Journal of Organometallic Chemistry, 373 (1989) 377–384
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20067

Rhodium-catalyzed C–C coupling reactions involving ring opening of strained molecules

III *. Reaction of *N*-allylamides of organic acids

Gian Paolo Chiusoli, Mirco Costa, Fausto Pivetti
Istituto di Chimica Organica dell'Università, Viale delle Scienze, I-43100 Parma (Italy)

(Received April 10th, 1989)

Abstract

The rhodium-catalyzed reaction of diphenyl(methylene)cyclopropane with *N*-allylamides of organic acids involves ring opening followed by regioselective coupling with the internal carbon atom of the allylamide double bond. Formation of an intermediate rhodacycle is postulated.

Introduction

In previous papers [1] we showed that activated olefins or chelating unsaturated acids couple with diphenylmethylenecyclopropanes via Rh^{I}-catalyzed ring opening of the latter. Activated olefins underwent insertion regioselectively, only the terminal carbon atom being involved in carbon–carbon bond formation. In contrast, chelating unsaturated acids underwent non-regioselective reactions, which was rather surprising in view of the high regioselectivity (attack on the terminal carbon atom of the double bond) we had observed [2] in similar reactions of the same acids with alkynes and 1,2- and 1,3-dienes. The absence of regioselectivity was attributed to operation of different mechanisms, true double bond insertion being involved in the latter cases, and metallacycle formation in the case of the cyclopropane ring opening reactions [1].

Extension to other chelating substrates led us to study the behaviour of *N*-allylamides of organic acids, which have been reported to react with rhodium(I) complexes in isomerization reactions [3].

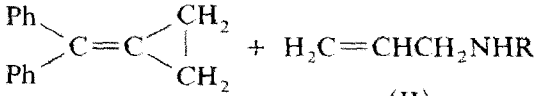
* For part II see ref. 1.

0022-328X/89/$03.50

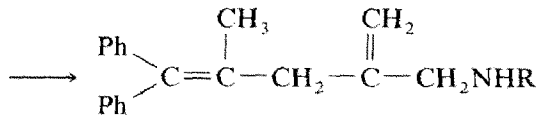
Results and discussion

(Diphenylmethylene)cyclopropane (I) reacts with *N*-allylamides (II) regioselectively. Surprisingly, however, the products, which are mixtures of isomeric 5,5-diphenyl-2-methylene-4-methyl-4-pentenylamine (IIIa) and 5,5-diphenyl-2,4-dimethylpentadienylamines (IIIb and IIIc), are essentially derived from attack on the internal carbon atom of the double bond, and not on the terminal one as was observed [2] in the case of regioselective reactions.

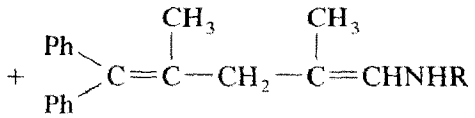
The reaction takes place according to eq. 1 (R = alkyl, aryl), and *E*-isomers are mainly formed.



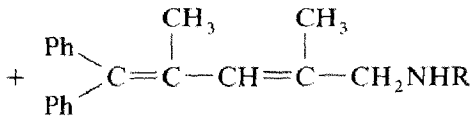
(I) (II)



(IIIa)



(IIIb)



(IIIc)

(R = $COCH_3$, COPh, $COOCH_2CH_3$, $COCH{=}CHCH_3$-(*E*), $SO_2(C_6H_4)$-*p*-CH_3)

The conditions are mild: compound I and the *N*-allylamide are heated in toluene at 90 °C in the presence of $RhCl(PPh_3)_3$ under nitrogen. The type of isomer formed depends on the substrate, solvent, temperature and time. In ethyl alcohol the less stable isomer is present in higher proportion than in toluene.

The *E* stereochemistry of the major isolated isomer (IIIc) has been unambiguously determined by X-ray diffraction for R = PhCO [4]. The corresponding isolated compound IIIb is suggested to be *E* on the basis of similar ^1H NMR coupling constants.

The reaction does not take place with other cyclopropanes, such as methylenecyclopropane, 1-phenyl-2-methylenecyclopropane and 1,1-diphenyl-2-methylenecyclopropane, but other amides can be used successfully. *E*- and *Z*-enamides also are reactive, although at a much lower rate. Allylamine and *N*-alkylallylamines are not reactive under the same conditions.

Some results are shown in Table 1.

Table 1

Reaction of I (1.0 mmol) with *N*-allylamides of organic acids (2.0 mmol) and $RhCl(PPh_3)_3$ (0.02 mmol) in toluene (3.0 ml) at 90 °C for 60 h

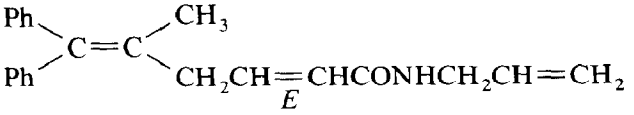
R in II	Conversion [a] (%)	Total yield [a] III + other stereoisomers (%)	Product yields [a] %					
			IIIa	IIIb	IIIc	other IIIa–IIIc stereoisomers	Isomers and hydrogenated derivatives of I	
$COCH_3$	93	72		4	56	12 [b]	8 [c]	3 [d]
$COCH_3$ [e]	92	53		15	22	16 [b]	12 [c]	17 [d]
COPh	98	73	4	10	40	19 [f]	4 [c]	2 [d]
COOEt	92	60	6		46	8 [b]	6 [c]	2 [d]
$COCH{=}CHCH_3$-(*E*)	90	58			43	15 [g]	7 [c]	2 [d]
$SO_2C_6H_4$-*p*-CH_3	90	36	10 [h]		12 [h]	14 [i]	9 [c]	3 [d]

[a] By GLC, based on substrate I. [b] Three IIIa–IIIc stereoisomers. Closely spaced GLC peaks (1/1.5/1.5 ratio areas) which could not be isolated. [c] Three isomers of I [1]. [d] Two hydrogenated derivatives of I [1]. [e] In EtOH at 75 °C. [f] Two IIIa–IIIc stereoisomers. Closely spaced GLC peaks (1/1.01) which could not be isolated. [g] Four IIIa–IIIc stereoisomers. Closely spaced GLC peaks (1/1/1.7/1.3) which could not be isolated. [h] Yield based on isolated products. [i] Yield estimated by GLC.

Yields are limited by self-reaction and hydrogenation (hydrogen transfer from the medium, particularly in ethanol) of the cyclopropane moiety, leading to isomers and dimers and to their hydrogenated derivatives [1]. Some (up to 15%) of the amide present in excess is transformed into *E*- and *Z*-enamides [3], along with small amounts of dimers (< 10%), the synthesis of which is described in the following paper. *N*-Methyl-*N*-allyl amides do not react with the cyclopropane compound but isomerize to enamides.

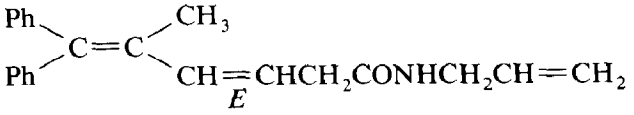
It is noteworthy that allyl acrylamide exclusively reacts at the terminal carbon atom of the acrylic site, while the allylic species undergoes some isomerizations (eq. 2, yields: IVa, 26%; IVb, 10%; IVc (*E*,*E*) 15%; IVc (*E*,*Z*) 18%), showing that *N*-allylamides are not as reactive as acrylic compounds.

$$\text{I} + \text{II} \xrightarrow{\text{Rh cat.}} \text{(R = COCH=CH}_2\text{)}$$



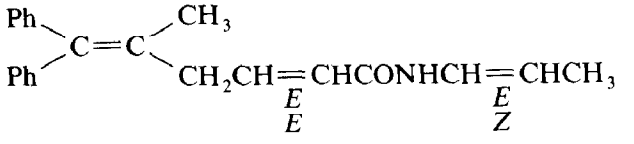
+

(IVa)

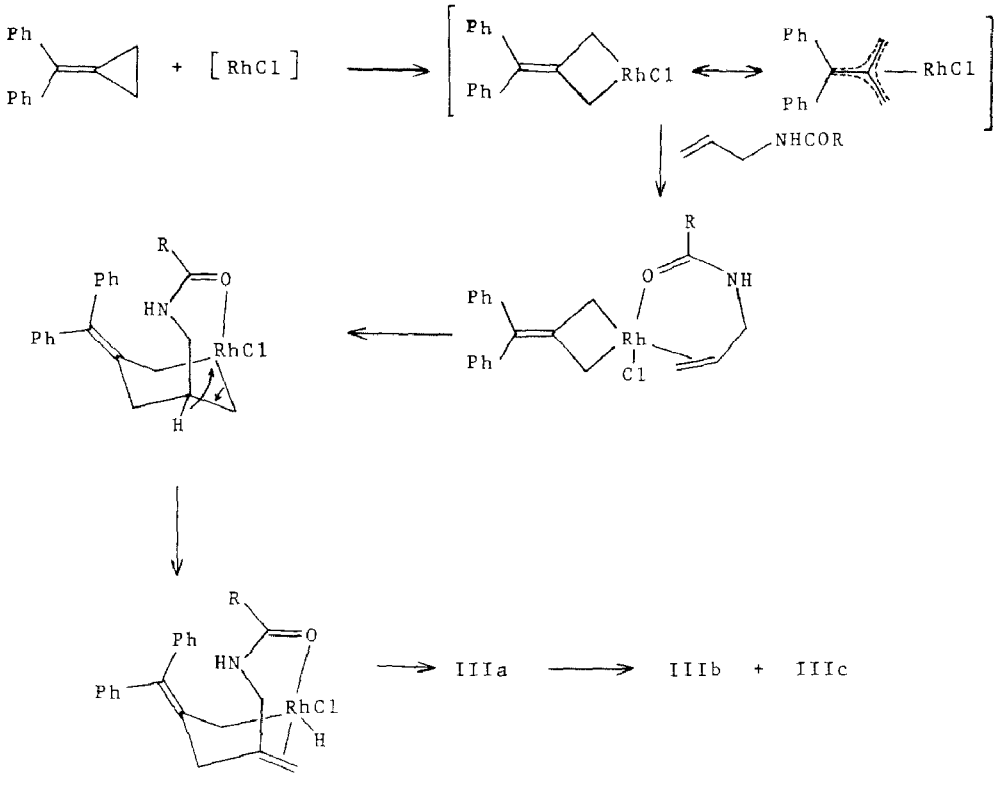


+

(IVb)



(IVc) (2)



Scheme 1.

Steric effects can reverse the outcome; however, simply adding a terminal methyl group to the acrylic species causes C–C bond formation to occur at the allylic site (eq. 1). A methyl group on the terminal allyl carbon atom also hinders the reaction, as shown with $PhCONHCH_2CH{=}CHCH_3$.

From a mechanistic point of view the reaction can be rationalized in terms of metallacycle formation (Scheme 1, inert ligands are omitted for simplicity). The reason for the preference for the internal position of the double bond is not yet clear. Prior isomerization to enamides can be discarded in view of the fact that both *E*- and *Z*-1-propenyl amides react much more slowly.

We conclude that *N*-allylamides are suitable substrates for the introduction of a three-carbon amine chain into a cyclopropane substrate susceptible to cleavage by rhodium. Regioselective reaction has been achieved, probably via metallacycle formation.

Experimental

Products were analyzed and quantitatively determined by GLC on a methylsilicone (OV-101 stationary phase) capillary column by use of an internal standard, and were isolated by HPLC, preparative TLC, or flash chromatography. Compounds were identified by comparison with authentic samples or by mass, IR, and NMR spectroscopy. Mass spectra were obtained with a Finnigan 1020 instrument at

70 eV, and IR spectra were recorded on a Perkin–Elmer 298 IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded with AC100 and CXP200 Bruker spectrometers; chemical shifts are in ppm (δ) from TMS as reference. Melting points were determined with an Electrothermal apparatus, and are uncorrected.

The complex $RhCl(PPh_3)_3$ [5] and the methylenecyclopropane derivatives (I) [6], (diphenyl)methylenecyclopropane [7], 1-methylene-2-phenylcyclopropane [8] and methylenecyclopropane [9]) were prepared by published methods.

N-Allylacetamide was prepared as described in ref. 3 and *N*-allylamides and carbamates, and allyl-*p*-toluenesulfonamide were prepared by standard methods [10]. The amides and carbamates are colourless liquids except for *p*-toluensulfonamide, which is a solid, m.p. 67–69°C. Crotylamine was made by the Gabriel synthesis [11] starting from crotyl bromide and potassium phthalimide. All the substrates showed analytical and spectral data consistent with their assigned structures.

General procedure for the reaction of methylenecyclopropanes with N-allylamine derivatives

In a Schlenk tube 0.02 g (0.02 mmol) of $RhCl(PPh_3)_3$, 1.0 mmol of substrate I, and 2.0 mmol of allylamine derivatives II were dissolved in toluene (3.0 ml) under nitrogen (eq. 1). The solution was stirred magnetically at 90°C for 60 h, then allowed to cool to room temperatue; 15 ml of Et_2O were then added and the solution was filtered and the solvent distilled off under vacuum. Components were separated from the product mixture (R = COMe) as described below. Hydrogenation of compounds III gave two diastereoisomers.

Compounds IIIa–IIIc and IVa–IVc were isolated by the following chromatographic procedures (eluent composition in parentheses): IIIb (R = COMe): preparative TLC on silica gel (n-hexane/EtOAc 4/6); IIIc (R = COMe): flash chromatography on silica gel (n-hexane/EtOAc 9/1); further purified by HPLC on C-18 reverse phase column ($MeOH/H_2O$ 76/24); IIIa, IIIb, IIIc (R = COPh): flash chromatography on silica gel (n-hexane/EtOAc 9/1); product IIIc was recrystallized from THF, H_2O solution; IIIa, IIIc (R = COOEt and $SO_2C_6H_4$-*p*-Me): flash chromatography on silica gel (n-hexane/EtOAc 9/1 and 85/15, respectively); IIIc (R = *E*-COCH=CHMe): flash chromatography on silica gel (n-hexane/EtOAc 8/2); IVa–IVc (R = $COCH{=}CH_2$): flash chromatography on silica gel (n-hexane/EtOAc 6/4); purified by HPLC on C-18 reverse phase column ($MeOH/H_2O$ 73/27).

Melting points, and the ^1H, ^{13}C NMR, mass and IR spectral data for the new compounds III–IV are listed below (NMR spectra were recorded in $CDCl_3$ solution unless otherwise indicated).

The *E*-configuration at the trisubstituted double bond has been established for compound IIIc (R = COPh), and the similar values of the $CH{=}CCH_3$ ^1H NMR coupling constant found for the other IIIb and IIIc compounds make the same configuration seem likely also for these compounds. This point was not investigated further, however.

IIIb (R = COMe), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H_2\overset{a}{C}(CH_3){=}\overset{e}{C}H\overset{f}{N}H\overset{c}{C}OCH_3$, oil. MS: (*m/e*): 305 (M^+), 246, 231, 191, 165, 138, 96, 91, 73(100), 69. IR film (cm^{-1}): 3330, 2960, 1675, 1530, 1460, 1385, 1290, 815, 780, 720. ^1H NMR: δ 1.53, d, 3H, H^a, J_{ae} 1.2 Hz; 1.68, s, 3H, H^b; 2.06, s, 3H, H^c; 2.84, s, 2H, H^d; 6.62, br d, 1H H^e, J_{ef} 10.4 Hz; 6.80–7.10, br s, 1H, H^f; 7.10–7.41, m, 10H, 2Ph.

IIIc (R = COMe), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H{=}C(\overset{a}{C}H_3)\overset{e}{C}H_2\overset{f}{N}H\overset{}{C}O\overset{c}{C}H_3$, m.p. 109–112 °C. MS: (*m/e*): 305 (M^+), 247, 246, 233, 231, 215, 191, 165, 96, 91, 73(100). IR (KBr) cm^{-1}: 3220, 3050, 2930, 1630, 1550, 1435, 1365, 1285, 1045, 765, 695. ^1H NMR: δ 1.38, d, 3H, H^a, J_{ad} 1.3 Hz; 1.85, d, 3H, H^b, J_{bd} 0.5 Hz; 1.90, s, 3H, H^c; 3.67, d, 2H, H^e, J_{ef} 5.7 Hz; 4.9–5.3, br s, 1H, H^f; 5.93, br s, 1H, H^d; 7.01–7.45, m, 10H, 2Ph. ^1H NMR (C_6D_6): δ 1.34, d, 3H, H^a, J_{ad} 1.3 Hz; 1.50, s, 3H, H^c; 1.85, d, 3H, H^b, J_{bd} 0.5 Hz; 3.56, d, 2H, H^e, J_{ef} 5.4 Hz; 4.30–4.60, br s, 1H, H^f; 5.87, br s, 1H, H^d; 6.84–7.46, m, 10H, 2Ph. Hydrogenation of IIIc gave two diastereoisomeric products with MS: (*m/e*): 309 (M^+), 218, 168, 167(100), 165, 152, 143, 115, 100, 91, 83, 72, 60, 55.

IIIa (R = COPh), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H_2C(=\overset{a}{C}H_2)\overset{e}{C}H_2\overset{f}{N}HCOPh$, oil. MS: (*m/e*); 367 (M^+), 246, 231, 205, 191, 160, 134, 105(100), 77, 71, 57. IR (film) cm^{-1}: 3380, 2940, 1645, 1530, 1500, 1455, 780, 715. ^1H NMR: δ 1.78, s, 3H, H^b; 2.96, s, 2H, H^d; 3.97, d, 2H, H^e, J_{ef} 5.9 Hz; 5.02, 5.10, 2s, 2H, H^a; 5.90–6.15, br s, 1H, H^f; 7.05–7.84, m, 15H, 3Ph.

IIIb (R = COPh), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H_2C(\overset{a}{C}H_3){=}\overset{e}{C}H\overset{f}{N}HCOPh$, m.p. 107–110 °C. MS: (*m/e*): 367 (M^+), 246, 246, 231, 205, 160, 134, 105(100), 91, 77. IR (KBr) cm^{-1}: 3420, 2940, 1660, 1520, 1495, 1455, 1280, 780, 770, 715. ^1H NMR: δ 1.63, d, 3H, H^a, J_{ae} 1.3 Hz; 1.73, s, 3H, H^b; 2.91, s, 2H, H^d; 6.86, br d, 1H, H^e, J_{ef} 10.0 Hz; 6.95–7.86, m, 16 H, H^f and 3Ph.

IIIc (R = COPh), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H{=}C(\overset{a}{C}H_3)\overset{e}{C}H_2\overset{f}{N}HCOPh$, m.p. 123–125 °C. MS: (*m/e*): 367 (M^+), 246, 231, 205, 160, 105(100), 91, 77, 57. IR (KBr) cm^{-1}: 3310, 3040, 2910, 1630, 1535, 1480, 1410, 1285, 1250, 795, 760, 690. ^1H NMR: δ 1.47, d, 3H, H^a, J_{ad} 1.2 Hz; 1.88, s, 3H, H^b; 3.88, d, 2H, H^e, J_{ef} 5.2 Hz; 5.80, br s, 1H, H^f; 6.03, br s, 1H, H^d; 7.05–7.67, m, 15H, 3Ph. ^{13}C NMR: δ 16.36, 21.09, 2Me; 47.51, CH_2; 126.14, 126.61, 126.93 (2C), 127.46 (2C), 127.28 (2C), 128.42 (2C), 129.29, 130.02 (2C), 130.23 (2C), 131.31 (16C, =CH); 131.72, 132.45, 134.58, 140.68, 142.71, 143.48 (6qC); 167.30 (CO).

IIIa (R = COOEt), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H_2C(=\overset{a}{C}H_2)\overset{e}{C}H_2\overset{f}{N}H\overset{}{C}O\overset{g}{O}\overset{}{C}H_2\overset{c}{C}H_3$, oil. MS: (*m/e*): 335 (M^+), 247, 246(100), 231, 217, 204, 191, 167, 115, 91, 56. ^1H NMR: δ 1.23, t, 3H, H^c, J_{cg} 7.1 Hz; 1.74, s, 3H, H^b; 2.86, s, 2H, H^d; 3.65, d, 2H, H^e, J_{ef} 6.0 Hz; 4.09, q, 2H, H^g, J_{gc} 7.1 Hz; 4.60, br s, 1H, H^f; 4.94, 5.02, 2s, 2H, H^a; 7.06–7.32, m, 10H, 2Ph.

IIIc (R = COOEt), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H{=}C(\overset{a}{C}H_3)\overset{e}{C}H_2\overset{f}{N}H\overset{}{C}O\overset{g}{O}\overset{}{C}H_2\overset{c}{C}H_3$, oil. MS: (*m/e*): 335 (M^+), 246, 233(100), 231, 215, 205, 191, 115, 103, 91. IR (film) cm^{-1}: 3370, 3000, 2950, 1720, 1530, 1455, 1260, 780, 715. ^1H NMR: δ 1.23, t, 3H, H^c, J_{cg} 7.1 Hz; 1.38, d, 3H, H^a, J_{ad} 1.0 Hz; 1.83, s, 3H, H^b; 3.58, d, 2H, H^e, J_{ef} 6.0 Hz; 4.09, q, 2H, H^g, J_{gc} 7.1 Hz; 4.45, br s, 1H, H^f; 5.92, s, 1H, Hd; 7.06–7.35, m, 10H, 2Ph.

IIIc (R = *E*-$\overset{h}{C}\overset{c}{C}H{=}CHMe$), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H{=}C(\overset{a}{C}H_3)\overset{e}{C}H_2\overset{f}{N}H\overset{}{C}O\overset{g}{C}H{=}\overset{h}{C}H\overset{c}{C}H_3$, oil. MS: (*m/e*): 321 (M^+), 263, 247(100), 232, 216, 206, 192, 165, 97, 85, 69. IR (film) cm^{-1}: 3310, 2940, 1685, 1640, 1560, 1450, 1235, 980, 780, 715. ^1H NMR: δ 1.37, d, 3H, H^a, J_{ad} 1.3 Hz; 1.84, d, 3H, H^b, J_{bd} 0.7 Hz; 1.85, dd, 3H, H^c, J_{ch} 6.8 Hz, J_{cg} 1.6 Hz; 3.73, dd, 2H, H^e, J_{ef} 5.8 Hz, J_{ed} 1.0 Hz; 5.13, br s, 1H, H^f; 5.68, dq, 1H, H^g, J_{gh} 15.2 Hz, J_{gc} = 1.6 Hz; 5.94, m, 1H, H^d; 6.78, dq, 1H, H^h, J_{hg} 15.2 Hz, J_{hc} 6.8 Hz, 7.01–7.42, m, 10H, 2Ph.

IIIa (R = $SO_2C_6H_4$-*p*-Me), $Ph_2C{=}C(\overset{b}{C}H_3(\overset{d}{C}H_2C(=\overset{a}{C}H_2)\overset{e}{C}H_2\overset{f}{N}HSO_2C_6H_4\overset{c}{C}H_3$, oil. MS: (*m/e*): 418 ($M+1^+$), 247, 171, 155, 105, 91, 86, 84(100), 77, 65, 49. ^1H

NMR: δ 1.66, s, 3H, H^b; 2.41, s, 3H, H^c; 2.75, s, 2H, H^d; 3.42, d, 2H, H^e, $J_{ef} = 9.8$ Hz; 4.40–4.75, br s, 1H, H^f; 4.91, 5.02, 2s, 2H, H^a; 6.96–7.76, m, 14H, 2Ph and 4 aromatic H.

IIIc (R = $SO_2C_6H_4$-*p*-Me), $Ph_2C{=}C(\overset{b}{C}H_3)\overset{d}{C}H{=}C(\overset{a}{C}H_3)\overset{e}{C}H_2\overset{f}{N}H\overset{c}{S}O_2C_6H_4CH_3$, oil. MS: (*m/e*): 418 ($M+1^+$), 263, 247, 334, 205, 167, 155, 105, 91(100), 65. IR (film) cm^{-1}: 3300, 2950, 1745, 1670, 1610, 1500, 1455, 1340, 1175, 1110, 830, 780, 750, 720, 680. ^1H NMR: δ 1.33, s, 3H, H^a; 1.76, s, 3H, H^b; 2.41, s, 3H, H^c; 3.34, d, 2H, H^e, J_{ef} 6.2 Hz; 4.40–4.65, br s, 1H, H^f; 5.89, br s, 1H, H^d; 6.97–7.76, m, 14H, 2Ph and 4 aromatic H.

IVa (*E*), $Ph_2C{=}C(\overset{a}{C}H_3)\overset{b}{C}H_2\overset{c}{C}H{=}\overset{d}{C}H\overset{e}{C}ONH\overset{f}{C}H_2\overset{g}{C}H{=}\overset{h}{C}H\overset{i}{H}$, oil. MS: (*m/e*): 317 (M^+), 233, 218, 217, 205, 203, 181, 171, 165, 155, 150, 141, 128, 123, 115, 105, 99(100), 91, 84, 57, 55. IR (film) cm^{-1}: 3295, 3040, 2940, 1680, 1640, 1560, 1455, 1290, 995, 930, 915, 780, 720. ^1H NMR: δ 1.76, s, 3H, H^a; 2.95, dd, 2H, H^b, J_{bc} 6.7 Hz, J_{bd} 1.4 Hz; 3.93, pseudo t, 2H, H^f, $J_{fe} = J_{fg} = 5.7$ Hz; 5.12, d, 1H, H^i, J_{ig} 10.5 Hz; 5.18, d, 1H, H^h, J_{hg} 17.2 Hz; 5.82, d, 1H, H^d, J_{dc} 15.0 Hz; 5.84, ddt, 1H, H^g, J_{gh} 17.2 Hz; J_{gi} 10.5 Hz, J_{gf} 5.7 Hz; 6.08, brt, 1H, H^e, J_{ef} 5.7 Hz; 6.88, dt, 1H, H^c, J_{cd} 15.0 Hz, J_{cb} 6.7 Hz; 7.07–7.35, m, 10H, 2Ph.

IVb (*E*), $Ph_2C{=}C(\overset{a}{C}H_3)\overset{b}{C}H{=}\overset{c}{C}H\overset{d}{C}H_2\overset{e}{C}ONH\overset{f}{C}H_2\overset{g}{C}H{=}\overset{h}{C}H\overset{i}{H}$, oil. MS: (*m/e*): 317 (M^+), 233, 218, 203, 191, 155, 115, 99(100), 91, 84, 57. IR (film) cm^{-1}: 3310, 2940, 1665, 1650, 1455, 990, 980, 930, 915, 780, 750, 715. ^1H NMR: δ 1.95, s, 3H, H^a; 3.01, dd, 2H, H^d, J_{dc} 7.4 Hz, J_{db} 1.0 Hz; 3.86, pseudo tt, 2H, H^f, $J_{fg} = J_{fe} = 5.7$ Hz, $J_{fi} = J_{fh} = 1.5$ Hz; 5.13, ddt, 1H, H^h, J_{hg} 10.0 Hz, $J_{hi} = J_{hf} = 1.5$ Hz; 5.15, ddt, 1H, H^i, J_{ig} 17.3 Hz, $J_{ih} = J_{if} = 1.5$ Hz, 5.40–5.70, br s, 1H, H^e; 5.82, ddt, 1H, H^g, J_{gi} 17.3 Hz, J_{gh} 10.0 Hz, J_{gf} 5.7 Hz; 5.88, dt, 1H, H^c, J_{cb} 15.6 Hz, J_{cd} 7.4 Hz; 6.43, dt, 1H, H^b, J_{bc} 15.6 Hz, J_{bd} 1.0 Hz; 7.05–7.36, m, 10H, 2Ph.

IVc (*E,E*), $Ph_2C{=}C(\overset{a}{C}H_3)\overset{b}{C}H_2\overset{c}{C}H{=}\overset{d}{C}H\overset{e}{C}ONH\overset{f}{C}H{=}\overset{g}{C}H\overset{h}{C}H_3$, oil. *MS*: (*m/e*): 317 (M^+), 260, 233, 218, 203, 191, 155, 115, 99, 91(100), 84, 57. IR (film) cm^{-1}: 3350, 1680, 1650, 1270, 1030, 985, 810, 780, 710. ^1H NMR: δ 1.68, dd, 3H, H^h, J_{hg} 6.7 Hz, J_{hf} 1.4 Hz; 1.76, s, 3H, H^a; 2.97, dd, 2H, H^b, J_{bc} 6.7 Hz, J_{bd} 1.4 Hz; 5.18, dq, 1H, H^g, J_{gf} 13.8 Hz, J_{gh} 6.7 Hz; 6.72, d, 1H, H^d, J_{dc} 15.2 Hz; 6.79, m, 1H, H^f; 6.93, dt, 1H, H^c, J_{cd} 15.2 Hz, J_{cb} 6.7 Hz; 7.05–7.33, m, 11H, 2Ph and H^e.

IVc (*E,Z*), $Ph_2C{=}C(\overset{a}{C}H_3)\overset{b}{C}H_2\overset{c}{C}H{=}\overset{d}{C}H\overset{e}{C}ONH\overset{f}{C}H{=}\overset{g}{C}H\overset{h}{C}H_3$, oil. MS: (*m/e*): 317 (M^+), 260, 233, 219, 205, 191, 165, 115, 105, 99, 91(100), 55. IR (film) cm^{-1}: 3300, 2950, 1670, 1640, 1530, 1275, 990, 815, 775, 715. ^1H NMR: δ 1.62, d, 3H, H^h, J_{hg} 7.2 Hz; 1.78, s, 3H, H^a; 3.00, dd, 2H, H^b, J_{bc} 6.8 Hz, J_{bd} 1.5 Hz; 4.85, dq, 1H, H^g, J_{gf} 8.4 Hz, J_{gh} 7.2 Hz; 5.79, d, 1H, H^d, J_{dc} 15.2 Hz; 6.87, m, 1H, H^f; 6.98, dt, 1H, H^c, J_{cd} 15.2 Hz, J_{cb} 6.8 Hz; 7.10–7.33, m, 11H, H^e and 2Ph.

Acknowledgements

Financial support by Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione is acknowledged. The facilities of Centro Interfacoltà di Misure of the University of Parma were used for recording NMR and mass spectra.

References

1 G.P. Chiusoli, M. Costa, P. Schianchi and G. Salerno, J. Organomet. Chem., 315 (1986) C45; G.P. Chiusoli, M. Costa and L. Melli, J. Organomet. Chem., 358 (1988) 495.

2 G.P. Chiusoli, L. Pallini and G. Salerno, J. Organomet. Chem., 235 (1982) C85; G. Salerno, F. Giliotti and G.P. Chiusoli, J. Organomet. Chem., 314 (1986) 231; G. Salerno, C. Gallo, G.P. Chiusoli and M. Costa, J. Organomet. Chem., 317 (1986) 373.
3 G.K. Stille and Y. Becker, J. Org. Chem., 45 (1980) 2139.
4 G. Bocelli, J. Crystallographic and Spectroscopic Research, submitted.
5 J.A. Osborn and G. Wilkinson, Inorg. Synth., 10 (1967) 67.
6 K. Friedrich and H.G. Henning, Chem. Ber., 92 (1959) 2576; K. Sisido and K. Utimoto, Tetrahedron Lett., (1966) 3267.
7 A.R. Pinhas, A.G. Samuelson, R. Risenberg, E.V. Arnold, J. Clardy and B.K. Carpenter, J. Am. Chem. Soc., 103 (1981) 1668.
8 S. Arora and P. Binger, Synthesis, (1974) 801.
9 J.R. Salaun, J. Champion and J.M. Conia, Org. Synth., 57 (1977) 36.
10 T.W. Greene, Protective Groups in Organic Synthesis, J. Wiley, New York, 1981, p. 218; J.W. Barton in J.F.W. McOmie (Ed.), Protective Groups in Organic Chemistry, Plenum Press, London, 1973, p. 43.
11 M.S. Gibson and R.U. Bradshaw, Angew. Chem. Int. Ed. Engl., 7 (1968) 919.