phosphane react catalytically with CO_2 in refluxing decalin (ca. 185 °C) to give OPR_3 in the rate order $PPh_3 < PBuPh_2 < PEt_3$.[11] The rate for the PPh_3 derivative is about 20 turnovers per day. In the current studies, it appears that CO_2 undergoes reaction with the catalyst to give $OPMe_3$. In the presence of an excess of CO $[Rh(CO)_2(PMe_3)Cl]$ is formed, while in the absence of CO $[Rh_2(CO)_2(PMe_3)_2(\mu\text{-}Cl)_2]$ is formed. We are presently investigating the mechanism of this reaction.

These studies have established the feasibility of carrying out photocatalysis of ethane to propionaldehyde in either single-phase ethane or CO_2 mixtures. A competing side reaction probably involving CO_2 cleavage and phosphine oxide formation may preclude the use of CO_2 as a medium for these rhodium catalysts.

Experimental Section

A thermostated, stainless steel, high-pressure photolysis cell fitted with CaF_2 IR windows and a sapphire photolysis window was used in all high-pressure studies. The cell volume is about 12 mL and the IR pathlength is 0.1 mm. A small spin bar inside the cell was used for mixing. The cell was designed with a maximum pressure rating of 700 atm. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT IR Spectrometer. $[Rh(CO)(PMe_3)_2Cl]$ was prepared by standard literature methods.[12]

In a typical reaction, the rhodium catalyst was added to the cell as a solid, then the sealed cell was charged with reactant gases using a high-pressure line equipped with a syringe pump. Gases such as CO_2 and ethane were condensed into the syringe pump by chilling the pump with ice packs and then charged into the heated cell.

Reaction mixtures were photolyzed by using a 350-W high-pressure Hg lamp. A 30-mm quartz-windowed, water filter was used to remove IR wavelengths from the incident beam. Photolysis times of 6 – 12 h were used, and IR spectra were recorded at the beginning of each photolysis reaction and at regular intervals during the photolysis. Samples for mass spectrometric and NMR analysis were recovered by venting the sample through a restrictor tube directly into $DCCl_3$ in a N_2-flushed Schlenk flask immersed in an ice water bath.

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Rearrangement of a Tricyclic 2,5-Cyclohexadienone: Towards a General Synthetic Route to the Daphnanes and (+)-Resiniferatoxin**

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The daphnane resiniferatoxin[1] (RTX) and structurally related tiglianes possess complex, densely functionalized architectures, along with important biological activity, that have inspired much innovative research in chemistry and biology. The recent isolation and cloning of the principal receptor targeted by resiniferatoxin holds great promise for the development of RTX-related therapeutics.[2, 3] In this regard, parallel advances in the design and synthesis of analogues is imperative because these may serve as cellular probes and useful pharmacologically important compounds.

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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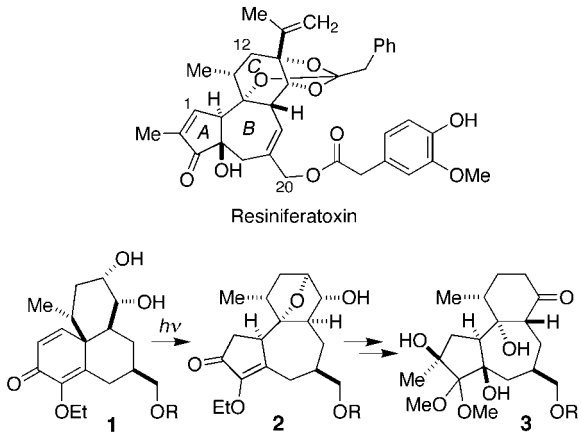
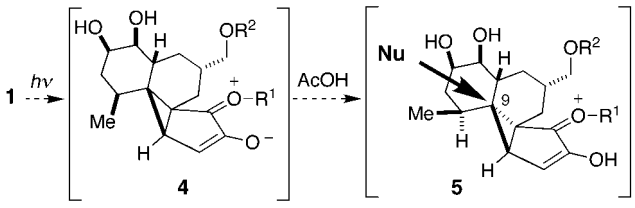
Progress in the synthesis of related bioactive tiglianes (such as phorbol) has generated methods for the construction of daphnanes,[4] and has culminated in the synthesis of resiniferatoxin by Wender et al.[5] We have been engaged in a program focussed on the synthesis of resiniferatoxin with an aim of developing an efficient, distinct approach to this daphnane skeleton. In this communication, we document a high yielding photorearrangement of **1** to a 5,7,6-tricyclic structure **2** (82% yield; Scheme 1). Utilization of this key transformation provides ready access to the conveniently functionalized, versatile template **2**, which can be elaborated as the daphnane skeleton to form **3**.



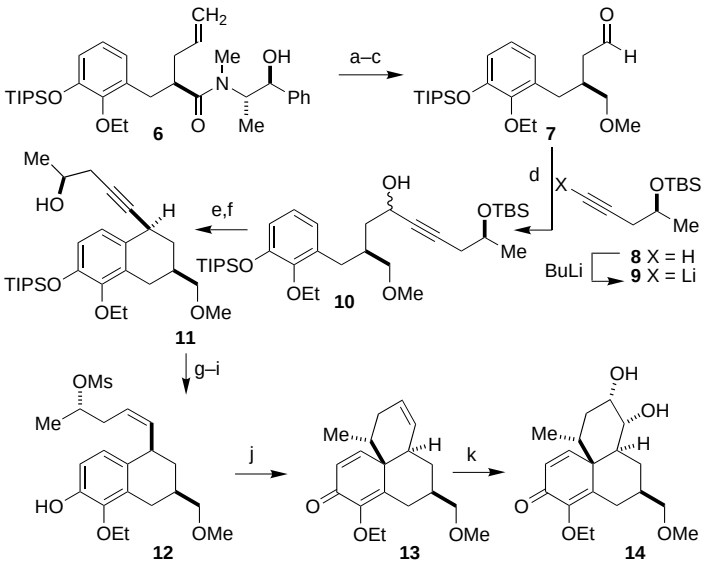
Scheme 1. The structure of resiniferatoxin, and the strategy of forming highly functionalized skeleton **3** through a key photorearrangement reaction.

In approaching the synthesis challenge, we were aware of the classic α-santonin to isophotosantonic lactone photorearrangement, which typically proceeds in 30–40% yield and which has inspired numerous studies and applications in the synthesis of bicyclic compounds.[6] At the outset of our synthetic analysis aimed at applying this photorearrangement reaction to **1** two critical issues were of concern: 1) the additional torsional strain associated with the tricyclic substrate may disfavor formation of the necessary cyclopropenyl intermediate [see **4**, Eq. (1)]; and 2) if this intermediate was



formed, the sterics associated at the C-9 electrophilic site might preclude stereoselective opening in the desired sense [see **5**, Eq. (1)]. In this regard, the failure of certain polycyclic dienones to undergo photorearrangement because of steric encumbrance has been documented.[7] Accordingly, precedence was lacking for the rearrangement of spirofused tricyclic systems.

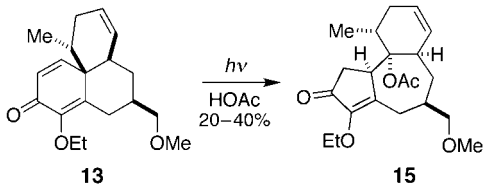
The synthesis of the requisite tricyclic photosubstrate commences with **6** (Scheme 2).[8] Through a short sequence



Scheme 2. a) $LiNH_2BH_3$, THF, 0 °C, 86%; b) MeI, NaH, THF, RT, 96%; c) 1. O_3, CH_2Cl_2, −78 °C; 2. PPh_3, 91%; d) THF, −78 °C, 81%; e) 1. $Co_2(CO)_8$, CH_2Cl_2, −78 °C; 2. $BF_3 \cdot OEt_2$, −78 °C, 76%; f) I_2, benzene, RT, 79%; g) H_2, Pd/C, pyridine, 92%; h) $MeSO_2Cl$, NEt_3, CH_2Cl_2, −78 °C, 98%; i) TBAF, THF, 0 °C, 97%; j) KO*t*amyl, HO*t*amyl, 102 °C, 74%; k) 0.1 equiv OsO_4, NMO, acetone, H_2O, 72%. Ms = mesyl = methanesulfonyl, NMO = 4-methylmorpholine *N*-oxide, TBAF = tetrabutylammonium fluoride, TBS = *tert*-butyldimethylsilyl, THF = tetrahydrofuran, TIPS = triisopropylsilyl.

of reactions amide **6** was transformed into aldehyde **7**. Addition of acetylide **9**[9] to **7** afforded alcohols **10** in 81% yield as an inconsequential mixture of diastereomers. These served as substrates for a cobalt-mediated ring annulation,[10] to furnish **11** in 60% yield as a single diastereomer.[11, 12] Semihydrogenation of **11** afforded a *cis* olefin which was elaborated to **12** in 90% overall yield. Cyclohexadienone **13** was formed from **12** (74% yield) through intramolecular *para-C*-alkylation.[13] Chemo- and stereoselective dihydroxylation of **13** afforded **14** in 72% yield and 90:10 diastereomeric ratio (d.r.).[11]

Dienones **13** and **14** can both serve as substrates for the strategic photorearrangement to furnish the daphnane skeleton. Photorearrangement of **13** with the conditions reported for α-santonin,[6a] afforded product **15** in 20–40% yield [Eq. (2)]. However, in TFA/HOAc **14** underwent the photo-



rearrangement cleanly (72%); moreover, in TFA/dioxane or TFA/pentane **16** was isolated in 78 and 82% yields, respectively [Eq. (3)]. Having established a route to the daphnane 5,7,6-tricyclic system, we proceeded to establish that **16** could be a useful template for further elaboration.[14]

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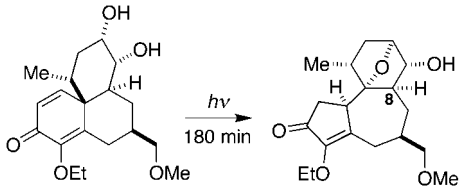
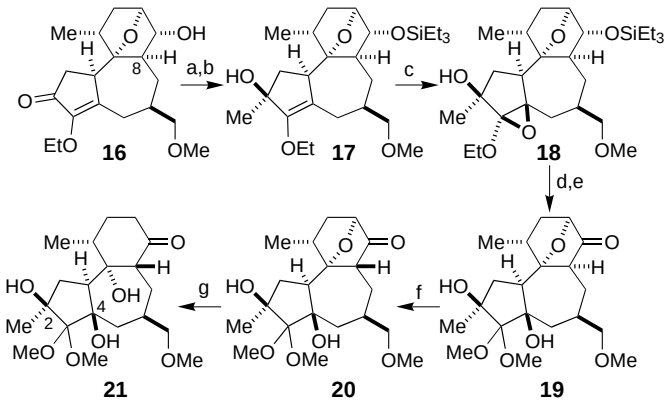


14 16

Conditions	Yield
33% TFA in HOAc	72%
33% TFA in pentane	82%
33% TFA in 1,4-dioxane	78%

The elaboration of **16** commenced with stereoselective addition of $MeLi/CeCl_3$ to the five-membered A ring (Scheme 3); the well-defined concave and convex domains of **16** furnish **17** as a single diastereomer.[11] This reaction



Scheme 3. a) Et_3SiCl, imidazole, CH_2Cl_2, 0 °C, 90 %; b) MeLi, $CeCl_3$, THF, −78 °C, 88 %; c) $VO(acac)_2$, TBHP, benzene, RT, 84 %; d) CSA, MeOH, RT, 95 %; e) TPAP, NMO, CH_2Cl_2, RT, 88 %; f) NaOMe, MeOH, 65 °C, 61 %; g) SmI_2, THF/H_2O, 0 °C, 80 %. acac = acetylacetone, CSA = (+)-camphorsulfonic acid, TBHP = *tert*-butylhydroperoxide, TPAP = tetrapropylammonium perruthenate.

provides an allylic alcohol suitably disposed to serve in subsequent stereoselective functionalization of the enol ether and, thus, installation of the requisite C-4 alcohol with the desired stereochemistry. Directed epoxidation of allylic alcohol **17** afforded exclusively the stable epoxy acetal **18** (84 %). Simultaneous transketalization and deprotection of the TES ether at the C-13 position generated intermediate dimethyl ketal **19**, after oxidation to the corresponding ketone. Through this short reaction sequence, the compatibility of the strategy with the appropriate functionalization reactions of the A ring is established.

We subsequently set out to determine the viability of the strategy in connection with functionalization of the six-membered C ring. Elaboration of this subunit commenced from ketone **19**. This ketone undergoes epimerization cleanly (10 mol % NaOMe) to yield a separable mixture of epimers **19** and **20** (1.6:1). Little material is lost through this transformation, and iterative application of the alkaline conditions to recovered ketone **19** yields > 90 % of the desired epimer **20** after three cycles. Treatment of **20** with SmI_2 in THF/H_2O resulted in C–O bond cleavage to furnish hydroxy ketone **21** (80 %).[15] It is noteworthy that the conversion of ring C proceeds smoothly without the observation of potentially complicating retroaldol or elimination reactions.

We have demonstrated the utility of a 2,5-cyclohexadienone photorearrangement within a complex tricyclic system for the formation of a highly functionalized template structure for the daphnanes. The five-membered A ring of the advanced intermediate can be functionalized in a series of stereoselective reactions to incorporate the C-2 methyl group and the C-4 tertiary hydroxy group with the latter in the stereochemical configuration found in many daphnanes. The C ring is similarly amenable to synthetic elaboration. The chemistry we have described should not only find use in the ongoing approaches to the synthesis of resiniferatoxin and related daphnanes, but also, importantly, be useful in the preparation of potentially useful analogues for pharmacological studies. It is worth noting with respect to the latter that, commencing from **6**, the tricyclic core **16** is accessed in only 12 steps with an overall yield of 9 %.

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  1433-7851/01/4014-2696 $ 17.50+.50/0

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Activation, Tuning, and Immobilization of Homogeneous Catalysts in an Ionic Liquid/ Compressed CO_2 Continuous-Flow System**

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Dedicated to Professor Ernst-Gottfried Jäger on the occasion of his 65th birthday

The quest for new strategies to immobilize organometallic catalysts is one of the major challenges in homogeneous catalysis. Ionic liquids (ILs) are emerging as excellent solvents for transition metal catalysts. In many applications they are used for multiphasic reaction systems because of their miscibility gap with the reaction products.[1] Supercritical carbon dioxide ($scCO_2$) is also of increasing interest because it combines an environmentally benign character with favorable physico-chemical properties for chemical synthesis.[2, 3] Catalyst separation schemes have been devised on the basis of the tuneable phase behavior of $scCO_2$ (CESS process).[4] We report here a new continuous-flow catalytic system based on the combination of these two solvents systems, which are at the extreme ends of the volatility and polarity scale. We provide convincing evidence that the interplay of their complementary properties offers new intriguing possibilities for catalytic synthesis.

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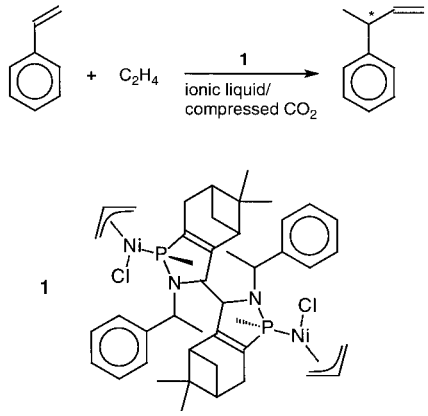
Recently, the research groups of Brennecke and Beckman described the phase behavior of biphasic systems consisting of an IL and supercritical CO_2.[5] They demonstrated that $scCO_2$ is highly soluble in some ILs, while the same ILs show no detectable solubility in the $scCO_2$ phase. Moreover, it was found that $scCO_2$ can be used to extract high-boiling organic substances from ILs without any cross-contamination of the extract with the IL. Intrigued by these pioneering studies, we and others[6, 7] started to explore this unique phase behavior for homogeneous catalysis. While our investigations were in progress, Jessop et al. used $scCO_2$ to isolate the products of a catalytic hydrogenation that was carried out in an IL.[6a] Baker, Tumas, and co-workers conducted catalytic hydrogenations of, for example, 1-decene directly in a biphasic reaction mixture consisting of the IL 1-*n*-butyl-3-methylimidazolium (BMIM) hexafluorophosphate and $scCO_2$. The ionic catalyst solution could be re-used in up to four consecutive batch experiments.[6b]

We demonstrate here that the combination of a suitable IL and compressed CO_2 can offer much more potential for process optimization than just a simple protocol for batchwise catalyst recycling. By using this unusual biphasic system we were able to activate, tune, and immobilize Ni-catalyst **1** in a continuous flow system for the hydrovinylation of styrene (Scheme 1).



Scheme 1. The hydrovinylation reaction and the Wilke's catalyst **1**.

Hydrovinylation is the transition metal catalyzed codimerization of alkenes with ethene to yield 3-substituted 1-butenes.[8] This powerful carbon–carbon bond forming reaction can be achieved with high enantioselectivity using Wilke's complex **1** as a catalyst precursor.[9] In conventional solvents pre-catalyst **1** needs to be activated with a chloride-abstracting agent, for example, the highly flammable $Et_3Al_2Cl_3$.[8, 9] Some of us reported the use of complex **1** in liquid and supercritical CO_2 after activation with alkali salts of weakly coordinating anions such as Na[BARF] (BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate).[10] In a first set of experiments we aimed to identify suitable ILs that would allow the activation of **1** for the enantioselective hydrovinylation of styrene in the presence of compressed CO_2 (Table 1).[11]

The synthesis of the ILs comprising the bistriflic amide anion ($(CF_3SO_2)_2N$, Tf_2N) and the cations 1-ethyl-3-methyl-

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