

Facile and Effective Synthesis of Unusually Substituted Aromatic *N*-Phenylamides

Uwe Kobs²⁾ and Wilhelm P. Neumann*

Lehrstuhl für Organische Chemie I der Universität Dortmund,
Otto-Hahn-Straße 6, D-4600 Dortmund 50

Received April 11, 1990

Key Words: Electrophilic aromatic substitution / Carbo-destannylation / Amides, synthesis of / Trialkylarylstannanes, application of / Aryl isocyanates

A mild and effective new method for the preparation of a variety of arylamides **3a–i** as well as heterocyclic **5a, b** and **6** and olefinic amides **7, 9** is described. The reaction of trialkylstannyl-substituted aromatic, heterocyclic or vinylic hydrocarbons with aryl isocyanates in the presence of aluminium trichloride provides the corresponding *N*-aryl-substituted am-

ides in good to excellent yields. The stannyl group serves as a powerful leaving group superior to hydrogen by several powers of ten which allows, via *ipso* substitution, to obtain isomer patterns not accessible by normal electrophilic substitution reactions, e.g. substitution in *meta* position with respect to a methoxy group.

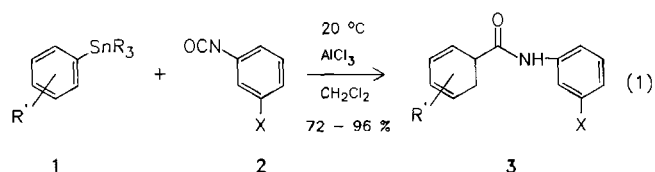
Increasing interest in the synthesis of natural products has led to an extensive use of aromatic amides as synthons in modern organic synthesis^{3,4)}. Despite of this growing need for mild and efficient synthetic methods for the preparation of various amides most approaches^{3,5)} still require drastic conditions like high temperature or strongly basic media. To avoid this, Effenberger and Gleiter^{6a)} have developed the earlier method of Leuckart^{6b)} which yields the *para* isomers of *N*-substituted arylamides by reacting the corresponding aromatic hydrocarbon with the appropriate isocyanate in the presence of aluminium trichloride. The sole disadvantage of this method is – besides the need of a 7–8-fold excess of the aromatic hydrocarbon with respect to the isocyanate – that it provides, in the examples investigated so far, access only to the *para*-substituted amides according to the normal rules for electrophilic aromatic substitution reactions. To circumvent these problems we present in this paper a new route to unusually substituted amides which makes use of the trialkylstannyl group as a superior leaving group in aromatic substitutions.

The ability of the trialkylstannyl group to act as a powerful leaving group superior to hydrogen by several powers of ten has first been demonstrated by Eaborn in kinetic experiments⁷⁾. The Sn–C bond is cleaved 10¹⁰ times faster than the corresponding H–C bond, thus allowing regioselective substitution reactions^{7b)}. In our group this concept has been extended to the *ipso*-selective synthesis of ketones and aldehydes by tin-mediated Friedel-Crafts acylations and Vilsmeier formylations^{1a,8)}. A number of compounds have been obtained in high yields or isomer distributions not obtainable in usual electrophilic substitution reactions. These results have led us to the investigation of the reaction of trialkylarylstannanes with the complex of aryl isocyanates and aluminium trichloride. This purpose is backed by the

recent, efficient, and versatile methods to obtain the trialkylstannyl-substituted precursors conveniently (for a compilation, see ref.^{1a)}).

Results and Discussion

Trialkylarylstannanes **1** react easily under very mild conditions (20 °C) with aryl isocyanates **2** in the presence of aluminium trichloride to yield the corresponding *N*-substituted benzamides **3**. Only the *ipso* isomer is obtained, eq. (1), the yields are excellent. A comparison of the yields of amides obtained from **1c** and **1d** shows that the toxicologically much less suspicious tributylstannyl group is at least as effective as leaving group as the trimethylstannyl group. For spectroscopic reasons the methyl derivatives are still used in this investigation in some cases. An excess of the



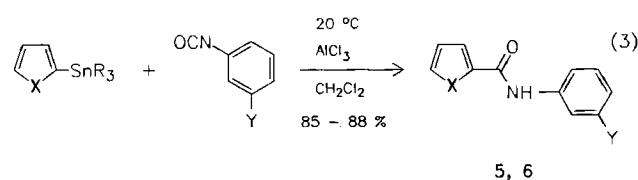
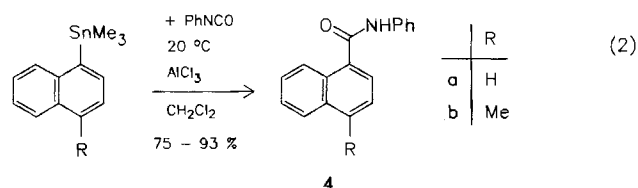
	R	R'	X		R'	X	
a	Bu	4-Me	a	H	a	4-Me	H
b	Me	4-Cl	b	Cl	b	4-Cl	H
c	Me	3-Me			c	4-Cl	Cl
d	Bu	3-Me			d	3-Me	H
e	Bu	2-Et			e	3-Me	Cl
f	Me	3-Cl			f	2-Et	H
g	Me	3-OMe			g	3-Cl	Cl
					h	3-OMe	H
					i	3-OMe	Cl

aryl component^{6a}) is no longer necessary, and the reaction conditions (formerly^{6a}) up to 130 °C) are considerably milder now. Therefore, this method should be applicable also to the synthesis of high-value natural compounds.

It is remarkable how easily the directive effects of substituents in the aromatic nucleus are overcome. The *meta*-substituted compounds **1c, d** react with the isocyanates **2a, b** to the corresponding *ipso*-substitution products **3d, e** exclusively. The *ortho/para* directing effect of the methyl group is not effective here. This demonstrates the efficiency of the stannyl group as a leaving group. Even the effect of the very strongly *ortho/para* directing methoxy group is overcompensated to give the *ipso* products **3h, i** in high yields and exclusively. This has led us to the assumption that a close, σ -analogue complex between the electrophile and the stannane with the extension of the coordination sphere of the tin atom via the lone electron pair of the nitrogen atom is responsible for this result. In other cases where such a complexation is weaker or not possible, e.g. in acylations or brominations of anisole, no *ipso* destannylations or desilylations has been observed^{2,8a,9,10}, which has led to the postulation that no such reactions can be carried out in *meta* position with respect to a methoxy group¹¹). However, our results show that the ability of the tin atom to enlarge its coordination sphere provides an additional effect for influencing electrophilic substitutions.

Even the deactivating effect of a chloro substituent (**1b, f**) can easily be overcome. The powerful leaving ability of the stannyl group allows substitutions in *para* (**3b, c**) as well as in *meta* (**3g**) position with respect to the chloro substituent. Only the strong deactivating effects of a trifluoromethyl or cyano group cannot be overcompensated by the stannyl group².

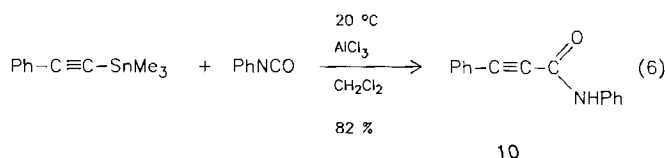
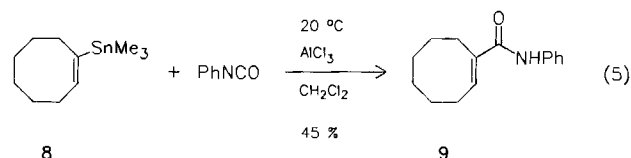
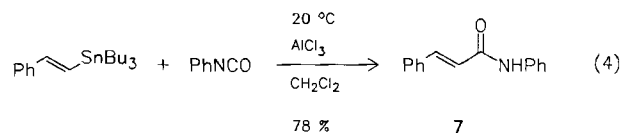
This method for synthesizing *N*-aryl-substituted amides can easily be extended to polycyclic (**4a, b**), eq. (2), and heterocyclic (**5a, b, 6**) amides, eq. (3), as demonstrated by a few typical examples. In each case the nonstannylated hydrocarbons are much less reactive than the stannylated ones, e.g. 1-methylnaphthalin yields only 16% **4b** whereas with



	X	Y
5a	O	H
5b	O	Cl
6	NMe	H

1-methyl-4-trimethylstannyl-naphthalin the yield of **4b** is 93%.

Vinylstannanes have received considerable interest¹² since the beginning of modern organotin chemistry. Two typical examples **7, 9**, eqs. (4), (5), show that the reaction described in this paper is also advantageous for the preparation of olefinic amides. Even stannyl-substituted alkynes like 1-phenyl-2-(trimethylstannyl)ethyne react to yield the corresponding amide **10**, eq. (6), although earlier studies¹³ showed that with an excess of isocyanate hydantoin can be obtained. In both cases a *N*-stannyl-substituted amide may be postulated as an intermediate.



Since preliminary investigations² have shown that the tin-mediated synthesis of amides is also possible with vinyl isocyanates, further work concerning the expansion of this reaction and the application to the synthesis of natural products are under investigation.

U. K. is grateful to the *Studienstiftung des Deutschen Volkes* for a Postgraduate Fellowship. This work was supported by the *Fonds der Chemischen Industrie*.

Experimental

All melting points were determined with a Büchi SMP 20. — IR spectra: Shimadzu 3289. — NMR spectra: Varian EM 360 (60 MHz, ¹H) and Bruker AM 300 (300 MHz, ¹H, 75.47 MHz, ¹³C, and 111.92 MHz, ¹¹⁹Sn). — Mass spectra: Finnigan MAT 8230, 70 eV. — Elemental analyses: Carlo Erba 1106.

N-Arylbenzamide **3a–i**. — *General Procedure*: The solution of an aryl isocyanate (11 mmol) in 20 ml of anhydrous dichloromethane is treated under argon with sublimed aluminium trichloride (11 mmol) at 20 °C for 15 min. After adding a trialkylstannane¹⁴ (10 mmol) during 5 min the mixture is stirred at 20 °C for 2 h. The solution is then poured on ca. 50 g ice and stirred for 30 min. Separation of the organic phase is followed by twofold extraction of the aqueous phase with 10 ml of dichloromethane. The combined organic phases are treated with 10 ml of a saturated solution of KF in water, stirred vigorously for 3 h, and the precipitated R₃SnF is filtered off. The filtrate is extracted thrice with 10 ml of dichloromethane, the combined organic phases are dried with 5 g of MgSO₄ and after filtration concentrated at

15 Torr/30°C. For purification the crude product is recrystallized from the appropriate solvent.

4-Methyl-*N*-phenylbenzamide (3a): From 4.0 g (10.5 mmol) of **1a**, 1.4 g (11.7 mmol) of **2a**, and 1.5 g (11.5 mmol) of AlCl₃, 2.0 g (89%) of **3a** is obtained, recrystallisation from petroleum ether, m. p. 144°C (ref.^{6a}) 145–146°C). — ¹H NMR (CDCl₃): δ = 2.35 (s, 3H, Me), 7.2–7.6 (m, 9H, aromatic H), 8.2 (s, 1H, NH).

4-Chloro-*N*-phenylbenzamide (3b): From 2.0 g (7.3 mmol) of **1b**, 1.3 g (10.9 mmol) of **2a**, and 1.4 g (10.5 mmol) of AlCl₃, 1.4 g (81%) **3b** is obtained, m. p. 197–198°C from petroleum ether (ref.^{6a}) 200–201°C). — ¹H NMR (CDCl₃): δ = 7.2–7.8 (m, 9H, aromatic H), 8.40 (s, 1H, NH).

4-Chloro-*N*-(3-chlorophenyl)benzamide (3c): From 2.0 g (7.3 mmol) of **1b**, 2.2 g (14.5 mmol) of **2b**, and 1.9 g (14.5 mmol) of AlCl₃, 1.5 g (78%) of **3c** is obtained, m. p. 133°C from methanol (ref.¹⁵) 137°C). — IR (KBr): $\tilde{\nu}$ = 1480 cm⁻¹, 1530, 1590, 1645, 3300. — ¹H NMR (CDCl₃): δ = 7.15–7.90 (m, 8H, aromatic H), 8.50 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 118.39, 120.52, 124.81, 128.46, 128.98, 134.68 (CH), 129.99, 132.75, 138.35, 138.73 (C), 164.92 (C=O).

3-Methyl-*N*-phenylbenzamide (3d): From 2.0 g (7.8 mmol) of **1c**, 1.1 g (9.2 mmol) of **1a**, and 1.2 g (9.2 mmol) of AlCl₃, 1.4 g (87%) of **3d** is obtained, m. p. 130°C from ethanol (ref.¹⁵) 129°C). — IR (KBr): $\tilde{\nu}$ = 1330 cm⁻¹, 1440, 1490, 1535, 1595, 1650. — ¹H NMR (CDCl₃): δ = 2.60 (s, 3H, Me), 7.1–7.9 (m, 9H, aromatic H), 8.2 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 21.2 (CH₃), 120.4, 124.0, 124.3, 127.8, 128.3, 128.8, 132.3 (CH), 134.7, 137.9, 138.3 (C), 166.3 (C=O).

***N*-(3-Chlorophenyl)-3-methylbenzamide (3e):** From 4.0 g (10.5 mmol) of **1d**, 1.8 g (11.5 mmol) of **2b**, and 1.5 g (11.5 mmol) of AlCl₃, 2.2 g (88%) of **3e** is obtained after recrystallisation from petroleum ether, m. p. 84–85% (ref.¹⁵) 79°C). — IR (KBr): $\tilde{\nu}$ = 1510 cm⁻¹, 1580, 1650, 3280. — ¹H NMR (CDCl₃): δ = 2.40 (s, 3H, Me), 7.0–7.85 (m, 8H, aromatic H), 8.15 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 20.71 (CH₃), 118.25, 120.19, 123.61, 123.99, 127.62, 127.85, 129.31, 132.05 (CH), 133.78, 134.13, 137.77, 139.41 (C), 166.29 (C=O).

2-Ethyl-*N*-phenylbenzamide (3f): From 4.0 g (10.1 mmol) of **1e**, 1.3 g (10.7 mmol) of **2a**, and 1.4 g (10.7 mmol) of AlCl₃, 1.6 g (72%) of **3f** is obtained, m. p. 134°C from ethanol. — IR (KBr): $\tilde{\nu}$ = 1540 cm⁻¹, 1595, 1640, 3260. — ¹H NMR (CDCl₃): δ = 1.40 (t, *J* = 8 Hz, 3H, CH₃), 3.0 (q, *J* = 8 Hz, 2H, CH₂), 7.2–8.0 (m, 10H, aromatic H und NH). — ¹³C NMR (CDCl₃): δ = 15.8 (CH₃), 26.2 (CH₂), 119.9, 124.4, 125.7, 126.5, 128.9, 129.4, 130.2 (CH), 136.1, 137.9, 142.3 (C), 168.3 (C=O).

3-Chloro-*N*-(3-chlorophenyl)benzamide (3g): From 2.0 g (7.3 mmol) of **1f**, 1.7 g (10.9 mmol) of **2b**, and 1.5 g (10.9 mmol) of AlCl₃, 1.6 g (86%) of **3g** is obtained, m. p. 118°C from ethanol (ref.¹⁵) 120°C). — IR (KBr): $\tilde{\nu}$ = 1420 cm⁻¹, 1515, 1585, 1650, 3300. — ¹H NMR (CDCl₃): δ = 7.10–8.00 (m, 8H, aromatic H), 8.65 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 118.03, 119.98, 123.65, 125.28, 127.09, 129.32, 131.09, 133.85 (CH), 129.32, 133.71, 136.06, 139.28 (C), 164.27 (C=O).

3-Methoxy-*N*-phenylbenzamide (3h): From 2.0 g (7.6 mmol) of **1g**, 1.1 g (9.2 mmol) of **2a**, and 1.2 g (9.0 mmol) of AlCl₃, 1.3 g (75%) of **3h** is obtained, m. p. 121°C from methanol (ref.¹⁶) 120°C). — IR (KBr): $\tilde{\nu}$ = 1430 cm⁻¹, 1470, 1530, 1585, 1645, 3250. — ¹H NMR (CDCl₃, 300 MHz): δ = 3.00 (s, 3H, OMe), 6.3–6.9 (m, 9H, aromatic H), 7.60 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 55.3 (OCH₃), 112.4, 117.9, 118.8, 120.4, 124.5, 128.9, 129.5 (CH), 136.3, 137.9, 159.7 (C), 165.9 (C=O).

***N*-(3-Chlorophenyl)-3-methoxybenzamide (3i):** From 2.0 g (7.6 mmol) of **1g**, 1.8 g (11.4 mmol) of **2b**, and 1.5 g (11.4 mmol) of AlCl₃, 1.9 g (96%) of **3i** is obtained, m. p. 109°C from petroleum ether (ref.¹⁶) 111–112°C). — IR (KBr): $\tilde{\nu}$ = 1425 cm⁻¹, 1475, 1530, 1590, 1645, 3250. — ¹H NMR (CDCl₃): δ = 3.85 (s, 3H, OMe), 7.0–7.8 (m, 8H, aromatic H), 8.40 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 55.3 (OCH₃), 112.4, 118.1, 118.4, 118.8, 120.5, 124.5, 129.6, 129.9 (CH), 134.5, 135.8, 139.0, 159.8 (C), 166.0 (C=O).

***N*-Phenyl-1-naphthalenecarboxamide (4a):** According to the general procedure from 4.0 g (13.6 mmol) 1-(trimethylstannyl)naphthalene, 1.7 g (14.4 mmol) of **2a**, and 1.9 g (14.4 mmol) of AlCl₃, 2.5 g (75%) of **4a** is obtained, m. p. 163°C from ethanol (ref.¹⁷) 164–164.5°C). — IR (KBr): $\tilde{\nu}$ = 1315 cm⁻¹, 1430, 1500, 1590, 1640, 3280. — ¹H NMR (CDCl₃): δ = 7.10–8.20 (m, 12H, aromatic H), 8.40 (s, 1H, NH).

4-Methyl-*N*-phenyl-1-naphthalenecarboxamide (4b): According to general procedure from 1.0 g (3.3 mmol) of 4-methyl-1-(trimethylstannyl)naphthalene, 0.4 g (3.3 mmol) of **2a**, and 0.4 g (3.3 mmol) of AlCl₃, 0.8 g (93%) of **4b** is obtained, m. p. 184°C from ethanol (ref.¹⁸) 179°C). — IR (KBr): $\tilde{\nu}$ = 1321 cm⁻¹, 1439, 1524, 1596, 1647, 3275. — ¹H NMR (CDCl₃): δ = 2.75 (s, 3H, Me), 7.2–8.5 (m, 12H, aromatic H and NH). — ¹³C NMR ([D₆]DMSO): δ = 19.4 (CH₃), 120, 123.7, 124.6, 125.3, 125.6, 125.8, 126.4, 126.7, 128.8 (CH), 130.0, 132.3, 133.4, 136.7, 139.5 (C), 167.6 (C=O).

***N*-Phenyl-2-furancarboxamide (5a):** According to the general procedure from 1.0 g (4.3 mmol) of 2-(trimethylstannyl)furan, 0.5 g (4.3 mmol) of **2a**, and 0.6 g (4.5 mmol) of AlCl₃, 0.7 g (87%) of **5a** is obtained, m. p. 122°C from ethanol (ref.¹⁹) 124°C). — ¹H NMR (CDCl₃): δ = 6.55 (t, 2 Hz, 1H, CH), 7.00–7.80 (m, aromatic H), 8.20 (s, 1H, NH).

***N*-(3-Chlorophenyl)-2-furancarboxamide (5b):** According to the general procedure from 4.0 g (11.2 mmol) of 2-(tributylstannyl)furan, 1.8 g (11.7 mmol) of **2b**, and 1.5 g (11.3 mmol) of AlCl₃, 2.1 g (85%) of **5b** is obtained after recrystallisation from ethanol/petroleum ether (1:2), m. p. 113°C (ref.²⁰) 116°C). — IR (KBr): $\tilde{\nu}$ = 1426 cm⁻¹, 1530, 1598, 1666, 3270. — ¹H NMR (CDCl₃, 300 MHz): δ = 6.50 (m, 1H, CH), 7.05–7.77 (m, 6H, aromatic H), 8.26 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 112.56, 115.55, 117.91, 120.00, 124.41, 129.92, 144.39 (CH), 134.57, 138.47, 147.30 (C), 156.06 (C=O).

***N*-Methyl-2-pyrrolecarboxanilide (6):** According to the general procedure from 2.0 g (8.2 mmol) of *N*-methyl-2-(trimethylstannyl)pyrrole, 1.0 g (8.4 mmol) of **2a**, and 1.1 g (8.3 mmol) of AlCl₃ besides 10% *N,N'*-diphenylurea, 1.4 g (88%) of **6** is obtained after recrystallisation from petroleum ether, m. p. 117°C. — ¹H NMR (CDCl₃): δ = 3.8 (s, 3H, Me), 5.2, 5.7, 6.6 (s, je 1H, CH), 6.8–8.3 (m, 6H, aromatic H and NH).

***N*,3-Diphenyl-2-propenamamide (7):** According to the general procedure from 4.0 g (10.2 mmol) of 1-(tributylstannyl)-2-phenylethene, 1.3 g (10.9 mmol) of **2a**, and 1.4 g (10.5 mmol) of AlCl₃, 1.8 g (78%) of **7** is obtained, m. p. 152°C from ethanol (ref.²¹) 153.5–154°C). — ¹H NMR (CDCl₃): δ = 6.1 (d, *J* = 17 Hz, 1H, CH), 7.0–8.3 (m, 12H, aromatic H and NH).

1-(Trimethylstannyl)cyclooctene (8): To the Grignard reagent prepared from 50.0 g (0.26 mol) of 1-bromocyclooctene and 6.4 g (0.26 mol) of magnesium turnings in 250 ml of anhydrous THF is added a solution of 40.0 g (0.20 mol) of Me₃SnCl in 50 ml of anhydrous THF at 20°C during 30 min. After stirring at 66°C for 2 h the solution is hydrolysed with 150 ml of a saturated aqueous NH₄Cl. Twofold extraction of the aqueous phase with 100 ml of diethyl ether, drying of the combined organic phases with Na₂SO₄

and fractionating distillation yield after some (11.2 g) cyclooctyne (b. p. 62°C/15 Torr) 21.0 g (38%) of colourless **8**, b. p. 70–75°C/0.05 Torr. — ¹H NMR (CDCl₃, 300 MHz): δ = 0.04 (s, ²J_{SnH} = 52.9 Hz, 9H, SnMe₃), 1.41 (s, 8H, CH₂), 2.1 (m, 2H, CH₂), 2.3 (m, 2H, CH₂), 5.79 (t, J = 7.8 Hz, 1H, CH). — ¹³C NMR (CDCl₃): δ = -9.98 (¹J_{SnC} = 331.9 Hz, SnMe₃), 25.78, 26.47, 26.96, 29.08, 29.25, 30.24 (CH₂), 140.25 (CH, ²J_{SnC} = 31.4 Hz, C-2), 144.06 (C, ¹J_{SnC} = 476.0 Hz, C-1). — ¹¹⁹Sn NMR (CDCl₃): δ = -34.10.

C₁₁H₂₂Sn (273.0) Calcd. C 48.38 H 8.14
Found C 48.17 H 8.01

N-Phenyl-1-cyclooctenecarboxamide (**9**): According to the general procedure from 2.0 g (7.3 mmol) of **8**, 0.9 g (7.5 mmol) of **2a**, and 1.0 g (7.5 mmol) of AlCl₃, 0.75 g (45%) of **9** is obtained, m. p. 96°C. — ¹H NMR (CDCl₃, 300 MHz): δ = 1.45–1.62 (m, 8H, CH₂), 2.13–2.20 (m, 2H, CH₂), 2.43–2.47 (m, 2H, CH₂), 6.56 (t, J = 8.3 Hz, 1H, CH), 7.03 (t, 1H, aromatic H), 7.23 (m, 2H, aromatic H), 7.62 (d, 2H, aromatic H), 8.48 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 25.07, 25.50, 26.13, 26.58, 28.63, 29.13 (CH₂), 120.00, 123.44, 128.22, 135.70 (CH), 137.06, 138.13 (C), 167.61 (C=O).

C₁₅H₁₉NO (229.4) Calcd. C 78.55 H 8.37 N 6.11
Found C 78.29 H 8.18 N 6.27

N,3-Diphenyl-2-propyneamide (**10**): According to the general procedure from 2.5 g (9.4 mmol) of 2-(trimethylstannyl)ethyne, 1.2 g (10.1 mmol) of **2a**, and 1.3 g (9.8 mmol) of AlCl₃, 1.7 g (82%) of **10** is obtained, m. p. 129°C (EtOH) (ref.²² 128°C). — IR (KBr): $\tilde{\nu}$ = 1444 cm⁻¹, 1550, 1596, 1629, 2215, 3230. — ¹H NMR (CDCl₃, 300 MHz): δ = 7.07–7.73 (m, 10H, aromatic H), 9.31 (s, 1H, NH). — ¹³C NMR (CDCl₃): δ = 83.40, 86.05 (C≡C), 120.13, 124.55, 128.18, 128.70, 129.90, 132.35 (CH), 119.69, 137.49 (C), 151.64 (C=O).

CAS Registry Numbers

1a: 31614-66-1 / **1b**: 14064-15-4 / **1c**: 937-01-9 / **1d**: 68971-88-0 / **1e**: 127686-16-2 / **1f**: 17315-41-2 / **1g**: 17113-78-9 / **2a**: 103-71-9 / **2b**: 2909-38-8 / **3a**: 6833-18-7 / **3b**: 6833-15-4 / **3c**: 2447-96-3 / **3d**: 23099-05-0 / **3e**: 96749-32-5 / **3f**: 56776-51-3 / **3g**: 10286-92-7 / **3h**: 6833-23-4 / **3i**: 91612-04-3 / **4a**: 6833-19-8 / **4b**: 127686-13-9 / **5a**: 1929-89-1 / **5b**: 2008-49-3 / **6**: 123862-94-2 / **7**: 3056-73-3 / **8**: 127686-14-0 / **9**: 127686-15-1 / **10**: 7342-02-1 / Me₃SnCl: 1066-45-1 / 1-(trimethylstannyl)naphthalene: 944-85-4 / 4-methyl-1-(trimethylstannyl)naphthalene: 127686-17-3 / 2-(trimethylstannyl)furan: 51583-40-5 / 2-(tributylstannyl)furan: 118486-94-5 / *N*-methyl-

2-(trimethylstannyl)pyrrole: 107311-71-7 / 1-(tributylstannyl)-2-phenylethene: 79159-76-5 / 1-bromocyclooctene: 4103-11-1 / 2-(trimethylstannyl)-1-phenylethyne: 1199-95-7

- ¹⁾ ^{1a)} Part 1: W. P. Neumann, H. Hillgärtner, K. M. Baines, R. Dicke, K. Vorspohl, U. Kobs, U. Nußbeutel, *Tetrahedron* **45** (1989) 951. — ^{1b)} Part 2: U. Gerigk, M. Gerlach, W. P. Neumann, R. Vieler, V. Weintritt, *Synthesis* **1990**, 448.
- ²⁾ U. Kobs, *Dissertation*, University of Dortmund, 1990.
- ³⁾ A. L. J. Beckwith in *The Chemistry of Amides* (J. Zabicky, Ed.), Interscience, London 1970.
- ⁴⁾ ^{4a)} J. E. Baldwin, K. W. Bair, *Tetrahedron Lett.* **29** (1978) 2559. — ^{4b)} P. Beak, V. Snieckus, *Acc. Chem. Res.* **15** (1982) 306. — ^{4c)} I. Ninomiya, T. Naito in *The Alkaloids* (A. Brossi, Ed.), vol. XXII, p. 189, Academic Press, New York 1983.
- ⁵⁾ H. Henecka, P. Kurtz in *Methoden der Organischen Chemie* (Houben-Weyl, Ed.), vol. 8, Thieme, Stuttgart 1952.
- ⁶⁾ ^{6a)} F. Effenberger, R. Gleiter, *Chem. Ber.* **97** (1964) 472. — ^{6b)} R. Leuckart, *Ber. Dtsch. Chem. Ges.* **18** (1885) 873.
- ⁷⁾ ^{7a)} C. Faborn, K. C. Pande, *J. Chem. Soc.* **1960**, 1566. — ^{7b)} C. Eaborn, *J. Organomet. Chem.* **100** (1975) 43.
- ⁸⁾ ^{8a)} U. Nußbeutel, *Diplomarbeit*, University of Dortmund, 1987. — ^{8b)} A. Lube, *Diplomarbeit*, University of Dortmund, 1988. — ^{8c)} O. Thies, *Diplomarbeit*, University of Dortmund, 1989. — ^{8d)} C. Wicenc, *Diplomarbeit*, University of Dortmund, 1989.
- ⁹⁾ B. Bennetau, M. Krempp, J. Dunoguès, *J. Organomet. Chem.* **334** (1987) 263.
- ¹⁰⁾ C. Eaborn, D. E. Webster, *J. Chem. Soc.* **1960**, 179.
- ¹¹⁾ T. H. Chang, I. Fleming, *Synthesis* **1979**, 761.
- ¹²⁾ ^{12a)} W. P. Neumann, *The Organic Chemistry of Tin*, J. Wiley, New York 1970. — ^{12b)} M. Pereyre, J.-P. Quintard, A. Rahm, *Tin in Organic Synthesis*, Butterworth, London 1987. — ^{12c)} P. G. Harrison, *Chemistry of Tin*, Blackie, Glasgow 1989.
- ¹³⁾ W. P. Neumann, F. G. Kleiner, *Liebigs Ann. Chem.* **716** (1968) 29.
- ¹⁴⁾ All stannanes except for **8** were prepared according to published procedures. For a compilation of various procedures, see ref.^{1a)}.
- ¹⁵⁾ P. Grammaticakis, *Bull. Soc. Chim. Fr.* **1963**, 862.
- ¹⁶⁾ P. Grammaticakis, *Bull. Soc. Chim. Fr.* **1964**, 924.
- ¹⁷⁾ C. C. Price, E. C. Chapin, A. Goldmann, E. Krebs, H. M. Shafer, *J. Am. Chem. Soc.* **63** (1941) 1857.
- ¹⁸⁾ F. Mayer, A. Sieglitz, *Ber. Dtsch. Chem. Ges.* **55** (1922) 1835.
- ¹⁹⁾ L. Vargha, F. Gönczy, *J. Am. Chem. Soc.* **72** (1950) 2738.
- ²⁰⁾ N. P. Buu-Hoï, N. Hoán, *Recl. Trav. Chim. Pays-Bas* **68** (1949) 5.
- ²¹⁾ C. R. Hauser, R. S. Yost, B. I. Ringler, *J. Org. Chem.* **14** (1949) 261.
- ²²⁾ J. von Braun, H. Ostermayer, *Ber. Dtsch. Chem. Ges.* **70** (1937) 1002.

[132/90]