structure was solved by direct methods with SHELXS-86 and refined by the full-matrix least-squares procedure against F^2 with SHELXL-93. a) Crystal structure data for **1-CA**: $C_{24}H_{40}O_5 \cdot C_5H_{10}N_2O$, crystal size $0.6 \times 0.3 \times 0.07$ mm, $T = 100$ K, monoclinic, $P2_1$, $a = 13.268(4)$, $b = 7.909(2)$, $c = 13.818(4)$ Å, $\beta = 106.03(2)^\circ$, $V = 1393.6(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.246$ g cm^{-3}, $\mu = 0.086$ mm^{-1}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data were collected up to $2\theta = 48^\circ$ (θ-2θ scans). The structure was refined on 2058 reflections with positive F^2 values; 334 refined parameters; $R_1 = 0.044$, $wR_2 = 0.102$, GOF = 1.102 for 1691 reflections with $F > 4\sigma(F)$ ($R_1 = 0.106$, $wR_2 = 0.141$, GOF = 1.281 for all 2376 independent reflections). b) Crystal structure data for **2-CA**: $C_{24}H_{40}O_5 \cdot C_6H_{12}N_2O$, crystal size $0.6 \times 0.2 \times 0.07$ mm, $T = 100$ K, $P2_1$, $a = 12.353(2)$, $b = 7.675(1)$, $c = 16.359(4)$ Å, $\beta = 111.09(2)^\circ$, $V = 1447.1(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.232$ g cm^{-3}, $\mu = 0.085$ mm^{-1}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data were collected up to $2\theta = 52^\circ$ (θ-2θ scans). The structure was refined on 2823 reflections with positive F^2 values; 343 refined parameters; $R_1 = 0.043$, $wR_2 = 0.110$, GOF = 1.051 for 2425 reflections with $F > 4\sigma(F)$ ($R_1 = 0.076$, $wR_2 = 0.125$, GOF = 1.084 for all 3066 independent reflections). c) Crystal structure data for **3-CA**: $C_{24}H_{40}O_5 \cdot C_7H_{14}N_2O$, crystal size $0.6 \times 0.2 \times 0.1$, $T = 293$ K, monoclinic, space group $P2_1$, $a = 12.754(3)$, $b = 7.881(2)$, $c = 16.355(3)$ Å, $\beta = 111.97(3)^\circ$, $V = 1524.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.200$ g cm^{-3}, $\mu = 0.655$ mm^{-1}, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). Data were collected up to $2\theta = 140^\circ$ (θ-2θ scans). The structure was refined on 2534 reflections with positive F^2 values; 343 refined parameters; $R_1 = 0.041$, $wR_2 = 0.111$, GOF = 1.077 for 2340 reflections with $F > 4\sigma(F)$ ($R_1 = 0.052$, $wR_2 = 0.122$, GOF = 1.084 for all 2639 independent reflections). The guest *N*-nitroso group is disordered over two positions. Restraints were imposed on 1–2 and 1–3 distances and planarity of the *N*-nitrosamino group during refinement. d) Crystal data for **1-DCA**: $2\,C_{24}H_{40}O_4 \cdot C_5H_{10}N_2O$, crystal size $0.6 \times 0.45 \times 0.2$ mm, $T = 130$ K, orthorhombic, $P2_12_12_1$, $a = 26.730(4)$, $b = 13.228(2)$, $c = 13.971(4)$ Å, $V = 4346(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.209$ g cm^{-3}, $\mu = 0.081$ mm^{-1}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data were collected up to $2\theta = 48^\circ$ (ω-θ scans). The structure was refined on 4345 reflections with the positive F^2 values; 530 refined parameters; $R_1 = 0.056$, $wR_2 = 0.132$, GOF = 1.070 for 3459 reflections with $F > 4\sigma(F)$ ($R_1 = 0.080$, $wR_2 = 0.148$, GOF = 1.073 for all 4347 independent reflections). The guest molecule is disordered over three positions. It was refined isotropically as a rigid body with molecular geometry fitted to that of **1** in **1-CA**. Sum of the occupancy factors was refined to 1.00 (0.55(1) for the *pR* isomer and 0.30(1) and 0.15(1) for the *pS* isomer). e) Crystal structure data for **3-DCA**: $2\,C_{24}H_{40}O_4 \cdot C_7H_{14}N_2O$, crystal size $0.4 \times 0.2 \times 0.2$ mm, $T = 130$ K, orthorhombic, $P2_12_12_1$, $a = 26.845(5)$, $b = 13.583(3)$, $c = 14.001(3)$ Å, $V = 5105(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.206$ g cm^{-3}, $\mu = 0.080$ mm^{-1}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data were collected up to $2\theta = 48^\circ$ (ω-θ scans). The structure was refined on 3661 reflections with the positive F^2 values; 539 refined parameters; $R_1 = 0.059$, $wR_2 = 0.147$, GOF = 1.013 for 2496 reflections with $F > 4\sigma(F)$ ($R_1 = 0.176$, $wR_2 = 0.200$, GOF = 1.094 for all 4485 independent reflections). The guest molecule was refined anisotropically, but disorder was suspected because of poor molecular geometry, the shape of the elipsoids, and large residual peaks close to the *N*-nitroso atom. Therefore, the geometry of the guest was fitted to that found for **3** in the **3-CA** complex. Subsequently, the guest molecule was refined isotropically as a rigid body. Sum of the two occupancy factors of the guest molecules was kept fixed at 1.0. The occupancy of the higher populated *E* stereoisomer was refined at 0.67(1). f) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101943 – CCDC-101947. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Total Synthesis of (−)-Strychnine via the Wieland – Gumlich Aldehyde**

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Strychnine, the most famous of the *Strychnos* alkaloids,[1] is a natural product that has been known for a long time. Its complex heptacyclic structure, which is assembled from only 24 skeletal atoms and contains six contiguous asymmetric carbon atoms (five of which are in the core cyclohexane ring), represents a permanent challenge for synthetic organic chemists.[2] The classical, pioneering total synthesis by Woodward et al.[3] remained the only synthesis of strychnine for nearly 40 years, and five research groups have recently reported new total syntheses of this alkaloid, either via isostrychnine[4] or via the Wieland – Gumlich aldehyde.[5] However, only in one case has the enantioselective total synthesis of the natural enantiomer, (−)-strychnine, been achieved.[5c] The elegant enantioselective synthesis of (−)-strychnine by Overman et al. takes advantage of the tandem cationic aza-Cope rearrangement/Mannich cyclization strategy for the construction of the basic skeleton of the alkaloid and—with almost the same number of reaction steps as the synthesis by Woodward et al.—upped the overall yield by a factor of 10^5.

As the culmination of our studies on the synthesis of *Strychnos* alkaloids,[6] we present here a new synthesis of (−)-strychnine which proceeds via the Wieland – Gumlich aldehyde and starts with 1,3-cyclohexanedione (the core ring E of strychnine),[7] from which the pyrrolidine, piperidine, and indoline rings are successively built in three well-differenti-

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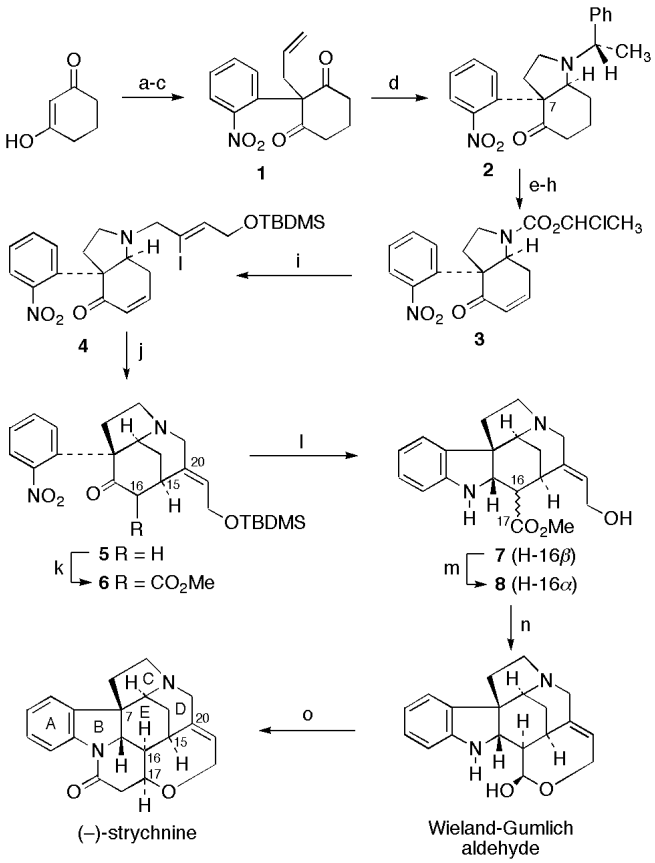
[**] This work was supported by DGICYT, Spain (Projects PB94-0214 and PB97-0877). Financial support for DGEU, Catalonia (1997SGR-0018 and 1997SGR-00166) is also acknowledged.

ated phases. This strategy has proved to be useful for the synthesis of pentacyclic *Strychnos* alkaloids of the curan type.[6d] The most remarkable aspects of the synthesis are 1) easy generation (in only four steps from 1,3-cyclohexanedione) of the first enantiopure intermediate, the 4-(2-nitrophenyl)octahydroindol-4-one **2**, which contains the crucial quaternary C7 center (Scheme 1); 2) closure of the piperidine



Scheme 1. Synthesis of (−)-strychnine: a) 2-$IC_6H_4NO_2$, K_2CO_3, DMSO, 85–90 °C, 72%; b) $BrCH_2CH{=}CH_2$, K_2CO_3, acetone, reflux, 85%; c) toluene, sealed tube, 180–190 °C, 80%; d) O_3, CH_2Cl_2, −78 °C, then (*S*)-$PhCH(CH_3)NH_2 \cdot HCl$, $NaBH_3CN$, *i*PrOH, 37%; e) $ClCO_2CHClMe$, 135 °C, 72%; f) $HN(SiMe_3)_2$, Me_3SiI, CH_2Cl_2/pentane 1/1, −20 °C; g) PhSeCl, $(PhSe)_2$, THF, 70%; h) O_3, CH_2Cl_2, −78 °C, then *i*Pr_2NH, 72%; i) MeOH, reflux, then (*Z*)-$BrCH_2CI{=}CHCH_2OTBDMS$, K_2CO_3, LiI, CH_3CN, 50 °C, 74%; j) $Pd(OAc)_2$, PPh_3, Et_3N, 90 °C, 53%; k) $LiN(SiMe_3)_2$, HMPA, THF, −78 °C, then $NCCO_2Me$, 67%; l) Zn dust, H_2SO_4, MeOH, reflux; m) NaH, MeOH, reflux, 26%; n) DIBAL, toluene, −40 °C, 65%; o) $CH_2(CO_2H)_2$, Ac_2O, NaOAc, AcOH, 110 °C, 49%. DMSO = dimethyl sulfoxide, HMPA = hexamethyl phosphoramide, TBDMS = *tert*-butyldimethylsilyl.

ring by a Pd-catalyzed reaction (formation of the C15–C20 bond), which ensures the stereoselective incorporation of the C20 *E*-configured double bond; and 3) closure of the indoline ring in an advanced synthetic stage by reductive cyclization of the α-(2-nitrophenyl) ketone moiety.

The chiral nonracemic *cis*-octahydroindolone **2** was prepared as previously reported[6d] from the prochiral dione **1** by a one-pot procedure consisting of an ozonolysis followed by a double reductive amination with (*S*)-1-phenylethylamine as the aminocyclization agent.[8] Removal of the α-phenylethyl substituent via a carbamate followed by generation of the enone moiety, deprotection of the pyrrolidine nitrogen atom, and finally alkylation of the resulting bicyclic secondary amine with (*Z*)-1-bromo-4-[(*tert*-butyldimethylsilyl)oxy]-2-iodobut-2-ene[9] led to the key intermediate **4**.

It was our original hope that the closure of the piperidine ring containing the ethylidene group and the introduction of the functionalized one-carbon substituent at C16 could be achieved in a palladium-catalyzed tandem process.[10] Disappointingly, however, numerous attempts to promote the tandem cyclization/carbonylation process (Pd catalyst, CO, MeOH)[11] failed. Instead, the ester resulting from methoxycarbonylation of the initially formed vinyl palladium derivative was isolated.[12] In light of these results, we turned our attention to a less direct strategy, in which cyclization and introduction of the functionalized C17 carbon atom would be achieved in two separate steps. After considerable experimentation with racemic compounds, the best results for the cyclization were obtained with $Pd(OAc)_2$ (0.3 equiv) and PPh_3 (0.6 equiv) as the catalyst in Et_3N at 90 °C for a short time (30 min). Under these conditions the tricyclic ketone **5** was isolated in 53% yield. This key Heck-type cyclization takes place in a reductive form, and is a variant of the Heck reaction which has received comparatively little attention from a synthetic standpoint.[13] Methoxycarbonylation of **5** with LiHMDS (HMDS = hexamethyldisilazane) and methyl cyanoformate provided β-keto ester **6** (55% yield), a compound containing all but the two acetate-derived carbon atoms of the heptacyclic target molecule.

The synthesis of the Wieland–Gumlich aldehyde from **6** only required closure of the indoline ring and reduction of the ester functionality to an aldehyde. Treatment of **6** with zinc dust in 10% sulfuric acid (in methanol) brought about both the removal of the TBDMS protecting group and the reductive cyclization of the α-(2-nitrophenyl) ketone moiety. Under the reaction conditions the initially formed anilinoacrylate intermediate undergoes further reduction to an epimeric mixture of esters **7** and **8** (ratio approximately 9:1). The mixture was equilibrated to pure **8**, which has the natural stereochemistry at C16, by treatment with NaH in refluxing MeOH. The pentacyclic ester **8**, which is also an intermediate in the synthesis by Overman et al.,[5c] was isolated in 26% overall yield from **6**. Finally, further adjustment of the oxidation level by partial reduction of ester **8** with DIBAH (DIBAH = diisobutylaluminum hydride) in toluene at −40 °C afforded the Wieland–Gumlich aldehyde.[14, 15]

Although the conversion of the Wieland–Gumlich aldehyde into strychnine was reported many years ago,[16] and there would therefore seem to be little need to perform such a conversion, for the sake of completion we followed the described protocol, thus fulfilling the total synthesis of the natural product. The resulting (−)-strychnine was identical to a natural specimen, as determined by thin-layer chromatography (TLC) as well as IR, ^1H NMR, and ^{13}C NMR spectroscopy. The $[\alpha]_D^{25}$ value was −119.4 ($c = 0.35$, $CHCl_3$; reference [16]: $[\alpha]_D^{25} = -139$ ($c = 2.0$, $CHCl_3$)), which represents 86% *ee*,[17] a value very similar to that obtained in our enantioselective synthesis of (−)-tubifolidine from azabicycle **2**.[6d]

We have accomplished a short enantioselective synthesis of (−)-strychnine (15 steps from commercially available 1,3-

  1433-7851/99/3803-0396 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **1999**, *38*, No. 3

cyclohexanedione), involving a transfer of chirality from (*S*)-1-phenylethylamine to generate an enantiopure 3a-(2-nitrophenyl)hexahydroindol-4-one, from which the additional rings of the target molecule are assembled with high stereocontrol. Taking into account our previous work,[6d] the strategy developed here provides a general synthetic route for the enantioselective synthesis of *Strychnos* alkaloids.

Received: July 14, 1998 [Z 12141 IE]
German version: *Angew. Chem.* **1999**, *111*, 408 – 410

Keywords: alkaloids · asymmetric synthesis · nitrogen heterocycles · palladium · total synthesis

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[11] $[Pd(PPh_3)_4]$, $Pd(OAc)_2$, and $[PdCl_2(PPh_3)_2]$ were used as catalysts in several solvents (C_6H_6, CH_3CN, DMF, DMF/H_2O) under a variety of experimental conditions.

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[13] a) In the Heck reaction with electron-deficient olefins, two competing reaction pathways can operate, namely, substitution (which involves β-H elimination) and 1,4-conjugate addition (which involves reduction of the σ-alkylpalladium intermediate); see, for example, G. K. Friestad, B. P. Branchaud, *Tetrahedron Lett.* **1997**, *38*, 5933 – 5936; H. Hagiwara, Y. Eda, K. Morohashi, T. Suzuki, M. Ando, N. Ito, *Tetrahedron Lett.* **1998**, *39*, 4055 – 4058, and references therein; b) the closure of the piperidine ring in the synthesis of strychnine by Rawal and Iwasa[4b] involves a nonreductive intramolecular Heck reaction from a tetracyclic ABCE intermediate.

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Nickel-Catalyzed Homoallylation of Aldehydes and Ketones with 1,3-Dienes and Complementary Promotion by Diethylzinc or Triethylborane**

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Allylation of carbonyl compounds is a fundamental process in organic syntheses, and many efficient methodologies have been developed.[1] Besides the allyl derivatives of alkali and alkaline earth metals, those of transition metals[2] and metalloids (e.g., allylstannanes, -silanes, -boranes, etc.)[1] have been utilized for the regio- and stereoselective allylation of carbonyl compounds. Homoallylation could have similar importance in organic transformations; however, this process has received little attention, probably owing to the limited variety of homoallylating agents $CH_2{=}CHCH_2CH_2M$, which are restricted to metals of high electropositivity such as Li and Mg, since the polarity of homoallylic C–M bonds is considerably lower than that of allylic C–M bonds.

By analogy with the stoichiometric homoallylation of carbonyl compounds with $[ZrCp_2(1,3\text{-diene})]$ (Cp = cyclo-

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[**] We thank Mr. Y. Ohhama, NMR Facility, for technical assistance. Financial support by the Ministry of Education, Science, Sports and Culture, Japanese Government, is gratefully acknowledged.