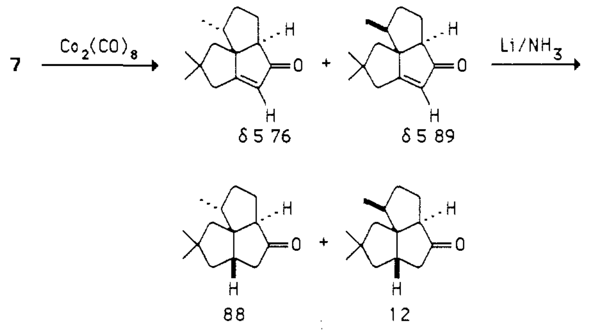

8

In the event, heating of 7-$Co_2(CO)_6$ in heptane at 110 °C (sealed tube) gives 51% of an 88:12 ratio of enones. The products have readily resolved proton NMR resonances at δ 5.76 (major isomer) and δ 5.89 (minor isomer), respectively, but no information concerning the stereochemistry of the major product could be inferred at this point. Reduction (Li/NH_3, 89%) gives a mixture of saturated ketones **8** whose major constituent clearly possesses the desired configuration at C-9, based on superimposability of its NMR signals with those of the minor constituent in spectra obtained by Piers for a 42:58 mixture of isomers of **8**. Completion of the synthesis of pentalenene was achieved by following the published procedure; spectroscopic data for the product were identical in all respects with that of authentic (±)-pentalenene.[11,12]

The interactions associated with the intramolecular Pauson–Khand reaction are more than sufficient to give rise to usable stereoselectivity in relatively complex situations. The interaction above is not obviously greater than those that give rise to rather modest *regio*selectivities in some intermolecular versions of the reaction.[13,14] The difference in transition state energy between endo and exo C-9 methyl leading to the intermediate shown is about 1 kcal/mol. Apparently the transition state associated with alkene insertion in the intramolecular process is more product-like, consistent with the high stereoselectivities found by Magnus in Pauson–Khand syntheses of substituted bicyclic systems.[15] It was necessary in the latter cases to generate the controlling interaction by attachment of a bulky group to the alkyne terminus. In our system this is unnecessary, as the control elements are already present in the framework of the incipient tricyclic itself.

Acknowledgment. We thank the National Institutes of Health (Grant GM26294) for financial support of this research. This material is based upon work supported under a National Science Foundation Graduate Fellowship to E.G.R. We also express our appreciation to Professor M. Cooke for helpful discussions and to Professor E. Piers for supplying copies of spectra and detailed experimental information.

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(11) We are extremely grateful to Prof. Edward Piers of the University of British Columbia for providing us with details of his conversion of **8** into **1** and for supplying IR and NMR spectra of these compounds for comparison purposes.

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[*n*]Staffanes: A Molecular-Size "Tinkertoy"[1] Construction Set for Nanotechnology. Preparation of End-Functionalized Telomers and a Polymer of [1.1.1]Propellane

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Received April 13, 1988

Nanotechnology,[2] custom design and construction of molecular-size mechanical structures, has been a subject of speculation for some time.[3] We have telomerized and polymerized [1.1.1]propellane (**1**) and obtained a family of end-functionalized inert, insulating, transparent, and straight beams with a van der Waals radius of 2.3 Å and a length increment of 3.35 Å for use as construction elements. We propose the trivial name [*n*]staffanes for the parent hydrocarbons.[4] Presently, we describe a one-step synthesis of singly functionalized telomers **[*n*]2**, with emphasis on the esters **[*n*]2a** and the acids **[*n*]2b**, including a low molecular weight polymer **[poly]2a**. A one-step preparation of doubly end-functionalized telomers of **1** will be reported separately.[5]

Previously described molecules of this type were the formal telomers **[*n*]3** of [2.2.2]propellane, originated by Zimmerman,[6] known up to *n* = 2, and used as spacers in studies of energy[6] and electron[7] transfer. Unlike the synthesis of **[*n*]2**, the preparation of the higher members of this series is laborious.

[1.1.1]Propellane[8] (**1**) is readily accessible from methallyl dichloride.[9] The formation of telomer side-products up to *n* = 3 during radical addition of cyanogen bromide to **1** has been detected,[10] and very recently a low-molecular weight polymer was obtained from a related monomer, 2,4-trimethylene-**1**, by anionic polymerization.[11]

We have detected the formation of numerous telomers under radical addition conditions, **[*n*]2a** – **[*n*]2i**, *n* = 1–4 or 5, and isolated many of them in pure state. Their relative amounts depend on the choice of reactant concentrations. Chlorocarbonylation of **[*n*]2a**, *n* = 2, 3, yielded derivatives of **[*n*]2j**. Some of the attempted telomerization reactions did not proceed smoothly; e.g., the reaction of $PhCH_2Br$ with **1** yielded some **[2]2k** and bibenzyl in addition to **[1]2l**.

Efficient preparation of **[*n*]2a** requires ether-free solutions of **1**, obtained in a 15% yield based on methallyl dichloride by substituting TMEDA for ether in the Szeimies synthesis. In a typical procedure, a 1.4 M solution of **1** in pentane (65 mL) reacted with methyl formate (800 mL) upon irradiation in the presence of benzoyl peroxide (0.4 g). The individual telomers **[*n*]2a** were separated by crystallization of the acids and potassium salts and by sublimation. On the basis of methallyl dichloride, the overall three-step yields of purified materials were about 3% for *n* = 1, 2, about 1.5% for *n* = 3, 4, and about 0.8% for *n* = 5, with about 3% of **1** accounted for as higher molecular weight material. It is possible to find reaction conditions under which only the

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(1) Tinkertoy is a trade-mark of the Questor Education Products Company, used to designate a children's toy construction set consisting of straight beams and connectors.

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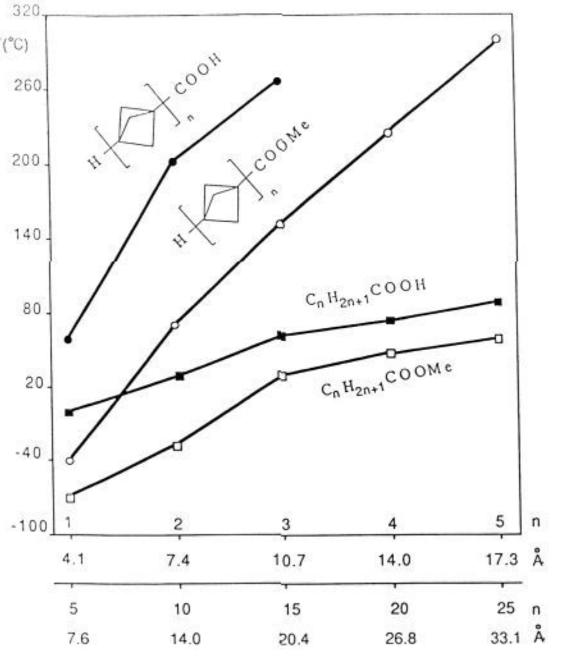
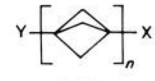


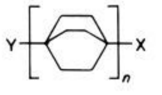
Figure 1. Melting points of (i) [***n***]**2b**, (ii) [***n***]**2a**, (iii) fatty acids $C_nH_{2n+1}COOH$, and (iv) their methyl esters. Horizontal scales give *n* and chain length. The upper one applies to (i) and (ii), the lower one to (iii) and (iv).

monomer ($n = 1$) is formed.[12] At low concentrations of methyl formate and also under anionic polymerization conditions (*n*-butyllithium, 2–25%), practically only **[poly]2** is obtained (unoptimized yield, ~50%).

1



[*n*] **2**



[*n*] **3**

		X	Y		X	Y		X	Y
[*n*] 2	**a**,	H	COOMe	**f**,	H	C(Ph)(COOEt)$_2$	**k**,	Br	Br
	b,	H	COOH	**g**,	H	CH(COMe)COOMe	**l**,	PhCH$_2$	Br
	c,	H	CH(COOEt)$_2$	**h**,	H	CH(CN)COOMe	**m**,	SCOMe	SCOMe
	d,	H	C(COOEt)$_3$	**i**,	H	P(O)(OEt)$_2$			
	e,	H	CH(CN)$_2$	**j**,	COOH	COOH			

The telomers [***n***]**2** have strikingly high melting points (Figure 1) and remarkable thermal stability up to about 300 °C, considering their high-energy content (the strain energy of bicyclo[1.1.1]pentane is 68 kcal/mol[13]). Differential scanning calorimetry on a sealed sample of **[4]2a** shows a decomposition exotherm at ~320 °C (145.7 kcal/mol). **[poly]2a** decomposes violently at 290 °C with an ~80% weight loss. In keeping with the high melting points, the solubility of the higher telomers is poor, and no solvent for **[poly]2a** was found. Its X-ray diffraction pattern shows a high degree of crystallinity. Its solubility is increased dramatically upon extensive chlorination,[14] and this clearly points the way toward improvements in the solubility of all the telomers.

X-ray structure analysis[15] on **[2]2a** (Figure 2) and **[2]2k** yields an inter-ring C–C bond length of only ~1.48 Å, in keeping with expectations,[16] and a bridgehead–bridgehead separation of ~1.9 Å. In **[3]2m**, obtained[5] by telomerization of **1** with $(CH_3COS)_2$, the inter-ring distances are even shorter, 1.47 Å.[5] Neighboring staffs are parallel and meshed in the crystal, with axes only 4.6 Å apart. This very efficient packing is undoubtedly responsible for the high melting points.

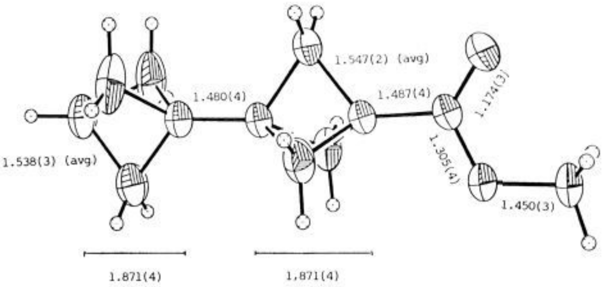


Figure 2. The structure of methyl [2]staffane-3-carboxylate.[14]

The salts of the acids [***n***]**2b** are surface active. In the concentration range $c = 1.4 \times 10^{-2}$–3×10^{-4} M, the surface tension[16] of an aqueous solution of the potassium salt of **[3]2b** follows $\gamma = -17.7 \log c - 0.2$ dyn/cm (107 Å^2 of surface area per molecule). Langmuir–Blodgett films have been prepared by using the Cd^{2+} salt of **[4]2b** (45 Å^2/molecule).[18]

The NMR spectra of the "staffs" clearly show each equivalent class of ^1H and ^{13}C nuclei up to $n = 5$. Large bridgehead–bridgehead coupling constants are attributed to transannular orbital interactions,[19] e.g., in **[2]2i**, $^7J[^{31}P^1H] = 1.7$ Hz. The CP-MAS ^{13}C NMR spectrum of **[poly]2a** consists of a peak at δ 50.8 (bridge), a sharp peak at δ 40.3 (bridgehead), and weak end-group signals at δ 169.7 (carbonyl) and δ 27.8 (methine).

Acknowledgment. This work was supported by the National Science Foundation (CHE 8796257) and The Robert A. Welch Foundation (F-1068). We are grateful to Prof. W. H. Wade for permission to use his spinning drop apparatus and to Dr. A. Orendt for a measurement of CP-MAS NMR in the laboratory of Prof. D. M. Grant.

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The Role of Oxygen in the Partial Oxidation of Methane over a Samarium Oxide Catalyst

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Received March 17, 1988

The reaction of methane with oxygen at high temperatures to form higher hydrocarbons such as ethane and ethylene was first reported by Ito et al.,[1] who used a lithium-doped magnesium oxide catalyst and suggested that the reaction involved the formation of methyl radicals on Li^+O^- sites and their subsequent gas-phase dimerization. The reaction presents an intriguing mechanistic problem, particularly as it is now known to be catalyzed by a wide range of materials.[2] Samarium oxide appears to be one of the most active catalysts.[3] Details of the reaction mechanism are obscure at present, but it is obvious that the formation of C2 hydrocarbons at these high temperatures in the presence of oxygen

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