Lewis Acids-Catalyzed Nucleophilic Addition of Allylstannane to Aroylhydrazone

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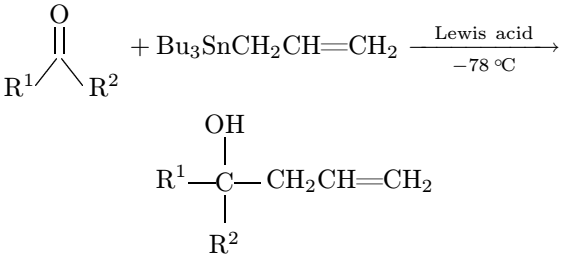
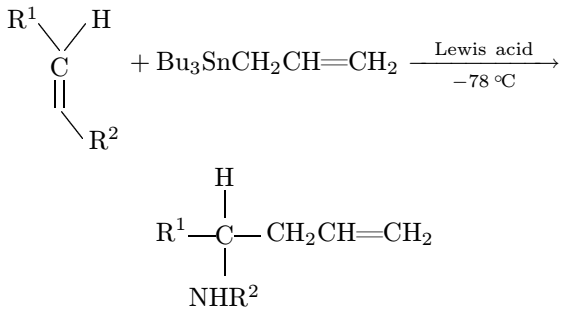
A convenient and selected synthetic method of N'-but-3-enylaroylhydrazide preparation has been performed *via* nucleophilic addition of allyltributylstannane to aroylhydrazone catalyzed by Lewis acids under mild conditions.

Allylstannane can add to carbonyl in aldehyde and ketone using Lewis acids, such as BF_3, $MgBr_2$, $SnCl_4$, $TiCl_4$, ZnI_2, *etc.* as catalysts [1—3] as shown



In addition, allylstannane can also add to C=N double bond in imine to form but-3-enylamine [4, 5] as shown



These additions are efficient in organic synthesis, especially in preparation of some natural products, such as Cembranolide [6], Benganide [7], (±)Statine [8], and (±)Coniine [9], but addition of allyltin to substrates containing simultaneously both C=O and C=N double bonds has not been reported so far.

Table 1. Substrates and Addition Products

Product	R^1	R^2	Yield/%
IVa	C_6H_5	C_6H_5	62
IVb	2-HOC_6H_4	C_6H_5	60
IVc	2-BrC_6H_4	C_6H_5	68
IVd	2-BrC_6H_4	2-HOC_6H_4	60
IVe	2-$MeOC_6H_4$	C_6H_5	64
IVf	2-$MeOC_6H_4$	2-HOC_6H_4	58
IVg		C_6H_5	56

In the present work we wish to describe a new and convenient synthesis of N'-(4-arylbut-3-enyl)aroylhydrazide *via* selective addition of allyltributylstannane to aroylhydrazone.

The aroylhydrazone undergoes the addition of allylstannane as shown in Scheme 1. The addition products for this reaction, but-3-enylaroylhydrazides (*IV*), are shown in Table 1.

This reaction is able to occur easily at room temperature and does not need a tedious condition (−78 °C). It is apparent the addition is nucleophilic and selective, and the organotin reagents add only to C=N bond without touching the C=O bond. Even when the mole ratio of aroylhydrazone to $Bu_3SnCH_2CH{=}CH_2$ was 1:2, the addition products on C=O bond have not been obtained. The reaction goes through an intermediate stage forming tin complex in the presence of $SnCl_4$ and the "exocyclic" N=C bond, which is not involved in the chelate *III* which is the only one accessible for the nucleophilic at-

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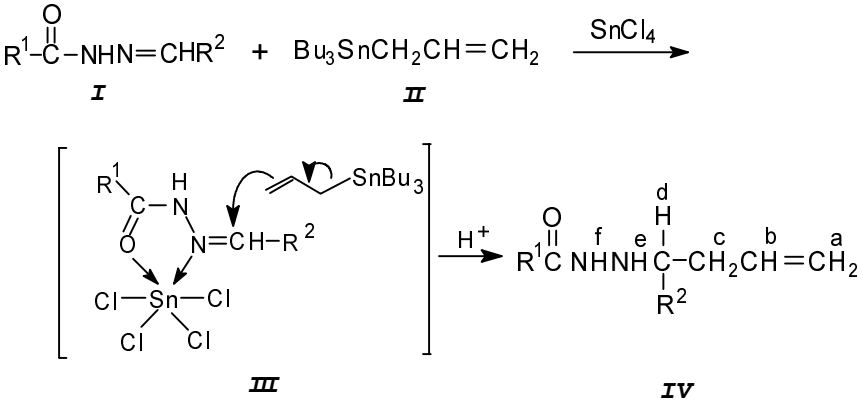

Scheme 1

tack. The similar tin-complex intermediate (*III*) had been separated and characterized in our previous work [10]. It can be seen from these results that this addition is a convenient and effective method for synthesizing *N′*-(but-3-enyl)aroylhydrazides.

EXPERIMENTAL

Aroylhydrazone and allyltributylstannane were prepared by literature methods [11, 12]. IR spectra were recorded on a Nicolet 170SX spectrometer using KBr discs. ^{1}H NMR spectra were measured on a PMX-60 spectrometer using CCl_4 or $CDCl_3$ as solvent and Me_4Si as internal standard. Mass spectra were taken on an HP 5988A spectrometer.

General Procedure for Addition

I (0.5 mmol) was dissolved in THF (10 cm^3) under an argon atmosphere at room temperature. After stirring for 20 min $SnCl_4$ (0.06 cm^3, 0.5 mmol) was added slowly, then *II* (0.34 cm^3, 1 mmol) was added dropwise. The content of container was stirred for 20 h until the reaction was complete according to thin-layer chromatography. After removing solvent, 10 % hydrochloric acid (5 cm^3) was introduced and the mixture was hydrolyzed. The solution was extracted with ether, separated on chromatographic sheet using petroleum ether—ether (volume ratio = 8:1) as developer and the product, yellow oil liquid, was obtained.

N′-(4-Phenylbut-3-enyl)benzoylhydrazide (IVa). ^{1}H NMR spectrum, δ: 2.46—2.60 (m, 2H, H*c*), 4.14—4.17 (t, 1H, H*b*), 5.09—5.19 (q, 2H, H*a*), 5.76—5.87 (m, 1H, H*d*), 7.23—7.26 (m, 10H, H_{arom}). IR spectrum, $\tilde{\nu}_{max}$/cm^{-1}: 3270 (NH), 3064 (=CH), 2923 (CH_2), 1637 (C=O), 1578 (C=C), 920 (δ (=CH)), 758 (aryl ring). MS, *m*/*z*: 266 (M^+), 225 (M − allyl), 105 (R^1CO), 131 ($R^2CH^+CH_2CH{=}CH_2$); for $C_{17}H_{18}N_2O$ calc. M_r = 266.

N′-(4-Phenylbut-3-enyl)2-hydroxybenzoylhydrazide (IVb). ^{1}H NMR spectrum, δ: 2.45—2.52 (m, 2H, H*c*), 4.05—4.08 (t, 1H, H*b*), 5.08—5.16 (q, 2H, H*a*), 5.72—5.81 (m, 1H, H*d*), 6.66—7.36 (m, 9H, H_{arom}), 11.25—12.15 (br, 1H, OH_{arom}). IR spectrum, $\tilde{\nu}_{max}$/cm^{-1}: 3288 (NH), 3060 (=CH), 2917 (CH_2), 1639 (C=O), 1599 (C=C), 919 (δ(=CH)), 754 (aryl ring). MS, *m*/*z*: 281 ($M^+ - 1$), 241 (M − allyl), 121 (R^1CO), 131 ($R^2CH^+CH_2CH{=}CH_2$); for $C_{17}H_{18}N_2O_2$ calc. M_r = 282.

N′-(4-Phenylbut-3-enyl)2-bromobenzoylhydrazide (IVc). ^{1}H NMR spectrum, δ: 2.41—2.49 (m, 2H, H*c*), 4.17—4.21 (t, 1H, H*b*), 5.04—5.13 (q, 2H, H*a*), 5.15—5.17 (d, 1H, H*e*), 5.73—5.81 (m, 1H, H*d*), 7.15—7.45 (m, 9H, H_{arom}). IR spectrum, $\tilde{\nu}_{max}$/cm^{-1}: 3274 (NH), 3066 (=CH), 2924 (CH_2), 1644 (C=O), 1589 (C=C), 917 (δ(=CH)), 753 (aryl ring). MS, *m*/*z*: 344 (M^+), 303 (M − allyl), 183 (R^1CO), 131 ($R^2CH^+CH_2CH{=}CH_2$); for $C_{17}H_{18}N_2O_2$ calc. M_r = 344.

N′-[4-(2-Hydroxyphenyl)but-3-enyl]2-bromobenzoylhydrazide (IVd). ^{1}H NMR spectrum, δ: 2.50—2.62 (m, 2H, H*c*), 4.30—4.34 (t, 1H, H*b*), 5.11—5.16 (q, 2H, H*a*), 5.35—5.48 (d, 1H, H*e*), 5.79—5.85 (m, 1H, H*d*), 6.74—7.47 (m, 8H, H_{arom}), 9.48 (br, 1H, H*f*). IR spectrum, $\tilde{\nu}_{max}$/cm^{-1}: 3264 (NH), 3070 (=CH), 2924 (CH_2), 1648 (C=O), 1588 (C=C), 918 (δ(=CH)), 753 (aryl ring). MS, *m*/*z*: 360 (M^+), 319 (M − allyl), 183 (R^1CO), 147 ($R^2CH^+CH_2CH{=}CH_2$); for $C_{17}H_{17}BrN_2O_2$ calc. M_r = 360.

N′-(4-Phenylbut-3-enyl)2-methoxybenzoylhydrazide (IVe). ^{1}H NMR spectrum, δ: 2.41—2.50 (m, 2H, H*c*), 3.55 (s, 3H, OCH_3), 4.05—4.09 (t, 1H, H*b*), 5.04—5.14 (q, 2H, H*a*), 5.25—5.60 (d, 1H, H*e*), 5.72—5.82 (m, 1H, H*d*), 6.78—8.09 (m, 9H, H_{arom}), 9.91 (s, 1H, H*f*). IR spectrum, $\tilde{\nu}_{max}$/cm^{-1}: 3273 (NH), 3066 (=CH), 2923 (CH_2), 1642 (C=O), 1597 (C=C), 916 (δ(=CH)), 753 (aryl ring). MS, *m*/*z*: 296 (M^+), 255 (M − allyl), 135 (R^1CO), 131 ($R^2CH^+CH_2$-$CH{=}CH_2$); for $C_{18}H_{20}N_2O_2$ calc. M_r = 296.

N′-[4-(2-Hydroxyphenyl)but-3-enyl]2-methoxybenzoylhydrazide (IVf). ^{1}H NMR spectrum, δ: 2.58—2.67 (m, 2H, H*c*), 3.67 (s, 3H, OCH_3), 4.24—4.27 (t, 1H, H*b*), 5.14—5.28 (q, 2H, H*a*), 5.70 (br, 1H, H*e*), 5.82—5.92 (m, 1H, H*d*), 6.79—8.15 (m, 8H, H_{arom}),

9.19 (s, 1H, H*f*), 10.00 (br, 1H, OH_{arom}). IR spectrum, $\tilde{\nu}_{max}$ /cm^{-1}: 3296 (NH), 3074 (=CH), 2923 (CH_2), 1652 (C=O), 1600 (C=C), 915 (δ(=CH)), 754 (aryl ring). MS, m/z: 311 ($M^+ - 1$), 271 (M – allyl), 135 (R^1CO), 147 ($R^2CH^+CH_2CH{=}CH_2$); for $C_{18}H_{20}N_2O_3$ calc. $M_r = 312$.

N′-(4-Phenylbut-3-enyl)2-furoylhydrazide (IVg). ^{1}H NMR spectrum, δ: 2.39—2.48 (m, 2H, H*c*), 4.04—4.10 (t, 1H, H*b*), 5.04—5.13 (q, 2H, H*a*), 5.70—5.81 (m, 1H, H*d*), 6.38—7.53 (m, 8H, H_{arom}, H_{furyl}). ^{13}C NMR spectrum, δ: 64.0 (C-1), 40.4 (C-2), 134.3 (C-3), 118.0 (C-4), 141.4 (C-1′), 128.5 (C-2′, C-6′), 127.6 (C-3′, C-5′), 127.6 (C-4′), 158.0 (C-1″), 146.6 (C-2″), 114.7 (C-3″), 111.9 (C-4″), 146.6 (C-5″). IR spectrum, $\tilde{\nu}_{max}$/cm^{-1}: 3280 (NH), 3066 (=CH), 2923 (CH_2), 1657 (C=O), 1590 (C=C), 917 (δ(=CH)), 755 (aryl ring). MS, m/z: 255 ($M^+ - 1$), 215 (M – allyl), 95 (R^1CO), 131 ($R^2CH^+CH_2CH{=}CH_2$); for $C_{15}H_{16}N_2O_2$ calc. $M_r = 256$.

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