field desorption mass spectrum ($m/e = 206$ for $CpV(NO)_3^+$)[4]; in nitromethane solution it behaves as a 1:1 electrolyte. The pronounced electron deficit at the central metal of *(1)* is reflected in the high ν(NO) frequencies in the IR spectrum and in the strong deshielding of the cyclopentadienyl protons in the ^{1}H-NMR spectrum. Table 1 shows the characteristic spectroscopic data of the cations *(1)* and *(2)*[5] and of the corresponding neutral complexes from which they can be obtained by reaction with $NOPF_6$.

Table 1. IR and ^{1}H-NMR data [a].

Complex	IR [b] ν(CO)	IR [b] ν(NO)	^{1}H-NMR [c] δ(Cp)
$CpCr(CO)_2(NO)$	2025, 1948	1693	5.23
$[CpCr(CO)(NO)_2]PF_6$	2142	1875, 1789	6.25
$CpV(CO)(NO)_2$	2064	1723, 1629	5.71
$[CpV(NO)_3]PF_6$	—	1912, 1794	6.55 [d]

[a] All measurements in nitromethane. [b] Perkin-Elmer 297; cm^{-1}. [c] Jeol C-60-HL; δ values rel. TMS int., calibration with TMS/$CHCl_3$. [d] Measurement at −25°C.

In contrast to the now complete series of the isosteric cations $[CpML_3]^+$ (L = CO, NO), the analogous series of the neutral half-sandwich complexes, $CpML_3$, remains incomplete since the end-member $CpTi(NO)_3$ is still unknown.

Experimental[6]

$CpV(CO)(NO)_2$: $CpV(CO)_4$ (1.27 g, 5.6 mmol) is dissolved in tetrahydrofuran and reduced to $Na_2[CpV(CO)_3]$ with 1% sodium amalgam[3b, 7]. The salt is dried in a high vacuum at +70°C, suspended in 50 ml diethyl ether, and nitrosylated with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("diazald") (2.38 g, 11.1 mmol; dissolved in 10 ml ether). The undissolved material is removed by filtration (G3 frit) and the solution evaporated to dryness; the resulting residue is then extracted with 5 × 20 ml pentane. Column chromatographic separation of the pentane solution on silica gel (pentane, 0°C) affords $CpV(CO)_4$ and $CpV(CO)(NO)_2$ in yields of 11% (0.14 g) and 34% (0.39 g), respectively.

$[CpV(NO)_3]PF_6$: A solution of $NOPF_6$ (0.32 g, 1.8 mmol) in 10 ml nitromethane is added dropwise to the orange-brown solution of $CpV(CO)(NO)_2$ (0.37 g, 1.8 mmol) in 50 ml nitromethane at −25°C. The resulting green solution is filtered through a G3 frit, cooled to −25°C, into 200 ml of cooled ether. After 12 h at −30°C, the resulting green crystals are separated from the mother liquor, washed several times with cooled ether and cooled pentane and then dried for 2 h at −70°C in a high vacuum. Yield 0.40 g (63%); decomposition above 160°C in a nitrogen-filled ampoule[8].

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$CpCr(CO)_2(NO)$, 36312-04-6; $[CpCr(CO)(NO)_2]PF_6$, 69439-82-3; $CpV(CO)(NO)_2$, 31811-51-5; $[CpV(NO)_3]PF_6$, 69439-84-5; $CpV(CO)_4$, 12108-04-2; *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 80-11-5; $NOPF_6$, 16921-91-8

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[8] *Note added in proof:* The salt $[CpV(NO)_3]PF_6$ is obtained directly when a nitromethane solution of $CpV(CO)_4$ is reacted with $NOPF_6$ at −25°C and then allowed to warm up in a stream of NO gas (*ca.* 90% yield).

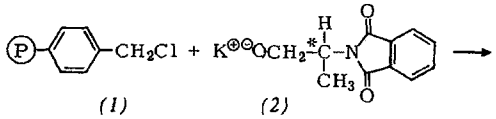
Asymmetric Synthesis of 2-Alkylcyclohexanones on Solid Phases[**]

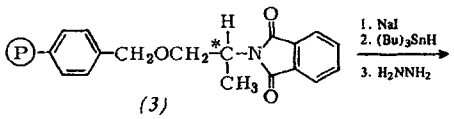
By *Paul M. Worster, Colin R. McArthur*, and *Clifford C. Leznoff*[*]

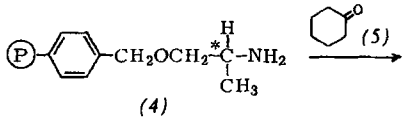
Asymmetric syntheses of 2-alkylcyclohexanones[1a] have been recently described in which the optical yields were remarkably high[1b]. The key step is alkylation of an optically active alkoxyiminocyclohexanone.

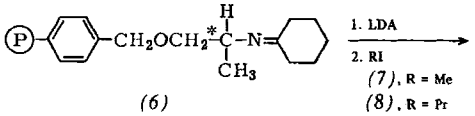
Insoluble polymer supports have been used in the preparation of enantiomerically pure organic compounds in several ways. Crosslinked polymers containing optically active phosphane ligands have been used as catalysts in asymmetric synthesis[2]. Crosslinked polymers containing chiral cavities have been used for resolving specific organic racemates[3]. In both of these applications the polymer is the reagent and the product remains in solution. In the Merrifield synthesis, however, the reaction product is attached to the polymer and the excess reagents and catalysts are removed by simple filtration. The latter approach was used in the asymmetric synthesis of atrolactic acid on crosslinked polystyrene polymers containing a chiral sugar[4]. The chemical and optical yields were somewhat better than those obtained in solution.

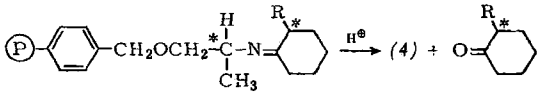
We feel that significant advantages can be gained by performing asymmetric syntheses on insoluble polymer sup-











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ports[5]. The expensive chiral reagent can be recovered by simple filtration at the end of the synthesis. In addition, the bulk of the polymer backbone and the reduced mobility of the polymer-bound substrate can mimic enzymatic reactions, giving high optical yields.

We were interested in determing whether the very high chemical and optical yields of the asymmetric synthesis of 2-alkylcyclohexanones[1b] could be achieved on solid phases. Merrifield's commercially available 1 % crosslinked divinylbenzene-styrene copolymer [*(1)*, containing 1.1 mmol of benzyl chloride groups/g of polymer] reacted with the potassium salt of (*S*)-2-phthalamido-1-propanol in benzene containing catalytic amounts of [18]crown-6 to give the polymer-bound phthalamido-blocked chiral amine *(3)*. Treatment of *(3)* with NaI in acetone and subsequent reaction with tri-*n*-butyltin hydride to remove the excess benzyl chloride groups[6] of *(3)*, followed by hydrazinolysis, gave the polymer-bound chiral amine *(4)*. Treatment of *(4)* with cyclohexanone *(5)* in benzene in a Soxhlet extractor [with 3-Å molecular sieves in the thimble] gave polymer-bound chiral alkoxyimine *(6)*. Acid cleavage[7] of *(6)* liberated 0.4 mmol of *(5)*/g of *(6)*. Treatment of *(6)* with lithium diisopropylamide (LDA) at 0°C followed by the addition of methyl iodide *(7)* or propyl iodide *(8)* at 22°C yielded the polymer-bound alkylated imines *(9)* or *(10)*, respectively. Mild acid cleavage[7] of *(9)* or *(10)* liberated *(4)* and (*S*)-2-methylcyclohexanone *(11)* ($[\alpha]_D^{26} = +15.5$) in 95% optical yield and 80% chemical yield or (*S*)-2-propylcyclohexanone *(12)* ($[\alpha]_D^{26} = +15.5$) in 60% optical yield and 80% chemical yield. The optical and chemical yields of *(11)* are at least as high as those reported[1b] for reactions performed in solution. The recovered chiral reagent *(4)* loses some of its capacity on recyclization, but the enantiomeric excesses of the product remain unchanged in subsequent cycles. We have thus demonstrated that asymmetric synthesis on solid phases is a practical reality which shows promise of high enantiomeric excesses of product comparable with those obtained in enzymatic systems.

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Novel Glycals as Synthons for Saccharide Syntheses[**]

By *Joachim Thiem, Petra Ossowski, and Jens Schwentner*[*]

The sequential construction of long-chain oligodeoxyoligosaccharides and linkage to complex aglycons require readily accessible reactive saccharide precursors and a readily manageable method of coupling. A suitable technique consists in the reaction of glycals with alcohols in the presence of *N*-iodosuccinimide (NIS)[1]. As a potential method for the production of cardenolide oligosaccharides, increasing interest is being focused on a synthesis of D-digitoxal *(3a)*, which proceeds independently of the natural product[2] and of the conventional glycal syntheses[3].

The epoxide ring in methyl 2,3-anhydro-6-deoxy-α-D-allopyranoside *(1)*[4], which is easily accessible in six steps from methyl α-D-glucopyranoside by a standardizable method[5], undergoes smooth nucleophilic cleavage with lithium iodide dihydrate in pyridine with addition of acetic acid. According to the Fürst-Plattner rule[6], the *trans*-diaxial 2,6-dideoxy-2-iodo-α-D-*altro* cleavage product *(2)* predominates (80 % yield, see Table 1 for physical data). In addition, the *trans*-diequatorial 3,6-dideoxy-3-iodo-α-D-*gluco* product (20 %) is also formed.

The reaction of iodohydrin *(2)* with methyllithium in ether[7] has proved to be of considerable advantage. Chromatographic separation of the isomeric iodohydrins formed in the first step is not necessary for the preparation since the stable compound *(3a)*[2] crystallizes directly after reaction of the mixture with methyllithium.

(3a) was acetylated to *(3b)* which could be condensed with the epoxide *(1)* by the *N*-iodosuccinimide method[1]

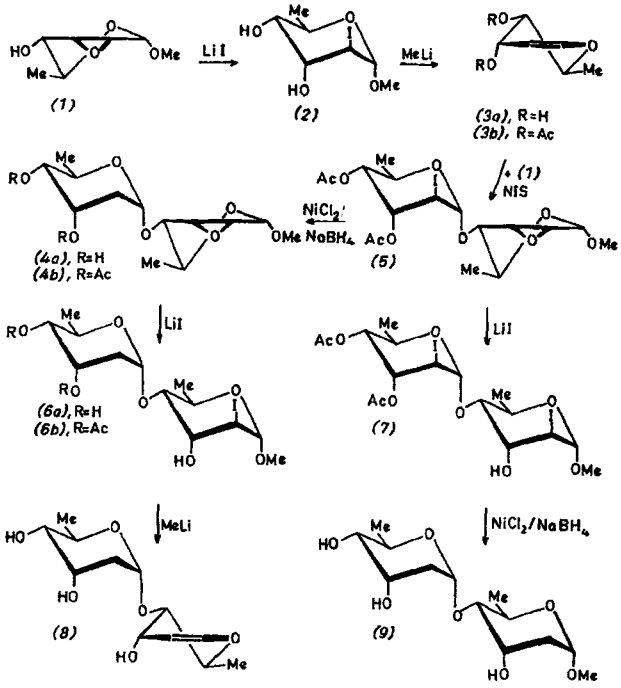

Table 1. Physical data (selection) of the sugar derivatives synthesized. ^{1}H-NMR at 270 MHz (Bruker WH 270) in $CDCl_3$ and CD_3OD.

(2), syrup, $[\alpha]_D^{20} = +44.3°$ ($CHCl_3$)
(3a), m.p. 115°C, $[\alpha]_D^{20} = +314.2°$ (CH_3OH)
(4b), m.p. 98°C, $[\alpha]_D^{20} = +256.9°$ ($CHCl_3$)
(5), syrup, $[\alpha]_D^{20} = +153.6°$ ($CHCl_3$); NMR: $\delta = 5.28$ (d, 1'-H), $J_{1',2'} = 2.4$ Hz
(6b), syrup, $[\alpha]_D^{20} = +157.7°$ ($CHCl_3$)
(7), syrup, $[\alpha]_D^{20} = +63.2°$ ($CHCl_3$); NMR: $\delta = 4.93$ (d, 1-H), 4.32 (dd, 2-H), 4.25 (m, 3-H), $J_{1,2} = 1.9$, $J_{2,3} = 4.3$, $J_{3,4} = 2.7$ Hz
(8), syrup, $[\alpha]_D^{20} = +324.1°$ (CH_3OH); NMR: $\delta = 6.31$ (d, 1-H), 4.89 (dd, 2-H), 4.27 (dd, 3-H), 3.64 (dd, 4-H), 4.15 (dq, 5-H), 1.35 (d, 6-CH_3), 5.13 (dd, 1'-H), 1.98 (ddd, 2a'-H), 2.25 (ddd, 2e'-H), 4.02 (ddd, 3'-H), 3.20 (dd, 4'-H), 3.88 (dq, 5'-H), 1.32 (d, 6'-CH_3), $J_{1,2} = 5.9$, $J_{2,3} = 4.9$, $J_{3,4} = 3.8$, $J_{4,5} = 8.5$, $J_{5,6} = 6.4$, $J_{1',2a'} = 3.4$, $J_{1',2e'} = 1.1$, $J_{2a',2e'} = -14.8$, $J_{2a',3'} = 3.5$, $J_{2e',3'} = 3.1$, $J_{3',4'} = 3.1$, $J_{4',5'} = 9.7$, $J_{5',6'} = 6.2$ Hz
(9), m.p. 155–157°C, $[\alpha]_D^{20} = +284.1°$ (CH_3OH)

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