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- [5] a) Diffraction measurement was made on an AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo α radiation at -180°C . The compound crystallized in the space group $P2_1/c$ with $a = 9.409(7)$, $b = 8.539(3)$, $c = 12.565(6)$ Å, $\beta = 104.64(4)^{\circ}$, $V = 976.8(8)$ Å 3 , $Z = 2$, $\rho_{\text{calcd}} = 1.313$ g cm $^{-3}$. A total of 2396 unique reflections was recorded in the range $6^{\circ} \leq 2\theta \leq 55^{\circ}$, of which 1968 were used ($F > 3\sigma(F)$) for solution and refinement. In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data. The structure was solved by the Patterson method (DIRDIF92, PATTY), and all hydrogen atoms were refined isotropically and all non-hydrogen atoms were refined anisotropically by using full-matrix least-squares techniques on F . The final structure of **4** was refined to $R = 0.027$, $R_w = 0.026$, for 167 parameters. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142856 (**4**), CCDC-142858 (**5**), and CCDC-142857 (**6**). 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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Asymmetric Alkylation of Nitroalkanes**

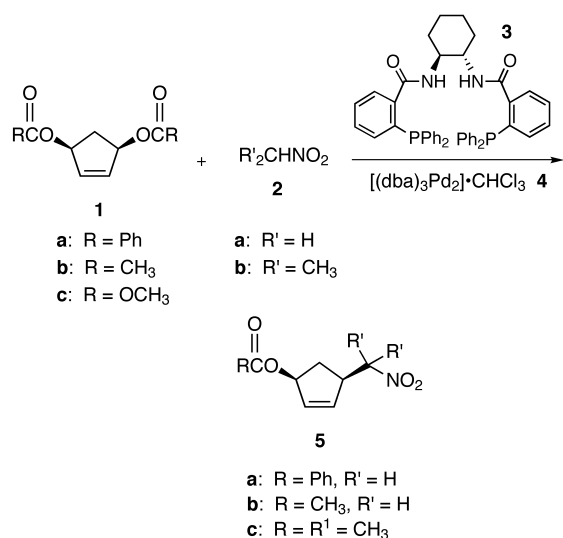
Barry M. Trost* and Jean-Philippe Surivet

The utility of nitro compounds as synthetic intermediates stems from the versatility of the reactivity of the nitro group.^[1] One feature arises from the ease of formation of nitronate anions; however, their low reactivity generally limits the reactions they undergo to carbonyl and conjugate addition.^[2] Alkylations do not normally proceed well. On the other hand, Pd-catalyzed allylic alkylations have had some success.^[3] This success stimulates the search for an asymmetric allylic alkylation (AAA) which has had good results in only one case (the 1,3-diphenylallyl system) and when nitromethane was used as solvent.^[4] We here report that the Pd-catalyzed AAA reaction^[5] of nitroalkanes with cyclic allyl esters can proceed in high yields and enantioselectivities and provide a short asymmetric synthesis of a carbanucleoside.

Our initial studies focused on desymmetrization of *meso* diesters [Eq. (1)].^[6] Our earlier results suggested the diben-

[*] Prof. B. M. Trost, Dr. J.-P. Surivet
Department of Chemistry
Stanford University
Stanford, CA 94305-5080 (USA)
Fax: (+1) 650-725-0002
E-mail: bmtrost@leland.stanford.edu

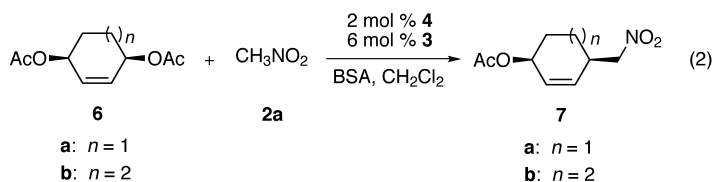
[**] We thank the National Science Foundation and the National Institutes of Health (NIH), General Medical Sciences, for their generous support of our programs. Rhône-Poulenc graciously provided a postdoctoral fellowship for J.-P. S. Mass spectra were provided by the Mass Spectrometry Facility of the University of California, San Francisco, supported by the NIH Division of Research Resources.



zoate **1a** would be superior for enantiodiscrimination. Surprisingly, using nitromethane (**2a**, 5 equiv) with the *S,S*-ligand **3** and a Pd⁰ complex **4** in DMSO with cesium carbonate as base led to no reaction. Similar results were obtained with the diacetate **1b** and dicarbonate **1c**. Switching the solvent to methylene chloride (but not THF nor acetonitrile) with the diacetate **1b** led to some reaction to produce **5b**^[7] (18 % yield) but, gratifyingly, with excellent enantioselectivity (99 %). Remarkably, changing the base from cesium carbonate to BSA (BSA = *O,N*-bis-trimethylsilylacetamide) in methylene chloride now led to smooth reaction producing **5b** in 75 % yield while maintaining high *ee* (99 %).^[8] Identical results were obtained with the dibenzoate **1a** to give **5a**^[7] however, the dicarbonate led to very low conversions.

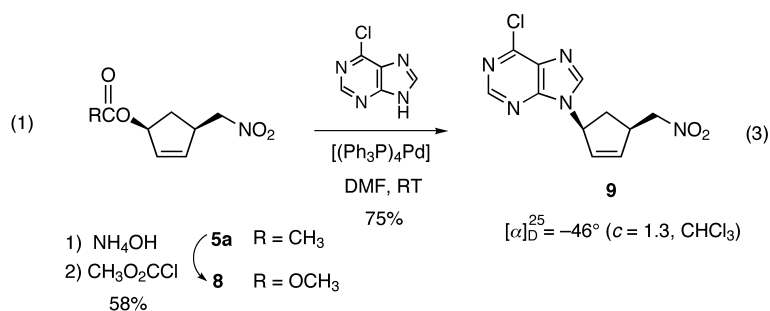
The complete reverse behavior was observed with 2-nitropropane (**2b**). Neither the dibenzoate **1a** nor the diacetate **1b** reacted to any appreciable extent in methylene chloride. On the other hand, the use of cesium carbonate in DMSO with the diacetate **1b** gave a 92 % yield of **5c**^[7] having 95 % *ee*.

The same trend was observed for nitromethane with the larger ring *meso* diesters **6a,b**. Using the optimal conditions established for **5b** [Eq. (2)], the corresponding monoalkylated products **7a**^[7] and **7b**^[7] were obtained in 82–84 % yield with near perfect enantioselectivity (99 % *ee*).

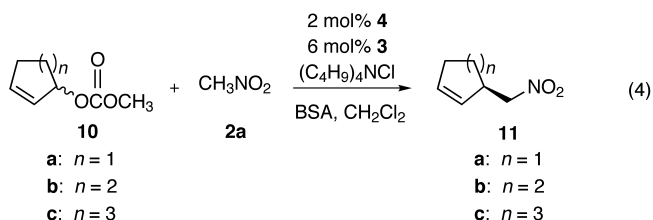


The absolute configuration is assigned by analogy.^[5, 6] Further support derives from conversion of **5b** to a known carbanucleoside intermediate **9** [Eq. (3)].^[3g] A (+) rotation is reported for the enantiomer corresponding to the “normal” enantiomeric series of the carbanucleosides, thus the (–) rotation observed for our synthetic sample indicates the absolute configuration as depicted. Since the nitromethyl side

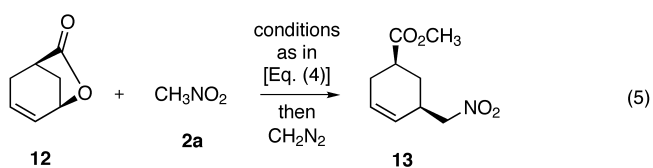
chain has been converted to a hydroxymethyl side chain in one step,^[9] this constitutes a rapid asymmetric synthesis of such carbanucleosides.



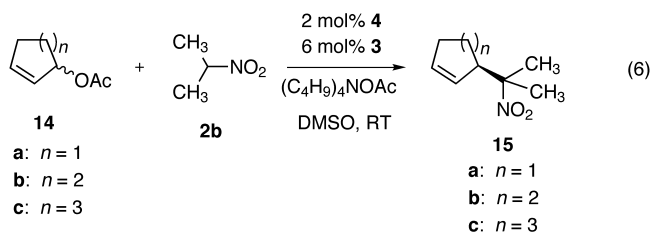
The success of the desymmetrization led to our investigation of the cycloalkenyl substrates [Eq. (4)].^[10] For the alkylations with nitromethane, the carbonates **10** proved



superior to the corresponding acetates. The conditions that proved successful in the desymmetrization with nitromethane also proved to be successful here. For the cyclopentenyl system **10a**, the alkylated product **11a**^[7] was obtained in 94 % yield (97 % *ee*). Equally satisfactory results were obtained for the six- (99 % yield, 99 % *ee* for **11b**) and seven-membered ring systems (94 % yield, 95 % *ee* for **11c**^[7]). The lactone **12** also followed the same pattern to provide, after esterification, the nitroester **13**^[7] in 74 % yield [99 % *ee*; Eq. (5)].

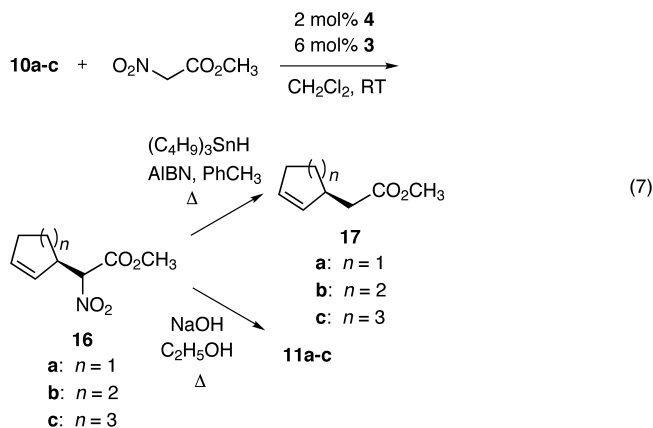


Use of 2-nitropropane allowed use of the allyl acetates as substrates [Eq. (6)]. The reactions performed in DMSO at room temperature with tetra-*n*-butylammonium acetate (for **14b**) or cesium carbonate (for **14a** and **14c**) as base gave



excellent results (**15a**^[7], 74 % yield, 97 % *ee*; **15b**^[7], 79 % yield, 94 % *ee*; **15c**^[7], 50 % yield, 96 % *ee*).

The absolute configuration was established by correlation as depicted in Equation (7). Alkylation of the allyl carbonates **10a–c** using methyl nitroacetate proceeds with no added base to give the desired products (**16a**^[7], 80 %; **16b**^[7], 93 %; **16c**^[7], 87 %). Radical denitration^[11] gave the known cycloalkenyl



acetates **17a–c**^[10] thereby establishing the absolute configuration of **16a–c**. Alternatively, hydrolysis with concomitant decarboxylation gave the nitroalkenes (**11a**, 64 % yield, 85 % *ee*; **11b**, 65 % yield, 95 % *ee*; **11c**, 72 % yield, >99 % *ee*) thereby establishing their absolute configurations as depicted.

The utility of nitroalkanes as building blocks makes a significant step forward as a result of the ability to effect AAA reactions using cyclic allyl esters. It is clear that the nitroalkane significantly influences the catalyst. The significantly different reactivity between nitromethane and 2-nitropropane highlight this fact. A possible explanation suggests that the nitronate derived from nitromethane may serve as a competitive ligand to palladium. The lack of polyalkylation of nitromethane is noteworthy especially considering that the higher nitroalkanes are better nucleophiles and the reported significance of this problem in another system.^[4] The current method provides a practical approach to these chiral nitroalkanes that enhances their utility as useful building blocks.

Received: March 28, 2000 [Z14909]

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Enantiomeric Self-Recognition: Cation-Templated Formation of Homochiral Isoguanosine Pentamers**

Xiaodong Shi, James C. Fetting, Mangmang Cai, and Jeffery T. Davis*

Stereochemical information embedded within the building blocks of biopolymers is often translated into higher organization. Both the protein α -helix and the DNA duplex, structures that require homochiral chains, rely on such a hierarchy.^[1] To illustrate the impact of stereochemistry in controlling the structure of noncovalent aggregates, we describe the enantiomeric self-recognition of the racemic 5'-*tert*-butyldimethylsilyl-2'-3'-di-*O*-isopropylidene-substituted isoguanosine, isoG **1**, to give homochiral, hydrogen-bonded pentamers.

Self-recognition is a process whereby a compound selectively associates with its own kind. Self-recognition relies on: 1) reversible processes^[2] and 2) a subunit's "pre-disposition"^[3] towards self-assembly. Stereochemistry can be crucial for self-recognition. Enantiomeric self-recognition in supramolecular systems has been achieved using metal ion coordination^[4,5] or hydrogen bonds.^[6–8]

[*] Prof. J. T. Davis, X. Shi, Dr. J. C. Fetting, M. Cai
Department of Chemistry and Biochemistry
University of Maryland
College Park, MD 20742 (USA)
Fax: (+1) 301-314-9121
E-mail: jd140@umail.umd.edu

[**] This research was sponsored by the Separations and Analysis Program, Chemical Sciences Division, Office of Basic Energy Sciences, U.S. Department of Energy. J.D. thanks the Dreyfus Foundation for a Teacher-Scholar Award. We thank Professors Giovanni Gottarelli and Steve Rokita for helpful discussions.

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