohexenyl), as was shown comparing its spectroscopic data with those of the corresponding *Z*-isomer, which was obtained in 80% yield from Ib and i-PrCu.

The reaction of Ib with $t\text{-}Bu_2AgMgCl$ gives a complex mixture of products, among which is the 2,4-alkadienenitrile(III).

The reason that $i\text{-}Pr_2AgMgCl$ and $t\text{-}Bu_2AgMgCl$ convert Ia partly or completely into allenic nitriles while n-alkylargentates do not, most probably lies in steric

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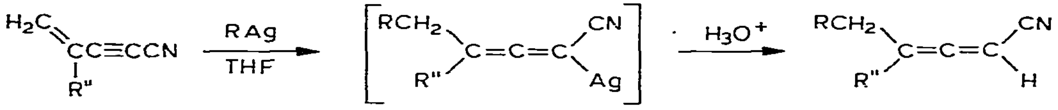
* The *Z*-isomer of III was obtained exclusively by treating Ia with i-PrCu (yield: 76%).

factors. Argentates with very bulky alkyl groups like t-Bu undoubtedly prefer to transfer their alkyl groups to the terminal, unsubstituted double bond carbon atom of Ia. In case of Ib this carbon atom bears a substituent, and this explains why in this case the i-Pr group from i-$Pr_2AgMgCl$ is transferred completely to the C—C triple bond *. It is not clear why t-$Bu_2AgMgCl$ does not convert Ib solely into III, but instead gives a complex mixture of products.

(b) Addition of RAg to enynenitriles

Under (a) we discussed the influence of R on the regiochemistry of reactions between enynenitriles and dialkylargentates. In this section attention is focused on reactions of enynenitriles with RAg compounds **. The results obtained with this type of silver(I) compound are remarkable. Thus we have found that treatment of enynenitrile Ia with RAg in which R is a primary, secondary, or tertiary alkyl group always gives exclusively 2,3-alkadienenitriles V (after protolysis of the intermediates VI) ***. Similar results were obtained from enynenitrile Ic, in which the double bond bears a very bulky substituent at the non-terminal carbon atom.



(VI) (V)

(Ia: R'' = Me;
Ic: R'' = t-Bu;
R = Et, n-Bu, i-Pr or t-Bu)

(yield: 85–90%)

This remarkable difference in stereochemistry for reactions of I with $R_2AgMgCl$ and RAg is quite unexpected, and may perhaps also be observed with other unsaturated substrates.

In a previous paper we already noted that organosilver(I) reactions are very susceptible to steric hindrance [1]. It is therefore conceivable that enynenitrile Ib is not a suitable substrate for preparing V. Treatment of Ib, for example, with an equimolar amount of EtAg, or with four molar equivalents of EtAg, gave several products, including 2,4-alkadienenitrile(III) and (as indicated by IR spectroscopy) an allenic compound (absorption at 1960 cm^{-1}). An absorption at 1960 cm^{-1} was likewise present in the IR spectrum of the product mixture obtained from Ib and t-BuAg; the ^1H NMR spectrum did not give any evidence for the presence of compound III in this case.

For a smooth formation of 2,3-alkadienenitriles it thus seems necessary that the terminal carbon atom of the double bond should be free of substituents. If this carbon atom is unsubstituted, RAg reagents can readily give compounds V. Such 2,3-alkadienenitriles † are potentially useful intermediates in the syntheses

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* It should be noted that for transfer of R to the double bond of Ib, the R group enters in the axial position. When R is a bulky group, this is an unfavourable process.

** The RAg compounds were prepared from RMgCl and AgBr · 3 LiBr.

*** No suitable reaction conditions have hitherto been found for preparing V with R is Me or Ph in reasonable yield from I and the corresponding RAg compounds.

† See ref. 9 for a preparation of 2,3-alkadienenitriles from bromoallenes and cuprous cyanide.

of allenic amides and acids [9], enamines [10], and several heterocyclic compounds [11—13].

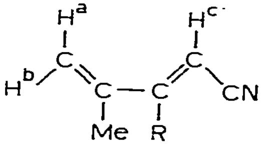
Experimental

All reactions with organosilver(I) and organocopper(I) compounds were performed under dry nitrogen. The products were analysed by GLC (SE 33 column) and by NMR (Varian EM-390 and CFT-20 spectrometers) and IR spectroscopy.

(a) General procedure for the reaction of I with $R_2AgMgCl$ *

To a stirred solution of AgBr · 3 LiBr (0.010 mol) in THF (35 ml) a solution of RMgCl (0.020 mol) in THF (~20 ml) at —60 to —50°C was added cautiously. The resulting homogeneous solution was stirred for 20 min at —60°C, then a solution of I (0.018 mol) in THF (10 ml) was added and the mixture was stirred for 1 h more at —60 to —50°C. The mixture was then poured into a saturated aqueous solution of ammonium chloride (200 ml) containing sodium cyanide (2 g). The products III and/or V were extracted with diethyl ether/n-pentane (90/10 v/v) and the extracts were washed with water and dried over $MgSO_4$. After evaporation of the solvent in vacuo the residue was distilled. Physical constants and some spectroscopic data for the distilled products *E*-III are given below (data found for the allene $t\text{-}BuCH_2C(Me){=}C{=}CHCN$ (yield: 90%) are given under (d)).

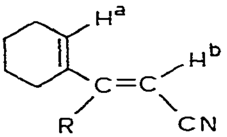
Compounds



R = Et (yield: 85%): b.p. 78—79°C/19 mmHg; n_D^{20} 1.4963. IR (NaCl) 2218, 1583 cm^{-1}. ^1H NMR (CCl_4, TMS): δ 1.16 (CH_3CH_2), 1.90 ($CH_3C\leqq$), 2.63 (CH_2CH_3), 5.26 (H^c), 5.26 + 5.40 (H^a + H^b).

R = Bu (yield: 90%). b.p. 103—105°C/19 mmHg; n_D^{20} 1.4907. IR (NaCl) 2220, 1581 cm^{-1}. ^1H NMR (CCl_4, TMS): δ 0.90 ($CH_3(CH_2)_3$), 1.10—1.75 (2 × CH_2), 1.90 ($CH_3C\leqq$), 2.58 ($(CH_2)\overset{|}{C}{=}\overset{|}{C}CN$), 5.28 ($H^c$), 5.28 + 5.38 ($H^a$ + H^b).

Compounds



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* The reaction of Ib with $Me_2AgMgCl$ and physical and spectroscopic data for the adduct were described in reference [2].

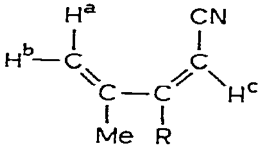
R = Et (yield: 80%): b.p. 75—77°C/0.06 mmHg; n_D^{20} 1.5395. IR (NaCl) 2210, 1620 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 1.13 (CH_3CH_2), 1.38—1.87 ($2 \times CH_2$), 1.94—2.40 ($2 \times CH_2$), 2.60 ($CH_2\overset{|}{C}=\overset{|}{C}CN$), 5.12 ($H^b$), 6.23 ($H^a$).

R = i-Pr (yield: 70%): b.p. 80—83°C/0.06 mmHg; n_D^{20} 1.5210. IR (NaCl) 2212 1620 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 1.26 ($(CH_3)_2CH$), 1.38—1.85 ($2 \times CH_2$), 1.93—2.35 ($2 \times CH_2$), 1.93—2.35 ($2 \times CH_2$), 3.03 (${>}CH\overset{|}{C}=\overset{|}{C}CN$), 5.09 ($H^b$), 5.94 ($H^a$).

(b) General procedure for the reaction of I with RCu *

To a stirred solution of CuBr · LiBr (0.020 mol) in THF (40 ml) a solution of RMgCl (0.020 mol) in THF (~20 ml) at —50 to —60°C was added cautiously. The mixture was stirred for 20 min at —60°C, and a solution of I (0.018 mol) in THF (10 ml) was then added. The reaction mixture was subsequently stirred for 30 min at —50°C. The product was isolated as described for (*E*)-III under (a). Physical constants and some spectroscopic data for the distilled products *Z*-III are given below.

Compounds

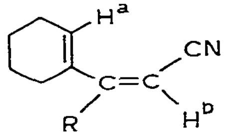


R = Et (yield: 90%): b.p. 79—80°C/19 mmHg; n_D^{20} 1.4751. IR (NaCl) 2218, 1610 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 1.02 (CH_3CH_2), 1.98 ($CH_3\overset{|}{C}{<}$), 2.30 ($CH_2\overset{|}{C}=\overset{|}{C}CN$), 5.10 ($H^c$), 5.18 ($H^a + H^b$).

R = n-Bu (yield: 86%): b.p. 105—106°C/19 mmHg; n_D^{20} 1.4743. IR (NaCl) 2217, 1612 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 0.90 ($CH_3(CH_2)_3$), 1.10—1.60 ($2 \times CH_2$), 1.96 ($CH_3\overset{|}{C}=$), 2.28 ($CH_2\overset{|}{C}=\overset{|}{C}CN$), 5.10 ($H^c$), 5.20 ($H^a + H^b$).

R = i-Pr (yield: 76%): b.p. 88—90°C/19 mmHg; n_D^{20} 1.4712. IR (NaCl) 2220 1605 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 1.07 ($(CH_3)_2CH$), 1.92 ($CH_3C=$), 2.58 (${>}CHC=CCN$), 5.03 (H^a), 5.09 (H^c), 5.18 (H^b).

Compounds



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* The reaction of Ib with MeCu, and physical and spectroscopic data for the adduct were reported in ref. 7.

R = Et (yield: 70%): b.p. 77—80° C/0.08 mmHg; n_D^{20} 1.5120. IR (NaCl) 2218, 1603 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 1.00 (CH_3CH_2), 1.30—1.90 (2 × CH_2), 1.95—2.30 (2 × CH_2), 2.28 ($CH_2C{=}CCN$), 5.00 (H^b), 5.92 (H^a).

R = i-Pr (yield: 80%): b.p. 77—80° C/0.08 mmHg; n_D^{20} 1.5039. IR (NaCl) 2219, 1600 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 1.04 ($(CH_3)_2CH$), 1.40—1.90 (2 × CH_2), 1.95—2.30 (2 × CH_2) 2.53 ($\sqsupset CHC{=}CCN$), 4.98 (H^b), 5.79 (H^a).

(c) Preparation of (E)-$H_2C{=}C(Me)C(R){=}CHCN$ (R = Et, n-Bu) from isopropenylacetylene

To a stirred solution of CuBr · LiBr (0.020 mol) in THF (60 ml) a solution of RMgCl (0.040 mol) in THF (~40 ml) at —60 to —50° C was added cautiously. After 20 min isopropenylacetylene (0.050 mol) was added at —60° C, and stirring of the mixture was continued for 30 min at —10° C. The mixture was then colled to —30° C, and a solution of ClCN (0.044 mol) in diethyl ether (20 ml) was carefully added. The mixture was then stirred for 45 min at —10° C, and the product was isolated as described under (a). The two 2,4-alkadienenitriles (*E*)-$H_2C{=}C(MeC(R){=}CHCN$ (R = Et or n-Bu) were obtained in 80% yield, and were identical to those described under (a).

(d) General procedure for the reaction of I with RAg

To a stirred solution of AgBr · 3 LiBr (0.020 mol) in THF (60 ml) a solution of RMgCl (0.020 mol) in THF (~20 ml) at —60 to —50° C was added cautiously. The mixture was stirred for 20 min at —60° C, and a solution of I (0.018 mol) in THF (10 ml) was added at this temperature. Subsequently, the mixture was stirred for 30 min at —30° C, and the product was isolated as described under (a). The following physical constants and characteristic spectroscopic data were found for the distilled compounds $RCH_2C_\gamma R''{=}\underset{\beta}{C}{=}\underset{\alpha}{C}HCN$ (V).

R = Et, R″ = Me (yield: 90%): b.p. 86—88° C/19 mmHg; n_D^{20} 1.4730. IR (NaCl) 2221, 1960 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 0.96 ($CH_3CH_2CH_2$), 1.60 (CH_3CH_2), 1.80 (R″), 2.08 (RCH_2), 5.07 ($=CHCN$). ^{13}C NMR ($CDCl_3$, TMS): δ 213.18 (C_β), 113.74 ($—C{\equiv}N$), 106.13 (C_γ), 66.65 (C_α).

R = n-Bu, R″ = Me (yield: 85%): b.p. 111—113° C/19 mmHg; n_D^{20} 1.4720, IR (NaCl) 2220, 1960 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 0.90 ($CH_3(CH_2)_4$), 1.10—1.65 (3 × CH_2), 1.79 (R″), 2.08 (RCH_2), 5.07 ($=CHCN$). ^{13}C NMR ($CDCl_3$, TMS): δ 213.11 (C_β), 113.56 ($C{\equiv}N$), 106.25 (C_γ), 66.76 (C_α).

R = i-Pr, R″ = Me (yield: 85%): b.p. 92—93° C/20 mmHg; n_D^{20} 1.4704. IR (NaCl) 2222, 1961 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 0.94 ($(CH_3)_2CH$), 1.78 (R″), 1.50—2.08 (RCH_2 + $(CH_3)_2CH$), 5.08 ($=CHCN$). ^{13}C NMR ($CDCl_3$, TMS): δ 213.53 (C_β), 113.62 ($C{\equiv}N$), 104.90 (C_γ), 66.14 (C_α).

R = t-Bu, R″ = Me (yield: 90%) *: b.p. 99—101° C/20 mmHg; n_D^{20} 1.4722. IR (NaCl) 2222, 1956 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 0.99 (t-Bu), 1.83 (R″), 1.98 (RCH_2), 5.06 ($=CHCN$). ^{13}C NMR ($CDCl_3$, TMS): δ 214.47 (C_β), 113.39 ($C{\equiv}N$), 103.26 (C_γ), 65.79 (C_α).

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* The same compound was obtained in 90% yield from Ia and $t\text{-}Bu_2AgMgCl$.

R = Et, R″ = t-Bu (yield: 90%): b.p. 108—110°C/20 mmHg; n_D^{20} 1.4713. IR (NaCl) 2225, 1950 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 0.94 ($CH_3CH_2CH_2$), 1.09 (R″), 1.40 ($CH_3CH_2CH_2$), 2.04 (RCH_2), 5.16 (=CHCN). ^{13}C NMR ($CDCl_3$, TMS): δ 212.00 (C_β), 120.08 (C_γ), 114.15 ($C{\equiv}N$), 68.45 (C_α).

R = t-Bu, R″ = t-Bu (yield: 90%): b.p. 120—123°C/20 mmHg; n_D^{20} 1.4724. IR (NaCl) 2225, 1945 cm^{-1}. ^{1}H NMR (CCl_4, TMS): δ 0.99 (t-Bu), 1.09 (R″), 2.02 (RCH_2), 5.15 (=CHCN). ^{13}C NMR ($CDCl_3$, TMS): 213.00 (C_β), 115.76 (C_γ), 113.82 ($C{\equiv}N$), 68.71 (C_α).

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