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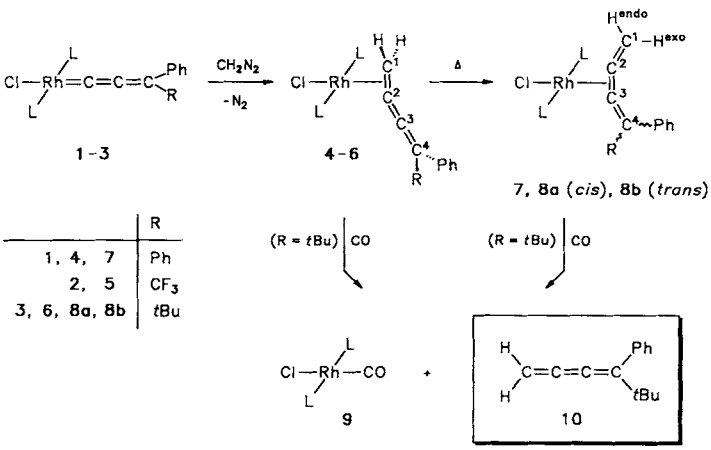
[27] X-ray crystal structure analysis of **7**: DIP2020 Image Plate from Enraf-Nonius, $Mo_{K\alpha}$ radiation, graphite monochromator. Structure resolution was performed with direct methods (SHELXS-86), refinement with full-matrix least-squares refinement at F^2 (SHELXL-93). $C_{50}H_{87}Co_3OP_4S_3$, $M_r = 1101.05$, orthorhombic, space group $Pna2_1$, $Z = 4$, $a = 23.446(3)$ $b = 22.794(2)$ $c = 10.531(2)$ Å, $V = 5628.1(14)$ Å^3, $\rho_{calcd} = 1.30$ g cm^{-3}, $\mu = 1.13$ mm^{-1}, 34477 measured reflections, 8159 independent, and 7446 observed reflections for $I > 2\sigma(I)$, temperature 20 °C. All non-hydrogen atoms were refined anisotropically, H atoms calculated for idealized positions. $R_1 = 0.0375$, $wR_2 = 0.0859$ (all data) for 569 parameters and 1 restraint. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404656.



Scheme 1. L = P*i*Pr$_3$.

Methyl Iodide as a Source of CH_2: Two Routes for Generating 1,1-Disubstituted Butatrienes in the Coordination Sphere of a Transition Metal**

Helmut Werner,* Matthias Laubender, Ralf Wiedemann, and Bettina Windmüller

Dedicated to Professor Max Herberhold on the occasion of his 60th birthday

Following the reports on the synthesis of vinylidene complexes of the general type *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$],[1] we recently also described an efficient preparative route to the corresponding allenylidene compounds *trans*-[RhCl(=C=C=CRR')(P*i*Pr$_3$)$_2$].[2] In the course of investigations into the reactivity of these compounds, we have now discovered that the allenylidene unit can be converted by two different pathways into 1,1-disubstituted butatrienes $H_2C{=}C{=}C{=}CRR'$, which because of their lability are otherwise hardly accessible. We note that up to now there is no precedent for the coupling of a CH_2 fragment, generated from CH_2N_2 or CH_3I, with an allenylidene moiety to yield a butatriene. Moreover, allenes can likewise be obtained from allenylidenerhodium complexes.

In contrast to compounds *trans*-[RhCl(=C=CHR)(P*i*Pr$_3$)$_2$] (R = Ph, *t*Bu, CO_2Me), which are inert in the presence of CH_2N_2,[3] complexes **1**–**3**[4] react with excess diazomethane at room temperature within a few minutes.[5] The red or orange butatriene complexes **4**–**6** (Scheme 1), which are only moderately sensitive to air and water, were isolated in nearly quantitative yield. The compositions of **4**–**6** have been confirmed by elemental analysis. The proposed structure shown in Scheme 1 is particularly supported by the ^{13}C NMR spectra (Table 1), which display four signals between $\delta = 180$ and 12 for the carbon atoms of the butatriene ligand. Two of these signals show a relatively large Rh–C coupling and are thus assigned to the C atoms of the butatriene ligand bonded to the metal. The chemical shift of the C^1 resonance as well as the ^1J(CH) coupling constant (161.4 Hz) of **4** indicate a predominant sp^3 character of this carbon atom which implies that the bonding between Rh, C^1, and C^2 is related to that of a metallacyclopropane.

The X-ray crystal structure analysis of **4** (Fig. 1)[6] reveals a distorted square-planar coordination around the central atom;

Table 1. Selected spectroscopic data of complexes **4**–**8** and **12**–**14**, and of the cumulenes **10** and **16** (without data for phosphane ligands, phenyl and *tert*-butyl groups); for assignment C^1–C^4 and H^{exo}, H^{endo} see Scheme 1.

4: ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.61$ [dvt, $N = 10.8$, J(H,H) = 1.6 Hz, CH_2]; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 181.50$ (s, C=CPh$_2$), 111.39 (s, CPh$_2$), 108.51 [dt, J(Rh,C) = 22.1, J(P,C) = 8.0 Hz, C=CH$_2$], 13.03 [d, J(Rh,C) = 13.6 Hz, CH$_2$]

5: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.87$ and 2.78 [each dddd, J(Rh,H) = 6.0, J(P^1,H) = 5.6, J(P^2,H) = 5.6, J(H,H) = 1.6 Hz, 1H each of CH$_2$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 183.83$ [s, C=C(Ph)CF$_3$], 125.02 [q, J(F,C) = 272.2 Hz, CF$_3$], 109.86 [dt, J(Rh,C) = 22.1, J(P,C) = 4.0 Hz, C=CH$_2$], 99.34 [q, J(F,C) = 34.0 Hz, C(Ph)CF$_3$], 16.12 [d, J(Rh,C) = 14.7 Hz, CH$_2$]; ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -58.60$ (s)

6: ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 179.30$ [s, C=C(Ph)*t*Bu], 100.17 [s, C(Ph)*t*Bu], 109.40 [dt, J(Rh,C) = 23.1, J(P,C) = 5.0 Hz, C=CH$_2$], 12.52 [d, J(Rh,C) = 13.4 Hz, CH$_2$]

7: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.46$ and 5.00 (each s, br, 1H each of CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 142.69$ [dt, J(Rh,C) = 17.1, J(P,C) = 4.0 Hz, C^2/C^3], 137.96 [dt, J(Rh,C) = 20.1, J(P,C) = 5.0 Hz, C^2/C^3], 127.59 (s, br, CPh$_2$), 98.36 (s, br, CH$_2$)

8a: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.62$ [t, J(P,H) = 2.4 Hz, 1H of CH$_2$], 5.21 (s, br, 1H of CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 143.57$ [dt, J(Rh,C) = 16.1, J(P,C) = 4.0 Hz, C^2/C^3], 134.27 [s, C(Ph)*t*Bu], 132.59 [dt, J(Rh,C) = 18.1, J(P,C) = 4.0 Hz, C^2/C^3], 100.20 (s, CH$_2$); ^{31}P NMR (162.0 MHz, $CDCl_3$): $\delta = 28.05$ [d, J(Rh,P) = 119.2 Hz]

8b: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.65$ and 4.19 (each s, br, 1H each of CH$_2$); ^{31}P NMR (162.0 MHz, $CDCl_3$): $\delta = 28.99$ [d, J(Rh,P) = 119.5 Hz]

10: IR (C_6H_6): $\tilde{\nu}$ [cm^{-1}] = 2050 (C=C=C); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.13$ and 5.05 [each d, J(H,H) = 7.6 Hz, 1H each of CH$_2$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 168.64$ and 158.69 (each s, =C=), 135.27 (s, CPh$_2$), 89.31 (s, CH$_2$)

12: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 5.13$ and 4.78 (each s, 1H each of CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 142.43$ [dt, J(Rh,C) = 18.1, J(P,C) = 3.0 Hz, C^2/C^3], 135.87 [dt, J(Rh,C) = 20.1, J(P,C) = 5.0 Hz, C^2/C^3], 127.49 (s, br, CPh$_2$), 98.31 (s, CH$_2$)

13: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.41$ [dt, J(Rh,H) = 2.1, J(P,H) = 5.1 Hz, CH$_2$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 173.34$ [dt, J(Rh,C) = 23.1, J(P,C) = 6.0 Hz, =C=], 123.10 (s, CPh$_2$), 16.40 [d, J(Rh,C) = 13.1 Hz, CH$_2$]

14: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.62$ (m, CH$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 179.00$ (m, =C=), 122.47 [q, J(F,C) = 277.4 Hz, CF$_3$], 112.85 [q, J(F,C) = 27.3 Hz, C(Ph)CF$_3$], 18.86 [d, br, J(Rh,C) = 13.9 Hz, CH$_2$]; ^{19}F NMR (188.3 MHz, $CDCl_3$): $\delta = -59.44$ (s)

16: MS (70 eV): m/z 184 (M^+); IR (C_6H_6): $\tilde{\nu}$ [cm^{-1}] = 1955 (C=C=C); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 4.75$ [q, J(F,H) = 3.2 Hz, CH$_2$]; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 210.20$ [q, J(F,C) = 5.0 Hz, =C=], 124.19 [q, J(F,C) = 273.7 Hz, CF$_3$], 102.02 [q, J(F,C) = 32.2 Hz, C(Ph)CF$_3$], 83.12 (s, CH$_2$); ^{19}F NMR (188.3 MHz, C_6D_6): $\delta = -60.70$ (s)

[*] Prof. Dr. H. Werner, Dipl.-Chem. M. Laubender, Dipl.-Chem. R. Wiedemann, Dipl.-Chem. B. Windmüller
Institut für Anorganische Chemie der Universität
Am Hubland, D-97074 Würzburg (Germany)
Fax: Int. code +(931)888-4605

[**] This work was supported by the Volkswagen Foundation, the Deutsche Forschungsgemeinschaft (SFB 347), and Degussa AG.

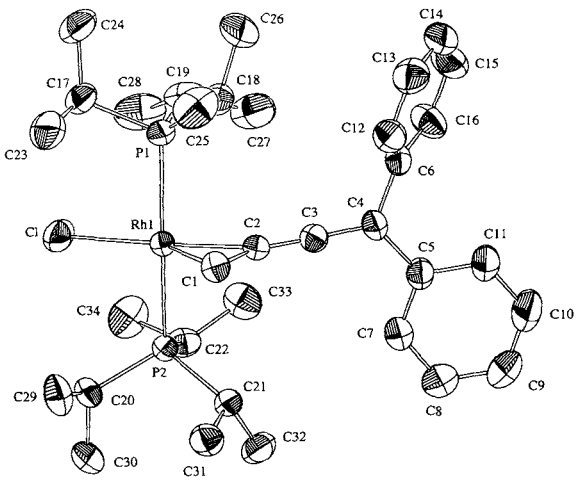


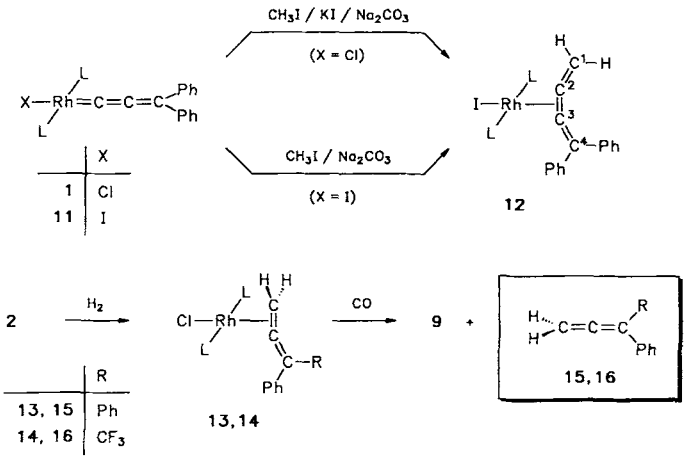
Fig. 1. Molecular structure of **4** (ORTEP plot) in the crystal. Selected bond lengths [Å] and angles [°]: Rh–P1 2.365(1), Rh–P2 2.355(1), Rh–Cl 2.349(1), Rh–C1 2.060(2), Rh–C2 2.063(2), C1–C2 1.408(3), C2–C3 1.272(3), C3–C4 1.335(3); P1-Rh-P2 166.45(2), P1-Rh-Cl 88.16(3), P1-Rh-C1 96.70(7), P1-Rh-C2 90.56(6), P2-Rh-Cl 87.42(2), P2-Rh-C1 94.35(7), P2-Rh-C2 92.89(6), Cl-Rh-C1 144.36(7), Cl-Rh-C2 175.65(6), C1-Rh-C2 40.0(1), Rh-C1-C2 70.1(1), Rh-C2-C1 69.9(1), C1-C2-C3 144.7(2), C2-C3-C4 174.8(2).

the Cl, Rh, and C1–C4 atoms lie in one plane. The Cl-Rh-C2 axis is almost linear (175.65(6)°), while the P1-Rh-P2 axis (166.45(2)°) deviates somewhat more from linearity. Despite the unsymmetrical coordination of the $C{=}CH_2$ unit to the metal, the Rh–C1 and Rh–C2 bond lengths are nearly identical. This is in contrast to the structurally similar compound *trans*-[RhCl{(1,2-η)-$C^1H_2{=}C^2{=}C^3HC^4O_2Et$}($P\mathit{i}Pr_3$)$_2$], in which the Rh–C1 and Rh–C2 bond lengths are 2.120(5) and 1.991(5) Å, respectively.[7]

Upon heating in toluene to 80–90 °C for several hours, compounds **4** and **6** rearrange to the thermodynamically more stable complexes **7** and **8**, respectively. The isomerization can easily be monitored by a change of color from red to yellow. In the case of **8**, a mixture of isomers **8a**/**8b** is formed that differ in the relative position of the phenyl and *tert*-butyl groups to the metal center. If the rearrangement of **6** is monitored by ^{31}P NMR spectroscopy, a **8a**:**8b** ratio of about 2:1 is observed initially that after 10 h in toluene at 90 °C changes to 10:1. Under these conditions, a complete conversion of **8b** to **8a** does not occur. Complex **8a** has been isolated analytically pure upon fractional crystallization from acetone (−78 °C) and, by comparison of the ^1H NMR data with those of **8b**, identified as the isomer in which the phenyl group at C^4 is directed towards the metal. The assignment of the signals for the H^{endo} and H^{exo} protons at C^1 follows from the work of Gladysz at al.[8] who assigned the resonances of the CH_2 protons of the allene complex $[C_5H_5Re(\eta^2\text{-}CH_2{=}C{=}CH_2)(NO)(PPh_3)]BF_4$ based on NOE measurements. We note that in all of the previously described 1,1,4,4-tetrasubstituted butatrienerhodium(I) compounds *trans*-[RhCl{(2,3-η)-$R_2C^1{=}C^2{=}C^3{=}C^4R'_2$}($PPh_3$)$_2$], which were prepared from [RhCl(PPh_3)$_3$] and corresponding butatrienes,[9] the central C=C bond is coordinated to the metal; the linkage of a terminal $R_2C{=}C$ bond not to rhodium(I) but to platinum(0) was recently reported by Stang.[10]

Similarly to the butenyne complex *trans*-[RhCl{(1,2-η)-$PhC^1{\equiv}C^2C^3H{=}C^4HPh$}($P\mathit{i}Pr_3$)$_2$],[11] compounds **4**–**8** also react rapidly with CO in benzene at room temperature yielding the carbonyl complex **9**[12] by ligand exchange. Of the butatrienes formed in these conversions, those with CPh_2 and $C(Ph)CF_3$ as the terminal unit are quite labile and undergo secondary reactions. The hitherto unknown compound **10** was characterized by GC/MS and by comparison of the spectroscopic data with those of other butatrienes.[13, 14]

Surprisingly, there is also a second route to convert a metal-bonded allenylidene moiety into a butatriene ligand (Scheme 2).



Scheme 2. L = $P\mathit{i}Pr_3$.

Complex **1** does not react, as we expected, with CH_3I to give a methylrhodium(III) compound. Instead, in the presence of excess Na_2CO_3, a mixture of products is formed, which besides **7** also contains the corresponding iodo derivative **12**.[15] A subsequent reaction of the mixture of products with KI yields **12** almost quantitatively. If compound **11**[2a] is treated with CH_3I and Na_2CO_3 in acetone/THF at room temperature, the butatriene complex **12** can be isolated in 76% yield. As far as the mechanism of formation of **12** is concerned, we assume that in the initial step an oxidative addition of CH_3I at the rhodium center takes place that is followed by an insertion of the allenylidene unit into the Rh–CH_3 bond. The intermediate $Rh{-}C(CH_3){=}C{=}CPh_2$ then reacts by a β-H shift to give a butatriene(hydrido)diiodorhodium(III) complex, which upon reductive elimination of HI generates the product **12**. Analogous to the first two steps is the formation of [IrCl(I){$C(CH_3){=}CH_2$}($P\mathit{i}Pr_3$)$_2$] and [IrI{$C(CH_3){=}CH_2$}-{$N(SiMe_2CH_2PPh_2)_2$}] from the corresponding vinylidene complexes and methyl iodide;[16] in these cases, however, a subsequent β-H shift does not occur. Preliminary studies indicate that under the same conditions the dideuterated compound *trans*-[RhCl{(2,3-η)-$C^1D_2{=}C^2{=}C^3{=}C^4Ph$}($P\mathit{i}Pr_3$)$_2$] is formed from **11** and CD_3I. Kinetic studies, now in progress, should provide a more detailed insight into the mechanism of this unexpected reaction.

Compounds **1** and **2** are hydrogenated by H_2 at a different rate. While the reaction of **1** with H_2 in benzene at room temperature is rather slow and completed after 40 h, the corresponding reaction of **2** takes only 30 min. In both cases, the allene complexes **13** and **14** are quantitatively formed by cleavage of the Rh=C double bond.[17] Remarkably, under the chosen conditions no hydrogenation of the allene ligand occurs. Only after increasing the reaction time to 10 days and raising the temperature of the reaction to 60 °C, is the formation of a new rhodium-containing product observed, which according to the NMR data is [$RhH_2Cl(P\mathit{i}Pr_3)_2$].[18] With regard to the structure of **13** and **14** it is important to note that the ^1H NMR spectra display only one signal for the CH_2 protons, thus confirming the coordination of the *unsubstituted* double bond of the allene to the metal center. A slippage of the [RhCl($P\mathit{i}Pr_3$)$_2$]

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fragment along the axis of the cumulene, as has been observed for $[Fe(\eta^2\text{-}Me_2C{=}C{=}CMe_2)(CO)_4]$[19] and $[PtCl_2(\eta^2\text{-}Me_2C{=}C{=}CMe_2)]$,[20] could not be detected.

In the same way as for **6** and **8**, on treatment of **13** and **14** with CO (benzene, 10 °C, 1 min) the olefinic ligand can be displaced leading to the 1,1-diphenylallene **15**, which is already known,[21] and the allene derivative **16**, which has been characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy (see Table 1).

Received: December 18, 1995 [Z8659IE]
German version: *Angew. Chem.* **1996**, *108*, 1330–1332

Keywords: allenylidene complexes · butatrienes · isomerizations · rhodium compounds

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[4] The synthesis of **1** has been reported [2a]; compounds **2** and **3** are analogously accessible from $[\{RhCl(P\mathit{i}Pr_3)_2\}_2]$ and HC≡CCPh(R)OH (R = CF_3, *t*Bu) in 90–95% yield.

[5] General procedure for **4**–**6**: A solution of **1**, **2**, or **3** (0.15 mmol) in benzene (3 mL) was treated dropwise with a 0.28 M solution of CH_2N_2 (1.5 mL) in ether at room temperature. After the solution had been stirred for 5 min, the solvent was removed, and the residue was recrystallized from pentane (−78 °C). Bright red (**4**), red (**5**), or orange crystals (**6**); yield 95%.

[6] Data for X-ray structure analysis: crystals from pentane (−10 °C), $C_{34}H_{54}ClP_2Rh$ (663.1); crystal dimensions 0.3 × 0.3 × 0.4 mm; monoclinic; space group $P2_1/c$ (No. 14); $a = 18.52(1)$, $b = 11.193(3)$, $c = 16.523(9)$ Å, $\beta = 93.35(3)°$, $Z = 4$, $V = 3420(3)$ Å^3; $\rho_{calcd.} = 1.288$ g cm^{-3}; $T = 293(2)$ K; max. $2\theta = 48°$; 5567 reflections measured; 5351 unique, 4654 observed [$I > 2\sigma(I)$]; Enraf-Nonius CAD4 diffractometer, Mo_{K_α} radiation (λ = 0.70930 Å), graphite monochromated, zirkon filter (factor 16.4); Lorentz polarization and empirical absorption correction (Ψ scan method, min. transmission 97.49%); Patterson method, refinement with full-matrix, least-squares method; $R1 = 0.0214$, $wR2 = 0.0568$ [for 4654 reflections with $I > 2\sigma(I)$], $R1 = 0.0305$, $wR2 = 0.0610$ (for all 5351 data); data-to-parameter ratio 8.33; residual electron density +0.296/−0.170 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-30. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

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[15] Preparative procedure for **12**: A solution of **1** (88 mg, 0.14 mmol) and Na_2CO_3 (500 mg, 4.72 mmol) in acetone/THF (1:1) (4 mL) was treated dropwise with CH_3I (60 µL, 135 mg, 0.95 mmol) at room temperature. After the solution had been stirred for 6 h, the solvent was removed, and the residue was extracted with CH_2Cl_2 (3 mL). The extract was concentrated to dryness in vacuo, the residue was dissolved in THF (4 mL), and KI (300 mg, 1.81 mmol) was added to the solution. After the mixture had been stirred at room temperature for 3 h, the solvent was removed, the residue was extracted with benzene (5 mL), the extract was concentrated, and the yellow precipitate was washed with acetone (3 × 2 mL) (0 °C); yield 83 mg (82%); m.p. 146 °C decomp.

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[17] General procedure for **13** and **14**: A solution of **1** or **2** (0.20 mmol) in benzene (5 mL) was stirred under a H_2 atmosphere for 40 h (**1**) or 30 min (**2**). After the solvent had been removed, the yellow residue was washed with pentane (0 °C) (2 × 1 mL) and dried in vacuo; yield 95%.

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Imine Substituent Effects on [2+2]Cycloadditions with Ketenes**

Claudio Palomo,* Jesus M. Aizpurua,* Marta Legido, Regina Galarza, Pere M. Deya, Jacques Dunoguès, Jean Paul Picard, Alfredo Ricci, and Giancarlo Seconi

The cycloaddition of imines with ketenes, generated from acid chlorides and tertiary amines, is recognized as one of the most convenient approaches to β-lactams.[1] However, virtually all of the investigations have dealt with the use of non-enolizable imines derived from aldehydes and, therefore, subsequent steps are often required to obtain the desired target product. In fact, ketene-enolizable aldimine cycloadditions, which would generate a wider range of substitution patterns at the C_4 position of the β-lactam ring, have not been viable, because of the instability of the starting imines and the presence of competitive deprotonations. We report herein on our initial findings on the development of this approach to a general asymmetric synthesis of 3-amino-4-alkyl β-lactams. The significance of these compounds as valuable precursors of β-lactam antibiotics, more complex organic compounds, large and medium heterocycles, and amino acid derivatives is apparent.[2] We thought that α-(trimethylsilyl)methyl imines[3] might provide a solution to the above-mentioned problems for two reasons: first, because of the ability of silyl groups to stabilize electron-deficient carbon centers in the β- and/or γ-position[4] and, second, because of the zwitterionic character of the reaction intermediate proposed for this kind of cycloaddition.[5]

[*] Prof. Dr. C. Palomo, Dr. J. M. Aizpurua, M. Legido, R. Galarza
Departamento de Química Orgánica
Universidad del País Vasco, Facultad de Química
Apdo 1072, E-20080 San Sebastián (Spain)
Fax: Int. code +(43)212236
e-mail: qppaiipj@sc.ehu.es

Dr. P. M. Deya
Departament de Química
Universitat de les Illes Balears, E-07071 Palma de Mallorca (Spain)

Prof. Dr. J. Dunoguès, Dr. J. P. Picard
Laboratoire de Chimie Organique et Organometallique Université de Bordeaux, F-33405 Talence (France)

Prof. Dr. A. Ricci
Dipartimento di Chimica Organica, Università di Bologna
I-40136 Bologna (Italy)

Dr. G. Seconi
C. N. R.-Istituto dei Composti del Carbonio contenenti Eteroatomi e loro Applicazioni
I-40064 Bologna (Italy)

[**] This work was supported by the E. U. (Project: SC1 CT 91/0646) and, in part, by Basque Government (Project: PI9386). Grants to M. L. from Spanish Education Ministry and to R. G. from Gobierno Navarro are acknowledged.