were separated by column chromatography on silica gel. The first fraction (elution with benzene–hexane (1:1)) contained the ozonide **8** (86% yield). From the second fraction (elution with benzene) was isolated the diketone **11** (2% yield).

Crystal data for solvent-participated product 9: $C_{22}H_{20}O_4$, colorless needles, M_r = 348.4, triclinic, a = 8.5201 (9) Å, b = 9.3045 (13) Å, c = 12.0403 (12) Å, α = 71.817 (9)°, β = 88.336 (8)°, γ = 83.044 (10)°, V = 900.1 Å^3, Z = 2, D_c = 1.285 g cm^{-3}, space group $P\bar{1}$ (No. 2) from successful structure solution and refinement, λ = 0.710693 Å, μ(Mo Kα) = 0.82 cm^{-1}, F(000) = 368, data crystal ~0.45 × 0.35 × 0.20 mm.

Structure Solution and Refinement. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer with use of ω–2θ scanning and graphite-monochromated Mo Kα X-radiation over the region $1.5 < \theta < 23°$. The 1897 observed intensities with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization, but not for absorption or crystal decay. The structure was solved by direct methods (SHELXS86[13]) and refined by use of full-matrix least-squares techniques (SHELX76[13]) with anisotropic temperature factors for the non-hydrogen atoms. All the hydrogen atoms were located on a difference Fourier map and included in the refinement process on idealized positions (C–H = 0.95 Å). The phenyl and methyl groups were treated as idealized rigid groups. At convergence, the conventional and weighted R factors ($w^{-1} = [\sigma^2(F) + 0.000386(F^2)]$) were 0.040 and 0.052, respectively. The final difference Fourier map contained no features greater than ±0.15 e Å^{-3}.

Acknowledgment. We thank Professor Karl Giesbaum, Universität Karlsruhe, for his helpful comments and Professor M. B. Hursthouse, Queen Mary-Westfield College, University of London, for access to X-ray data collection facilities through the SERC X-ray Service. M.N. thanks DAAD for providing financial support for a visit to Universität Karlsruhe (July–August 1987), and K.J.M. acknowledges financial support from the Carnegie Trust for the Universities of Scotland.

Registry No. *E*-**6**, 131618-93-4; *Z*-**6**, 131618-94-5; **7**, 5324-00-5; **8**, 131618-95-6; **9**, 131618-96-7; **10**, 131618-97-8; **11**, 53067-91-7; **12**, 131618-98-9.

Supplementary Material Available: Tables of atomic fractional coordinates, anisotropic vibration parameters, and torsion angles (3 pages); listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Stereoselective Intermolecular Radical Additions to Amide-Substituted Alkenes

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Abstract: The free-radical addition of carbon radicals to two alkenes substituted with chiral pyrrolidine amides has been studied. The two alkenes studied were both amides of 2,5-dimethylpyrrolidine, available as either the *R*,*R* or *S*,*S* enantiomer from D- or L-alanine. One alkene studied was the unsymmetrical monoamide derived from 4-oxo-2-pentenoic acid (**1**), while the other substrate examined was the diamide of fumaric acid, **2**. Hexyl, cyclohexyl, and *tert*-butyl radical addition to the amide of 4-oxo-2-pentenoic acid (**1**) gave approximately equal amounts of addition at the carbonyl and amide ends of the alkene. The two stereoisomeric products formed from addition at the carbonyl end were formed in nearly 1:1 product ratio while the products formed by addition at the amide end were formed in ratios as high as 40:1 (*tert*-butyl addition at 0 °C). Addition of cyclohexyl or *tert*-butyl radical to the fumaric diamide gives essentially only one stereoisomer, (diastereomeric ratio 50:1 and 80:1 at room temperature). This approach provides the highest reported stereoselectivity for radical addition to an acyclic chiral alkene. Furthermore, a rationale for the diastereoselectivity is presented that suggests that the amide selectivity is steric in origin and will be general.

Recent advances in the understanding of effects that influence chemo- and regioselectivities of radical reactions have dramatically increased the use of free-radical chemistry in organic synthesis.[1] The formation of C–C bonds by radical additions to alkenes is one of the most synthetically useful reactions that free radicals undergo and new radical chain sequences involving the formation of C–C bonds have greatly expanded the utility of this process.[2-7] Steric and polar effects (and to a lesser extent, radical stabilization) play important roles in addition reactions, and chemo- and regioselectivities of radical additions can be predicted and understood on the basis of these effects.[8-11] Unfortunately, the factors controlling stereochemistry in radical addition for acyclic radicals and for acyclic alkenes are poorly understood.[12] This limitation restricts the use of radicals in C–C bond forming reactions when compared to concerted reactions and reactions utilizing other

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(2) (a) Hart, D. J. *Science* **1984**, *223*, 883. (b) Stork, G.; Mah, R. *Tetrahedron Lett.* **1989**, *30*, 3609.
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(12) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969.

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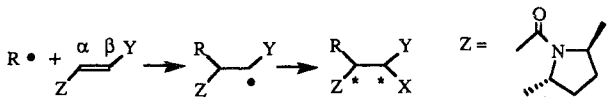
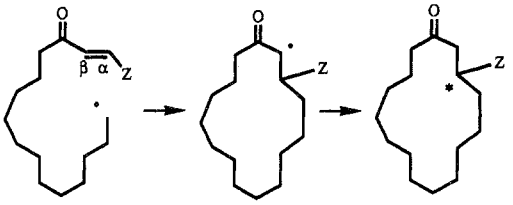
Scheme I



intermediates, particularly carbanions, because of the exquisite control of stereochemistry possible with these other approaches.[13-16] It seems clear that for radicals to take the last step to maturity as synthetic reactive intermediates, the factors governing the control of stereochemistry in radical reactions must be revealed.

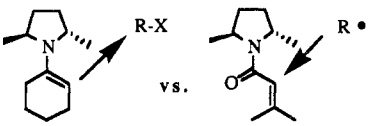
Additions of cyclic radicals to alkenes are fairly well understood.[12] The stereochemistry of addition of 2-substituted cyclopentyl radicals is controlled by steric factors, with the addition occurring preferentially on the least hindered face of the radical. Selectivities increase with the increasing steric demand of the substituent and more reactive alkenes tend to react with less selectivity.[17] There are also a few examples of the addition of radicals to chiral cyclic alkenes which suggest that steric effects lead to facial selectivity in the addition. Thus, addition to 4-substituted cyclic α,β-enones proceeds primarily to the face of the alkene opposite from the substituent, and this anti selectivity increases with increasing size of the radical.[18,19] The importance of steric effects in the radical reactions where selectivity has been observed suggests that this may also be a critical element in the design of acyclic olefins or acyclic radicals that are reasonable targets for study. Thus, acyclic alkenes with an auxiliary substituent such that one face of the alkene is sterically shielded and the other face is open for addition are reasonable candidates for showing selectivity in radical addition.

In the course of an investigation of free-radical macrocyclization,[20-23] we had occasion to consider control of stereochemistry of a stereogenic center formed in the cyclization.



The new stereocenter in this cyclization is formed at the alkene carbon undergoing radical attack, the α center, and the question naturally arose as to what Z groups would be suitable for exercising control of stereochemistry in this cyclization. Scheme I presents in a general fashion the control of stereochemistry at the α center of a radical addition. Two new stereocenters may be formed from the alkene if it is suitably substituted and the chain process is designed with this in mind.

In view of the success of amide control elements in carbanion and concerted reactions,[13-16] we chose to examine amide auxiliaries in radical macrocyclization[23,24] and we selected the amide derived from *trans*-2,5-dimethylpyrrolidine[24-27] as a Z controlling element.

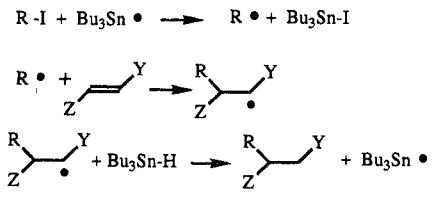


The pyrrolidine with C_2 symmetry was attractive for study because no chelation is required for this group to exert its effect, a feature that is desirable for neutral radical intermediates. The pyrrolidine is a useful auxiliary in alkylations of neutral enamines with alkyl halides, and the enamine alkylations have auxiliary steric relationships in the transition state similar to those we anticipated for radical addition reactions. This amide proved to be effective in controlling the stereochemistry of radical macrocyclization reactions,[23,24] and in a preliminary study we have also shown that this strategy is successful in intermolecular radical additions.[28,29] We report here on a more thorough study that shows the generality of this pyrrolidine amide auxiliary as an α center control element in free-radical additions. This group gives high selectivities in all of the examples studied and our results lead to the conclusion that acyclic stereocontrol in free-radical addition can be approached successfully.

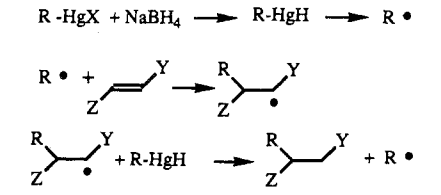
Results

Radical additions were carried out by either the "tin method"[30] or by the "mercury method".[31] Two alkenes, **1** and **2**, were used

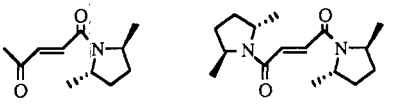
Tin Method



Mercury Method



as substrates in the addition of hexyl, cyclohexyl, and *tert*-butyl radicals. These alkenes were chosen for study since the fumaric diamide **2** is a symmetric alkene that should provide a simple product mixture while radical addition to the 4-oxopentenoic amide **1** not only raises issues of stereoselectivity but also of regioselectivity. The amides were prepared from 2,5-dimethylpyrrolidine



S-1 *S*-2

and the corresponding acids by either a mixed anhydride method in the case of **1** (acid and isobutyl chloroformate/*N*-methyl-

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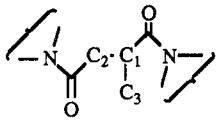
(31) Giese, B.; Meister, J. *Chem. Ber.* **1977**, *110*, 2588.

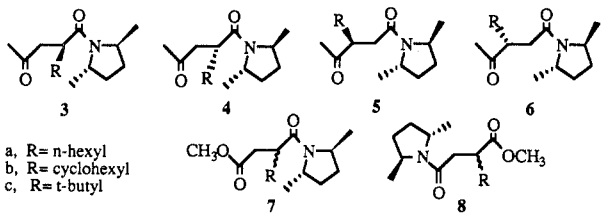
Table I. NMR Data for Addition Products **11b,c** and **12b,c**



	δ, ppm			J, Hz			δ, ppm		
	H-1	H-2	H-2′	J(1/2)	J(1/2′)	J(2/2′)	C-1	C-2	C-3
R-**11b** major isomer	3.13	2.43	2.60	6.8	5.6	16.0	44.96	34.93	42.07
S-**11c** major isomer (X-ray analysis)	3.24	2.53	2.60	5.1	6.8	16.3	47.72	33.73	34.40
R-**12b** minor isomer	2.89	2.35	2.68	3.1	10.5	14.3	45.77	35.93	40.49
S-**12c** minor isomer	3.00	2.29	2.83	2.2	11.0	13.8	48.18	35.44	33.31

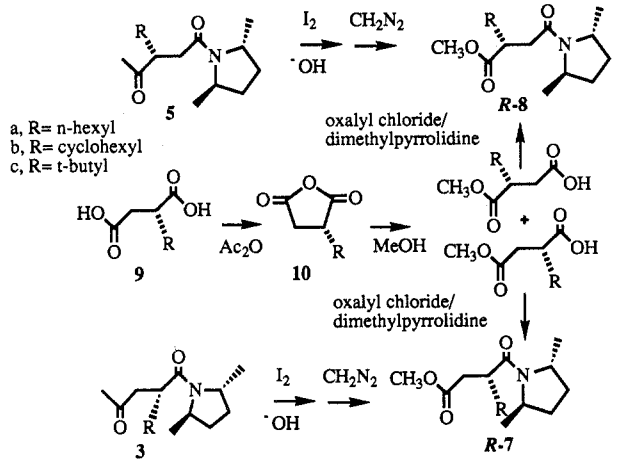
morpholine) or via the fumaric dichloride for formation of **2**. For **1**, the monoamide, either optically pure or racemic pyrrolidine was used, while for the diamide **2**, optically pure pyrrolidine was used in all studies. This was required for the diamide since diastereomers are formed if the racemic pyrrolidine is used in the synthesis. Dimethylpyrrolidine was prepared by the method of Schlessinger[32a] for both the 2*S*,5*S* or 2*R*,5*R* compound or by the Masamune method[32b] for the 2*R*,5*R* compound. Compounds identified with the index "*S*" indicates the use of (2*S*,5*S*)-dimethylpyrrolidine auxiliary, "*R*" indicates the use of (2*R*,5*R*)-dimethylpyrrolidine, and "*rac*" indicates the use of racemic dimethylpyrrolidine.[33]

Four products were formed as a result of the addition to **1** of hexyl, cyclohexyl, and *tert*-butyl radicals. Two of these products, **3** and **4**, are stereoisomers that result from addition of the radical



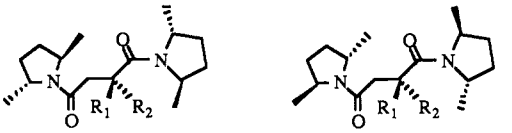
α to the amide substituent while two products, **5** and **6**, result from radical addition α to the ketone. The isomeric compounds **3**–**6** (**a**–**c**) can be separated by HPLC on silica gel with solvent 1:1 ethyl acetate/hexane. The stereochemistry of **3a** and **4a** was assigned by conversion to the 2-hexylsuccinic acid derivatives **7a** and independent synthesis of this compound from 2-hexylsuccinic acid.[34a] The isomeric **5a** and **6a** compounds could not be separated by silica gel chromatography. Proof of the stereochemistry of **3b**, **4b**, **5b**, and **6b** was achieved by conversion of these compounds to the corresponding succinic acid derivatives **7b** and **8b**, which were prepared independently from 2-cyclohexylsuccinic acid.[34b,35] These alkylsuccinic acids have been resolved by classical methods, and conversion of the optically pure acid to one stereoisomer each of **7** and **8** could be achieved by the sequence in Scheme II: conversion of the acid to the anhydride, reaction of the anhydride with methanol to give two isomeric half-esters, and conversion of the half-esters to pyrrolidine amide via reaction of the acid chloride with optically pure pyrrolidine. Conversion of the methyl ketones **3**–**6** to the succinates **7** and **8** was by an iodoform reaction[36] followed by conversion of the resultant acids to the methyl esters by reaction with diazomethane. Proof of stereochemistry of the α-amide products formed in the addition of *tert*-butyl radical

Scheme II

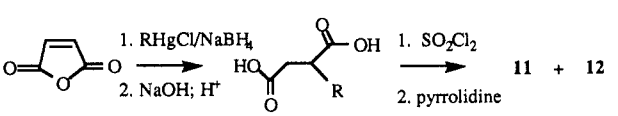


to **1** was obtained by the conversion of **3c** to the corresponding succinic diamide **11c** by an iodoform reaction followed by coupling of the resulting acid with the dimethylpyrrolidine by the mixed-anhydride method. The stereochemistry of **11c** has been established by a single-crystal X-ray analysis.[28]

Two stereoisomeric products result from the addition of cyclohexyl radical to fumaric diamide *R*-**2** and of *tert*-butyl radical to its enantiomer *S*-**2**. The main isomers *R*-**11b** and *S*-**11c** were



isolated by flash chromatography on silica gel with solvent 4:1 pentane/acetone in 55–70% yields. The major isomer *S*-**11c** was identified by single-crystal X-ray analysis.[28] The minor isomers *R*-**12b** and *S*-**12c** were synthesized by addition of either the *tert*-butyl or cyclohexyl radical to maleic anhydride, conversion of the racemic succinic anhydride to the 2-alkylsuccinic acid, and conversion of the diacid to the diastereomeric diamides via the diacid chloride. The diastereomers could be separated by flash chromatography or HPLC. In the case of the addition of cyclohexyl radical to *R*-**2**, the major product displayed chemical shifts and coupling constants in ^1H and ^{13}C NMR similar to the major product formed in the *tert*-butyl radical addition (Table I) and the stereochemistry of the isomers was assigned on the basis of this similarity. The enantiomers exhibit identical NMR spectra.



Product distribution at several temperatures was determined in the addition reactions by gas chromatography and by HPLC and these results are presented in Tables II and III. Product ratios

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(35) (*S*)-2-Cyclohexylsuccinic acid was prepared by hydrogenation of optically pure (*S*)-2-phenylsuccinic acid with a 5% Rh/Al_2O_3 catalyst.

(36) Morgan, K. J.; Bardwell, J.; Cullis, C. F. *J. Chem. Soc.* **1950**, 3190.

Table II. Product Ratios For Radical Additions to Amide **1**

				products			
alkene	radical	method	T, °C	**3a**[a]	**4a**	**5a**[b]	**6a**
rac-**1**	*n*-hexyl	tin	110	0.43	0.06	0.51	
rac-**1**	*n*-hexyl	tin	80	0.45	0.05	0.50	
rac-**1**	*n*-hexyl	mercury	0	0.48	0.03	0.49	
				3b[a]	**4b**	**5b**[c]	**6b**
rac-**1**	cyclohexyl	tin	110	0.42	0.04	0.30	0.24
rac-**1**	cyclohexyl	tin	80	0.43	0.037	0.30	0.23
R-**1**	cyclohexyl	mercury	0	0.48	0.02	0.28	0.23
				3c[a]	**4c**	**5c**[b]	**6c**
rac-**1**	*tert*-butyl	tin	80	0.55	0.04	0.41	
R-**1**	*tert*-butyl	mercury	0	0.49	0.01	0.50	

[a] Triplicate analyses of duplicate runs. GC on 0.25-i.d. 30-m SPB-1 capillary column. [b] Sum of isomers **5** and **6** formed. Separated incompletely by GC on SP-2230 30-m 0.25-i.d. ratio of **5** to **6** was close to 1:1. [c] Triplicate analyses of duplicate runs. Analysis on normal-phase HPLC, 5-μm silica, 4:1 ethyl acetate/hexane.

Table III. Product Ratios For Radical Additions to Diamide **2**

				products	
alkene	radical	method	T, °C	*R*-**11b**[a]	*R*-**12b**
R-**2**	cyclohexyl	mercury	110	0.93	0.07
R-**2**	cyclohexyl	mercury	65	0.94	0.06
R-**2**	cyclohexyl	mercury	20	0.975	0.025
R-**2**	cyclohexyl	mercury	0	0.98	0.02
				S-**11c**[a]	*S*-**12c**
S-**2**	*tert*-butyl	mercury	110	0.94	0.06
S-**2**	*tert*-butyl	mercury	65	0.96	0.04
S-**2**	*tert*-butyl	mercury	20	0.98	0.02
S-**2**	*tert*-butyl	mercury	0	0.988	0.012

[a] Triplicate analyses of duplicate runs, GC on 25-m OV1 capillary column.

were always determined from the crude reaction mixture. Product isolation by chromatography generally produced the addition products in yields of from 40 to 70%.

Discussion

There are only a few examples of intermolecular radical addition reactions with acyclic alkenes in which attack is more selective than 3:1. No examples of stereoselectivity with terminal alkenes have been reported, and it is therefore likely that the α-carbon must be substituted with the chiral auxiliary for observation of significant stereoselectivity. We have examined several acyclic alkenes with ester auxiliaries[37] and have found little selectivity in radical additions. Several fumarate and maleate systems have also been examined[38] and in only one example, a monomaleate phenylmenthyl ester, was significant stereoselectivity observed (60% diastereomeric excess). The experiments reported here show that the control of stereochemistry at the α olefin center in radical addition reactions to acyclic alkenes is possible with C_2 symmetric amide auxiliaries. The success of this auxiliary can be understood based on a consideration of the conformation of the amide-substituted alkene.

Carbon radicals are nucleophilic, and it has been suggested that transition states for addition of nucleophilic radicals to electron-deficient olefins such as **1** and **2** are reactant-like.[1a,8] For addition of carbon radicals to inactivated olefins, calculations suggest that the C(radical)–C(α) distance is in excess of 2.2 Å in the transition state and the angle of approach of the radical is close to the tetrahedral value.[39] Because of the early transition state, factors that influence the ground-state alkene conformation

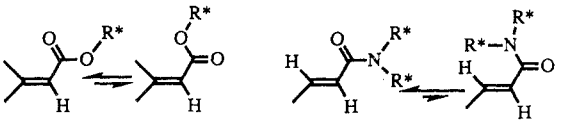

Figure 1.

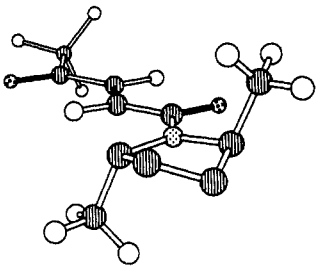

Figure 2. View of low-energy MM2 conformation for alkene **1**. (Pyrrolidine ring hydrogens are omitted for clarity.)

would also be expected to influence the transition state in the addition reaction.

The important conformations to be considered for ester and amide auxiliaries are presented in Figure 1. For esters, there is little control of the orientation of the C(α)–C(O) bond; the carbonyl oxygen and the ether-like oxygen are of comparable size.[40] The orientation of a chiral auxiliary substituted on an ester is therefore not fixed with respect to C(α) because of this conformational mobility. Experimental evidence suggests[41] that the conformation of amides is much less mobile than that of esters, allylic strain favoring the *Z* conformation as shown in Figure 1. Chiral groups substituted on the amide auxiliary are fixed relative to C(α) because of the lack of conformational mobility, and the promise for control of stereochemistry with chiral amides is therefore much more than that expected for ester auxiliaries. Control of the conformational orientation about the C(O)–N bond must also be considered in the analysis of amide auxiliary groups. In practice, the conformational problem of the C(O)–N bond has been solved by using amide auxiliaries with C_2 symmetry since, with such amides, both possible conformations present the same stereochemical environment to the C(α) center. In fact, amide auxiliaries with C_2 symmetry have been used extensively in cycloaddition and carbanion chemistry and excellent selectivity has been observed in many of these examples.[25-27,42-44]

A molecular mechanics analysis of the alkene **1** gives a low-energy arrangement that is in accord with the conformational analysis presented above. This planar conformation, shown in Figure 2, has the *Z*-amide conformation.[45] Approach of the radical to the amide end of the alkene on a nucleophilic trajectory suggests a facial bias in the addition, as can be seen in the figure. The proximate methyl substituent on the pyrrolidine protects the bottom face from addition while the other methyl substituent is remote from the trajectory of approach of the radical to the top face of the alkene. While the prediction of selectivity presented here is based on alkene ground-state arguments, the early transition state implied in these radical additions makes this assumption seem reasonable.

For each of the addition reactions reported here, significant stereoselectivity in the formation of the addition products is observed. The stereochemistry of the products was established rigorously in four of the reactions studied (in one case by a sin-

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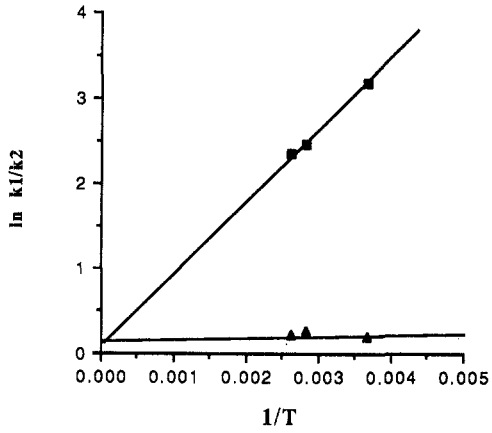

Figure 3. Arrhenius plot of selectivity for addition of cyclohexyl radical to **1**. ■, ln [**3b**]/[**4b**]; ▲, ln [**5b**]/[**6b**].

gle-crystal X-ray analysis), and in another example, comparison of NMR data allowed assignment of the stereochemistry of the addition products. In every case the stereochemistry of the major product can be understood by the model shown in Figure 1 and the selectivities observed range from 7:1 for the addition of hexyl radical to **1** at 110 °C to >40:1 for the addition of *tert*-butyl radical to either **1** or **2** at 0 °C. These selectivities are clearly superior to any previous examples of radical addition to acyclic alkenes and are in the range of selectivities that are synthetically useful. The results suggest further that "acyclic stereocontrol" is now a legitimate avenue of inquiry in free-radical chemistry and they provide a rational framework for approaching this problem.

The selectivity observed is temperature dependent, and the data can be treated by an Arrhenius approach to provide information about the competing transition states. In a competition experiment, a plot of ln k of the competing processes vs $1/T$ gives a line with slope related to $\Delta\Delta H^{\ddagger}$ and intercept related to $\Delta\Delta S^{\ddagger}$, according to eq 1. When the data presented in Tables II and III

$$\ln \frac{k_1}{k_2} = \frac{\Delta H_2^{\ddagger} - \Delta H_1^{\ddagger}}{RT} - \frac{\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}}{R} \qquad (1)$$

are treated in this way, $\Delta\Delta H^{\ddagger}$'s are obtained in the range of 1.5–3 kcal/mol along with $\Delta\Delta S^{\ddagger}$'s that are near 0 eu. This analysis suggests that the selectivity observed is enthalpy derived, and this is consistent with the qualitative analysis of the selectivity that is based on steric shielding of one face of the alkene by the pyrrolidine methyl. The transition-state enthalpy effects are greatest for tertiary *tert*-butyl radicals (~3 kcal/mol), smaller for secondary cyclohexyl radicals (1.7–2.7 kcal/mol), and smallest for primary hexyl radicals (~1.4 kcal/mol) in accord with the steric origins of the selectivity. The Arrhenius plot for the addition of cyclohexyl radical to the unsymmetrical olefin **1** presented in Figure 3 illustrates the fact that the selectivity observed is enthalpy derived. Note that the temperature range for the experiment is over 100 °C and that there is a good correlation of ln k vs $1/T$. Furthermore, the selectivity is greatest for the addition α to the amide center while addition α to the ketone group of the alkene **1** leads to little selectivity, although the same face of the alkene is favored in the addition at both the amide and the keto end. This differential selectivity at opposite ends of the alkene supports the arguments for selectivity based on conformation of the pyrrolidine amide auxiliary. From Figure 3, $\Delta\Delta H^{\ddagger}_{\mathbf{4b-3b}} = 1.7$ kcal/mol and $\Delta\Delta H^{\ddagger}_{\mathbf{6b-5b}} = 0$ kcal/mol. Similar Arrhenius plots of ln [**3b**]/[**5b**] and ln [**3b**]/[**6b**] give $\Delta\Delta H^{\ddagger}_{\mathbf{5b-3b}} = \Delta\Delta H^{\ddagger}_{\mathbf{6b-3b}} = 0.3$ kcal/mol.

Two general requirements for acyclic stereocontrol at the α-alkene center in radical addition are also suggested by the pyrrolidine amide precedent. These requirements would appear to be as follows: (1) control of the conformation of the α-2-, 2–3-, and 3,4-bonds (Figure 4) such that the orientation is anti–syn–anti for these bonds, (2) introduction of a chiral center at C-4 with substituents that have differing steric demand. In the pyrrolidine amide systems reported here, the α-2- and 2,3-bond conformations are controlled by amide stereoelectronic effects while the 3,4-conformation is fixed by the cyclic pyrrolidine structure and the C_2 symmetry element. It seems likely that other successful strategies can be developed to meet these same general structural requirements.

One problem that must be addressed before the radical method becomes of general synthetic utility is the ease of removal of the auxiliary after radical addition has been carried out. The dimethylpyrrolidine amides used in this study are hydrolyzed with difficulty unless the molecule is substituted such that there is intramolecular nucleophilic assistance in the hydrolysis.[24] This problem has been solved by the use of C_2 symmetric pyrrolidines that are substituted at positions 2 and 5 with protected hydroxymethyl groups that are ultimately used as internal nucleophiles in the removal of the pyrrolidine auxiliaries.[26,27,42–44] While these auxiliaries would appear to be ideal for use in free-radical reactions, it should be pointed out that the synthesis of the dimethylpyrrolidine and substituted pyrrolidines is tedious and improved procedures for the preparation of amine auxiliaries that fit the general requirements for selectivity and easy removal would be welcome.

Experimental Section

Tetrahydrofuran was freshly distilled from sodium benzophenone. Dichloromethane was distilled from calcium hydride and stored over molecular sieves. Benzene was distilled from sodium and stored over molecular sieves. Gas chromatography was done on a Hewlett-Packard 5890A gas chromatograph with a flame ionization detector coupled to a Hewlett-Packard 3393A integrator (conditions: 30-m SPB-1 column, 11 psi, 1 min at 100 °C to 280 °C at 15 °C/min) and on a Carlo-Erba 6000 with flame ionization detector coupled to a Shimadzu C-R4A (conditions: 25-m OV-1 column, 1 min at 120 °C to 220 °C at 10 °C/min). ^{1}H and ^{13}C NMR were run on either a Bruker WM 300, a Varian XL-300, or a Varian VXR-400 spectrometer (TMS as internal standard). Mass spectra were acquired on either a VG 70-250 or an HP-5990 spectrometer. Flash chromatography: Utekon silica gel, C 560 35–70 μm. Analytical HPLC was performed by using a Waters Model 590 pump with a Microsorb Si 80-125-C5 column and a refractive index detector. Preparative HPLC was done by using an Isco Model 2350 pump with a Dynamax 60A Si 83-121-C column and a refractive index detector or a Waters Delta Prep 3000. Melting points are uncorrected.

Synthesis of Alkenes. 4-Oxo-2-pentenoic Acid. To a stirred solution of 23.2 g (200 mmol) of freshly distilled levulinic acid in 80 mL of concentrated hydrochloric acid at −15 °C was added 33.6 g (210 mmol) of bromine over 2 h. After addition was complete, the solution was stirred for 3 h at room temperature. The reaction mixture was poured over 200 mL of crushed ice and water. The solution was cooled to 0 °C for 10 min and was then filtered. The filtrate was extracted thoroughly with ethyl ether. The organic solution was dried over magnesium sulfate and evaporated at reduced pressure to dryness. Without purification, the bromolevulinic acid (32.6 g, 167 mmol) was dissolved in 60 mL of glacial acetic acid [freshly distilled from acetic anhydride and 4-(dimethylamino)pyridine]. To this solution was added 33 g of sodium acetate (dried by melting under high vacuum). The mixture was stirred at room temperature until it became solid and was then warmed to 100 °C for 45 min. The hot mixture was poured over 200 mL of crushed ice and water. This aqueous solution was acidified to pH 2 while being shaken with ethyl ether. The acidified solution was washed three times with ethyl ether. All ethereal solutions were combined, dried over magnesium sulfate, and evaporated at reduced pressure. The crude residue was dissolved in chloroform, heated with activated carbon for 5 min, and filtered. The chloroform was evaporated at reduced pressure and the residue was allowed to stand under high vacuum with a sodium hydroxide trap for 24 h. The product was 18.5 g (81% yield) of a light brown solid. The product was recrystallized from chloroform twice to yield a white flaky solid: mp 120–121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.35 (s, (br), 1 H), 7.09 (d, J = 16.1 Hz, 1 H), 6.64 (d, J = 16.1 Hz, 1 H), 2.37 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.4, 170.7, 141.7, 130.4, 28.3.

[1(*E*)-2α,5β1-1-(2,4-Dioxo-3-pentenyl)-2,5-dimethylpyrrolidine (1). 4-Oxo-2-pentenoic acid (0.38 g, 3.3 mmol) was combined with 0.40 g (4.0 mmol) of *N*-methylmorpholine in 40 mL of dry THF. To this was added dropwise at −10 °C, with stirring, 0.43 mL (3.3 mmol) of isobutyl chloroformate. After being stirred for 0.5 h at −10 °C, the mixture was quickly filtered under argon into another reaction flask. *Trans*-(*rac*)-2,5-dimethylpyrrolidine hydrochloride (0.30 g, 2.2 mmol) was freed from HCl by dissolving in 8 mL of CH_2Cl_2 and washing with 4 mL of 5 N NaOH. The CH_2Cl_2 solution was dried over potassium carbonate and

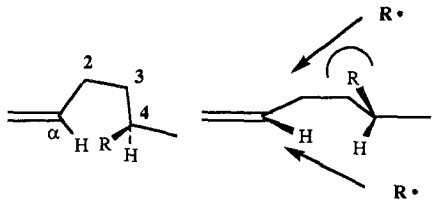

Figure 4. Elements required for α center stereoselection.

was added dropwise to the stirred solution of the mixed anhydride at −10 °C over 15 min. The reaction mixture was stirred for 30 min at −10 °C and then for 2 h at room temperature. The solution was evaporated to dryness under reduced pressure and purified by elution through silica gel with 1:1 ethyl acetate/hexanes, yielding 0.36 g (84%) of the amide **1** as a clear oil: TLC R_f = 0.14 (1:1 ethyl acetate/hexane); GC t_r = 6.21 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, J = 15.25 Hz, 1 H), 7.02 (d, J = 15.25 Hz, 1 H), 4.30 (m, 1 H), 4.19 (m, 1 H), 2.32 (s, 3 H), 2.14 (m, 2 H), 1.60 (m, 2 H), 1.17 (d, J = 6.6 Hz, 3 H), 1.15 (d, J = 6.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 197.7, 162.4, 136.4, 132.5, 53.6, 53.5, 30.5, 29.3, 28.7, 22.7, 18.8; MS (EI) m/z (relative intensity) 195 (3.7), 180 (20.0), 98 (30.3), 97 (22.3), 84 (100.0); exact mass for $C_{11}H_{17}NO_2$ calcd m/z 195.1259, measd (EIMS) m/z 195.1258 (−0.7 ppm).

Fumaric Bis[(2*S*,5*S*)-dimethylpyrrolidinide] (*S*-2). To a cooled (0 °C) and stirred solution of (2*S*,5*S*)-dimethylpyrrolidine (0.63 g, 6.4 mmol) and tetramethylguanidine (0.74 g, 6.4 mmol) in 40 mL of dry dichloromethane under argon was added dropwise fumaric dichloride (0.53 g, 3.5 mmol) dissolved in 20 mL of dichloromethane over a period of 1 h. After the addition was completed, the mixture was stirred 30 min at 0 °C and another 2 h at room temperature. The reaction mixture was washed twice with dilute hydrochloric acid, dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography (pentane/acetone 4:1) yielded diamide *S*-**2** (0.57 g, 64%) as a colorless solid. Recrystallization from ether/pentane afforded colorless needles: mp 126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (s, 2 H, HC=CH), 4.38–4.23 (m, 4 H, H_{pyr}-2, H_{pyr}-5), 2.31–2.06 (m, 4 H, H_{pyr}-3′, H_{pyr}-4′), 1.69–1.55 (m, 4 H, H_{pyr}-3, H_{pyr}-4) 1.20, 1.19 (2 d, J = 6.4 Hz, 12 H, 4 CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 162.88, 131.94, 53.93, 53.30, 30.48, 28.69, 22.61, 18.73; MS (EI) m/z (relative intensity) 278 (12, M^+), 263 (21), 180 (100), 152 (11), 124 (51), 98 (95), 84 (98), 83 (34), 55 (55), 41 (47). Anal. Calcd for $C_{16}H_{26}N_2O_2$ (278.40): C, 69.03; H, 9.41; N, 10.06. Found: C, 68.89; H, 9.32; N, 9.93. The same procedure was used in the synthesis of fumaric bis[(2*S*,5*S*)-dimethylpyrrolidinide] (*R*-**2**).

Radical Addition via the Tin Method. The olefin was combined with 4.0 equiv of alkyl iodide (hexyl, cyclohexyl, or *tert*-butyl) in dry benzene or toluene (30 mM in olefin) and the solution was degassed with argon for 30 min. The mixture was equilibrated to the reaction temperature and tributyltin hydride (4.4 equiv) and azobis(isobutyronitrile) (0.4 equiv) were added. The solution was stirred at the reaction temperature for 3 h under argon. The solvent was removed under reduced pressure and the residue was dissolved in ethyl ether. The ether solution was stirred for 24 h with an equal volume of 10% aqueous KF. Tributyltin fluoride was removed by filtration, the ether layer was dried over magnesium sulfate and evaporated to dryness, and the products were separated by chromatography.

Radical Addition via the Mercury Method. The olefin and 4.0–50 equiv of alkyl mercuric bromide or chloride (hexyl, cyclohexyl, or *tert*-butyl) were dissolved in dry CH_2Cl_2 (35–100 mmol in olefin). The solution was purged with argon for 15 min and equilibrated to the reaction temperature. Sodium borohydride (6.0–150 equiv) in a minimum volume of water or a pH 7 buffer solution (solution mixed and added immediately) was added to the stirred solution. The mixture was stirred at the reaction temperature for 30 min under argon. Mercury and water were removed from the reaction mixture by filtration through a short plug of magnesium sulfate; the dichloromethane layer was removed, washed with saturated aqueous NaCl, dried over magnesium sulfate, and evaporated to dryness. The products were separated by chromatography.

Product Isolation and Structural Information from Radical Additions. Separation and Analysis of Hexyl Radical Adducts 3a, 4a, and 5a,6a. Racemic **1** (0.585 g, 3.00 mmol) was treated with *n*-hexyl iodide (2.55 g, 12.0 mmol), tributyltin hydride (3.80 g, 13.2 mmol), and AIBN (0.20 g, 1.2 mmol) according to the procedure described above. Separation of reaction products was accomplished by preparative HPLC with 1:1 ethyl acetate/hexane at a flow rate of 12.0 mL/min. Four major peaks were detected by refractive index at 18, 27, 30, and 35 min. Injection of the collected fractions on GC and GC/EIMS allowed correlation of HPLC fractions with MS assignments. The fraction collected at 35 min was shown to be starting olefin by GC, ^{1}H NMR, ^{13}C NMR, and GC/MS. The combined yield of radical adducts was 362 mg (43%).

3a (major α-amide isomer): HPLC t_r = 27 min; GC t_r = 8.89 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.15 (m, 1 H), 4.01 (m, 1 H), 2.95 (m, 2 H), 2.42 (m, 1 H), 2.11 (s, 3 H), 2.18–2.04 (m, 2 H), 1.57 (m, 1 H), 1.47 (m, 1 H), 1.40 (m, 2 H), 1.32–1.14 (m, 8 H), 1.26 (d, J = 6.4 Hz, 3 H), 1.08 (d, J = 6.3 Hz, 3 H), 0.83 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 208.4, 173.5, 53.4, 52.7, 44.8, 38.7, 33.2, 31.6, 30.8, 30.7, 30.6, 29.3, 28.8, 26.9, 22.5, 21.5, 18.9, 14.0; MS (EI) m/z (relative intensity) 281 (7), 238 (9), 197 (29), 183 (25), 154 (100), 126 (22), 84 (67); exact mass for $C_{17}H_{31}NO_2$ calcd m/z 281.2355, measd (EIMS) m/z 281.2353 (−0.6 ppm).

4a (minor α-amide isomer): HPLC t_r = 30 min; GC t_r = 9.01 min; MS (EI) m/z (relative intensity) 281 (5), 238 (9), 197 (22), 183 (17), 154 (100), 126 (13), 84 (49).

Mixture of **5a** and **6a** (α-keto isomers): HPLC t_r = 18 min; GC t_r = 9.49 min; GC (SP-2330 column, 15 psi, 230 °C) t_r = 8.09 and 8.53 min (44% and 56%, respectively); ^{1}H NMR ($CDCl_3$) δ 2.24, 2.20 (s, 3 H, CH_3CO), 1.20, 1.12, 1.10, 1.06 (d, J = 6 Hz, 6 H, CH_3CHN); ^{13}C NMR ($CDCl_3$) δ 212.6, 169.8, 53.6, 53.3, 53.2, 53.0, 48.3, 47.7, 36.7, 36.4, 31.8, 31.60, 31.56, 30.83, 30.76, 30.4, 30.3, 29.4, 29.3, 29.0, 27.2, 22.5, 21.6, 21.2, 19.1, 19.0, 14.0; MS (EI) m/z (relative intensity) 281 (8), 238 (75), 197 (18), 183 (31), 141 (98), 126 (48) and 84 (100). Anal. Calcd for $C_{17}H_{31}NO_2$ (**5a** and **6a**): C, 72.55; H, 11.10. Found: C, 72.46; H, 11.14.

Separation and Analysis of 3b, 4b, and 5b and 6b. Optically pure *R*-**1** (0.36 g, 1.8 mmol) was treated with cyclohexyl iodide (1.6 g, 7.4 mmol), tributyltin hydride (2.4 g, 8.1 mmol), and AIBN (0.12 g, 0.74 mmol) according to the procedure described above. Separation and isolation of the products was done via preparative HPLC with 1:1 ethyl acetate/hexane at a flow rate of 10 mL/min. Five major peaks were detected by refractive index at 20, 23, 29, 32 and 36 min. Injection of the collected fractions on GC (11 psi, 1 min at 100 °C to 230 °C at 10 °C/min) and GC/EIMS allowed correlation with MS assignments. The fraction at 36 min corresponds to the starting olefin. The combined yield of radical adducts was 183 mg (36%).

3b (major α-amide isomer): HPLC t_r = 29 min; GC t_r = 11.66 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.17 (m, 1 H), 4.07 (m, 1 H), 3.01 (dd, 1 H, J = 17.1, 8.5 Hz), 2.89 (ddd, 1 H, J = 8.8, 5.3, 3.8 Hz), 2.43 (dd, 1 H, J = 17.2, 4.0), 2.14 (s, 3 H), 2.10 (m, 2 H), 1.76–1.54 (m, 6 H), 1.52–1.40 (m, 2 H), 1.27 (d, 3 H, J = 4.1 Hz), 1.11 (d, 3 H, J = 4.0 Hz), 1.30–0.86 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 208.9, 173.3, 54.1, 53.2, 44.4, 42.8, 41.8, 31.6, 31.2, 31.0, 30.1, 29.3, 27.1, 27.0, 26.7, 21.7, 19.5; $[\alpha]^{23}_D$ = +3.65° (c = 0.904, $CHCl_3$); MS (CI, CH_4/NH_3) MH^+ 280; MS (EI) m/z (relative intensity) 197 (9), 181 (5), 154 (36), 98 (9), 84 (38), 70 (12), 55 (30), 43 (100). Anal. Calcd for $C_{17}H_{29}NO_2$: C, 73.07; H, 10.46; N, 5.01. Found: C, 72.92; H, 10.43; N, 4.95.

4b (minor α-amide isomer): HPLC t_r = 32 min; GC t_r = 11.79 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.30 (m, 1 H), 4.17 (m, 1 H), 2.80 (dd, 1 H), 2.73 (ddd, 1 H), 2.58 (dd, 1 H), 2.12 (s, 3 H), 1.20 (d, 3 H), 1.10 (d, 3 H); MS (CI, CH_4/NH_3) MH^+ = 280; MS (EI) m/z (relative intensity) 197 (5), 181 (2), 154 (48), 98 (7), 84 (31), 70 (11), 55 (28), 43 (100).

5b (major α-keto isomer): HPLC t_r = 20 min; GC t_r = 12.53 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.11 (quintet, 1 H), 3.96 (quintet, 1 H), 3.06 (ddd, 1 H, J = 10.3, 6.3, 3.9 Hz), 2.78 (dd, 1 H, J = 16.1, 10.7 Hz), 2.32 (dd, 1 H, J = 16.1, 3.7 Hz), 2.26 (s, 3 H), 2.16–2.00 (m, 2 H), 1.80–1.42 (m, 8 H), 1.22 (d, 3 H, J = 6.1 Hz), 1.11 (d, 3 H, J = 6.4 Hz), 1.32–0.86 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 212.8, 170.1, 53.6, 53.0, 52.9, 39.6, 34.3, 31.8, 31.4, 30.8, 30.1, 29.0, 26.5, 26.4, 26.2, 21.1, 19.1; $[\alpha]^{23}_D$ = +49.8° (c = 0.502, $CHCl_3$); MS (EI) m/z (relative intensity) 279 (6), 236 (53), 222 (1), 197 (31), 181 (14), 154 (49), 141 (100), 126 (55), 84 (56) (mixture of **5b** and **6b**).

6b (minor α-keto isomer): HPLC t_r = 23 min; GC t_r = 12.52 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.10 (m, 1 H), 4.06 (m, 1 H), 3.07 (ddd, 1 H, J = 15.3, 5.9, 3.3 Hz), 2.67 (dd, 1 H, J = 15.3, 11.1 Hz), 2.27 (dd, 1 H, J = 15.3, 3.3 Hz), 2.21 (s, 3 H), 2.20–1.96 (m, 2 H), 1.80–1.41 (m, 8 H), 1.14 (d, 3 H, J = 6.6 Hz), 1.02 (d, 3 H, J = 6.4 Hz), 1.38–0.80 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 212.8, 170.3, 53.9, 53.3, 53.2, 39.7, 33.8, 31.9, 31.4, 30.7, 30.0, 29.0, 26.5, 26.4, 26.2, 21.6, 19.0.

Separation and Analysis of 3c, 4c, 5c, and 6c. Optically pure *R*-**1** (0.35 g, 1.8 mmol) was treated with *tert*-butyl mercuric chloride (2.1 g, 7.2 mmol) and sodium borohydride (0.41 g, 1.1 mmol) according to the procedure described above. Separation of reaction products was done via preparative HPLC with 1:1 ethyl acetate/hexane at a flow rate of 10 mL/min. Four major peaks were detected by refractive index at 17, 19, 21, and 23 min. Injection of the collected fractions are GC (11 psi, 1 min at 100 °C to 230 °C at 10 °C/min) and GC/EIMS allowed correlation with MS assignments. The yield of the major adduct, **3c**, was 128 mg (28%).

3c (major α-amide isomer): HPLC t_r = 21 min; GC t_r = 8.14 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.17 (m, 2 H), 3.06 (dd, 1 H, J = 17.2, 8.6 Hz), 2.86 (dd, 1 H, J = 8.6, 3.9 Hz), 2.47 (dd, 1 H, J = 17.2, 4.0

Hz), 2.12 (s, 3 H), 2.06–2.14 (m, 2 H), 1.55 (m, 1 H), 1.46 (m, 1 H), 1.24 (d, 3 H, J = 6.6 Hz), 1.13 (d, 3 H, J = 6.2 Hz), 0.93 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 208.7, 172.0, 54.4, 53.1, 46.8, 42.4, 34.0, 30.8, 30.7, 28.8, 27.9, 21.0, 19.2; $[\alpha]^{23}_D$ = +6.37° (c = 1.93, $CHCl_3$); MS (EI) m/z (relative intensity) 253 (3), 197 (13), 154 (78), 126 (18), 109 (21), 98 (34), 84 (100). Anal. Calcd for $C_{15}H_{27}NO_2$: C, 71.10; H, 10.74; N, 5.53. Found: C, 70.88; H, 10.69; N, 5.48.

4c (minor α-amide): HPLC t_r = 23 min; GC t_r = 8.14 min; MS (EI) m/z (relative intensity) 253 (5), 197 (22), 154 (100), 126 (18), 109 (23), 98 (16), 84 (47).

5c (major α-keto isomer): HPLC t_r = 17 min; GC t_r = 8.63 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.09 (m, 1 H), 3.95 (m, 1 H), 3.04 (dd, 1 H, J = 11.5, 2.7 Hz), 2.87 (dd, 1 H, J = 16.0, 11.6 Hz), 2.33 (dd, 1 H, J = 15.9, 2.7 Hz), 2.32 (s, 3 H), 2.20–1.98 (m, 2 H), 1.56 (m, 1 H), 1.47 (m, 1 H), 1.21 (d, 3 H, J = 6.4 Hz), 1.11 (d, 3 H, J = 6.4 Hz), 0.94 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 213.3, 170.3, 56.0, 53.6, 53.0, 34.6, 34.0, 32.6, 30.9, 29.0, 28.2, 21.1, 19.2; MS (EI) m/z (relative intensity) 253 (10), 210 (93), 196 (87), 154 (99), 139 (36), 126 (32), 98 (100), 84 (64) (mixture of **5c** and **6c**).

6c (minor α-keto isomer): HPLC t_r = 19 min; GC t_r = 8.63 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (m, 1 H), 4.02 (m, 1 H), 3.06 (dd, 1 H, J = 11.7, 2.9 Hz), 2.76 (dd, 1 H, J = 15.1, 11.7), 2.31 (dd, 1 H, J = 15.3, 3.0 Hz), 2.27 (s, 3 H), 2.22–1.96 (m, 2 H), 1.54 (m, 1 H), 1.46 (m, 1 H), 1.13 (d, 3 H, J = 6.4 Hz), 1.04 (d, 3 H, J = 6.3 Hz), 0.94 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 213.4, 170.4, 56.8, 53.4, 53.2, 34.2, 34.1, 32.8, 30.7, 29.0, 28.1, 21.6, 19.0.

Separation and Analysis of *R*-11b from Radical Addition. Fumaric diamide *R*-**2** (0.24 g, 0.86 mmol) was treated with cyclohexylmercuric chloride (13.7 g, 43.0 mmol) and sodium borohydride (6.5 g, 172 mmol) according to the procedure described above. The major product *R*-**11b** (0.22 g, 70%) was separated by flash chromatography (pentane/acetone 4:1) as a colorless oil: GC t_r = 20.78 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (m, 4 H, H_{pyr}-2, H_{pyr}-5), 3.13 (ddd, J = 6.8, 6.8, 5.6 Hz, 1 H, HC[c-C_6H_{11}]), 2.60 (dd, J = 16.0, 5.6 Hz, 1 H, H'HC), 2.43 (dd, J = 16.0, 6.8 Hz, 1 H, H'HC), 2.17–2.03 (m, 4 H, H_{pyr}-3′, H_{pyr}-4′), 1.61–1.45 (m, 4 H, H_{pyr}-3, H_{pyr}-4), 1.70–1.62, 1.26–0.85 (2 m, 11 H, c-C_6H_{11}), 1.32, 1.20, 1.13, 1.10 (4 d, J = 6.4 Hz, 12 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.79, 170.38, 53.91, 53.66, 52.95, 52.83, 44.96, 42.07, 34.93, 30.99, 30.84, 30.82, 30.0, 28.99, 28.92, 26.62, 26.55, 26.34, 21.84, 21.52, 19.10, 18.81; MS (El) m/z (relative intensity) 362 (0.4, M^+), 264 (24), 222 (46), 221 (13), 182 (21), 180 (8), 154 (26), 100 (10), 98 (100), 84 (18), 83 (15), 70 (12), 55 (39), 42 (10), 41 (10); HRMS (EI) calcd for $C_{22}H_{38}N_2O_2$ 362.2933, found 362.2954.

Separation and Analysis of *S*-11c from Radical Addition. Fumaric diamide *S*-**2** (0.24 g, 0.86 mmol) was treated with *tert*-butylmercuric chloride (5.0 g, 17.2 mmol) and sodium borohydride (2.6 g, 68.8 mmol) according to the procedure described above. The major product *S*-**11c** (0.15 g, 53%) was separated by flash chromatography (pentane/acetone 4:1) as colorless crystals: mp 90–92 °C (hexane); GC t_r = 12.64 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.29–4.07 (m, 4 H, H_{pyr}-2, H_{pyr}-5), 3.24 (dd, J = 6.8, 5.1 Hz, 1 H, $HC(CH_3)_3$), 2.60 (dd, J = 16.3, 6.8 Hz, 1 H, H'HC), 2.53 (dd, J = 16.3, 5.1 Hz, 1 H, H'HC), 2.22–2.03 (m, 4 H, H_{pyr}-3′, H_{pyr}-4′), 1.62–1.48 (m, 4 H, H_{pyr}-3, H_{pyr}-4), 1.34, 1.21, 1.16, 1.13 (4 d, J = 6.4 Hz, 12 H, 4 CH_3), 0.98 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 173.13, 170.75, 54.63, 53.84, 53.00, 52.85, 47.72, 34.46, 33.73, 30.84, 29.01, 28.83, 28.09, 21.74, 21.66, 19.25, 18.80; MS (EI) m/z (relative intensity) 336 (3, M^+), 308 (6), 238 (100), 222 (9), 210 (5), 182 (10), 180 (8), 156 (14), 154 (15), 126 (8), 98 (91), 83 (18), 70 (9), 55 (21), 41 (12); HRMS (EI) calcd for $C_{20}H_{36}N_2O_2$ 336.2777, found 336.2783; a sample for X-ray analysis[28] was recrystallized from hexane.

Independent Syntheses of Products. Iodoform Reaction and Esterification of 3a and 3b. The major α-amide adduct, **3a** or **3b**, (43 mg, 0.15 mmol) was dissolved in 0.75 mL of 1,4-dioxane and 0.75 mL of 5 N NaOH. To this was added dropwise a mixture of 0.5 g of I_2 and 1 g of KI dissolved in 5 mL of water. The iodine solution was added until a yellow color persisted. The solution was heated gently, turning the solution clear, and more iodine was added until the yellow color persisted again. NaOH (5 N) was added until the solution was clear, and the mixture was filtered through a plug of Celite to remove the iodoform. The solution was acidified with 5 N HCl and extracted with 2 × 20 mL of Et_2O. The combined ether layers were washed with 40 mL of 5% $Na_2S_2O_3$ and the aqueous phase was back-extracted with 40 mL of ether. The combined ether layers were dried over $MgSO_4$ and the ether was removed.

The crude acid was dissolved in 10 mL of diethyl ether. The solution was cooled to 0 °C and diazomethane was added dropwise until the solution was yellow. The solution was allowed to sit at 0 °C for 1 h and then the solvent and excess diazomethane were blown off under a stream of argon. The methyl ester product was isolated via preparative HPLC in 25% EtOAc/hexane.

Product from 3a: GC t_r = 9.05 min; GC/CIMS (NH_3) m/z (relative intensity) 327 ($M + NH_4^+$) (19), 310 (MH^+) (100); EIMS m/z (relative intensity) 297 (4), 266 (8), 213 (42), 199 (24), 154 (20), 126 (20), 84 (100); ^{1}H NMR ($CDCl_3$) δ 4.20 (m, 1 H, NCH(CH_3)CH_2), 4.04 (m, 1 H, NCH(CH_3)CH_2), 3.63 (s, 3 H, COOCH_3), 2.92 (m, 1 H, $CH_2CH(C_6H_{13})$CON), 2.78 (dd, J = 8.2, 16.8 Hz, 1 H, OCOCH(H)-CH), 2.39 (dd, J = 5.8, 16.8 Hz, 1 H, OCOCH(H)CH) 2.12 (m, 2 H, NCH(CH_3)CH(H)), 1.59 (m, 2 H, $CHCH_2C_5H_{11}$), 1.49 (m, 2 H, NCH(CH_3)CH(H)), 1.28 (d, J = 6.2 Hz, 3 H, NCHCH_3), 1.25 (8 H, $C_4H_8CH_3$), 1.12 (d, J = 6.2 Hz, 3 H, NCHCH_3), 0.85 (t, 3 H, $C_4H_8CH_3$); ^{13}C NMR ($CDCl_3$) δ 173.4, 173.1, 53.4, 52.9, 51.6, 39.6, 35.7, 33.4, 31.7, 30.8, 29.3, 28.9, 26.8, 22.5, 21.7, 18.9, 14.1; Exact mass for $C_{17}H_{31}NO_3$ calcd m/z 297.2304, measd (EIMS) m/z 297.2311 (+2.4 ppm).

Product from 3b: GC t_r = 9.39 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.20 (m, 1 H), 4.07 (m, 1 H), 3.62 (s, 3 H), 2.80 (m, 2 H), 2.39 (dd, 1 H, J = 19.7, 8.2 Hz), 2.21–2.02 (m, 2 H), 1.76–1.42 (m, 8 H), 1.25 (d, 3 H, J = 6.6 Hz), 1.13 (d, 3 H, J = 6.4 Hz), 1.22–0.86 (m, 5 H); ^{13}C ($CDCl_3$) δ 173.8, 172.5, 53.6, 52.9, 51.6, 45.0, 41.5, 33.4, 30.9, 30.8, 29.6, 28.9, 26.6, 26.5, 26.3, 21.5, 19.1; MS (CI, CH_4/NH_3) M^+ = 296; MS (EI) m/z (relative intensity) 213 (57), 171 (15), 154 (52), 119 (15), 84 (100), 55 (60).

Iodoform Reaction of 3c. The major α-amide product of *tert*-butyl radical addition was dissolved in 5 mL of 1,4-dioxane and 5 mL of 5 N NaOH. A mixture of I_2 (0.36 g, 4.5 equiv) and KI (0.74 g) in 4 mL of water was added dropwise with vigorous stirring. When the addition was complete, the solution was heated gently and then allowed to stir at room temperature for 30 min. The solution was acidified with concentrated HCl and extracted with 3 × 25 mL of ether. The combined ether layers were washed with 50 mL of $Na_2S_2O_3$, which was extracted with 50 mL of ether. The combined ether extracts were dried over $MgSO_4$ and the ether was removed.

2-*tert*-Butylsuccinic Bis[(2*S*,5*S*)-Dimethylpyrrolidinide] (11c). The unpurified acid (32.5 mg, 0.13 mmol) from above was dissolved in 5 mL of dry THF. *N*-Methylmorpholine (30.9 mg, 2.4 equiv) was added and the solution cooled to −10 °C in a brine/ice bath. Isobutyl chloroformate (1 equiv) was added dropwise, the solution was stirred at −10 °C for 30 min, and the N-methylmorpholine hydrochloride was filtered off. (2*R*,5*R*)-Dimethylpyrrolidine [(2*R*,5*R*)-dimethylpyrrolidine hydrochloride (54.6 mg, 3 equiv) dissolved in 5 mL of dry CH_2Cl_2, washed with 2 mL of 5 N NaOH, dried over KOH, and filtered through K_2CO_3] was added dropwise to the filtered solution at −10 °C. The solution was stirred for 30 min at −10 °C and then an additional 16 h at room temperature. The solvent was removed, leaving 39.3 mg of crude material. The desired product was isolated via preparative HPLC (1:1 hexane/EtOAc, 10 mL/min) and was spectroscopically identical with the major product, *S*-**11c**, isolated from the addition of *tert*-butyl radical to olefin **2**, for which an X-ray crystal structure was obtained.[28]

Resolution of 2-Hexylsuccinic Acid (*S*-9a). Quinine (50.0 g, 154 mmol) and 26.9 g of hexylsuccinic acid (133 mmol) were dissolved in 535 mL of 95% EtOH with gentle warming. Crystallization was allowed to take place at room temperature. Successive recrystallizations were performed by dissolving the quinine salt in 20 mL of ethanol for each gram of material. The progress of the resolution was followed by taking optical rotations of the acid recovered from the mother liquor. (The ethanol was removed under reduced pressure and the salt was decomposed with 10% H_2SO_4. This solution was washed with ethyl ether and dried over magnesium sulfate and the ether was removed under reduced pressure. The absolute rotations of the acids in ethanol from the filtrates were as follows: +13.1°, 0°, −12.2°, −19.9°.) The salt that comprised the fifth crop yielded acid with $[\alpha]^{23}_D$ = −24.9° (c = 4.00, ethanol). The reported rotation for the pure (*S*)-2-hexylsuccinic acid is $[\alpha]^{23}_D$ = −26.0° (c = 4.00, ethanol).[34a]

(*S*)-2-Hexylsuccinic Anhydride (*S*-10a). Fifteen milliliters of freshly distilled acetyl chloride was added to 2.70 g of (*S*)-2-hexylsuccinic acid. The mixture was refluxed for 30 min. Acetyl chloride was removed under reduced pressure and the residue was left under high vacuum until it solidified. The solid was recrystallized from hexane twice, yielding 1.35 g of white solid: TLC (1:1 ethyl acetate/hexane) R_f = 0.7; IR 1870 (weak), 1790 cm^{-1} (strong); ^{1}H NMR ($CDCl_3$) δ 3.08 (m, 1 H), 3.05 (dd, 1 H), 2.64 (dd, 1 H), 1.92 (m, 1 H), 1.63 (m, 1 H), 1.45–1.20 (8 H), 0.87 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 173.7, 170.1, 40.6, 34.1, 31.4, 30.9, 28.7, 26.6, 22.5, 14.0.

[2*S*-[1(*S*),2α,5β]]-β-Hexyl-γ-oxo(2,5-dimethyl-pyrrolidin-1-yl)butanoic Acid, Methyl Ester (*S*-7a). (*S*)-Hexylsuccinic anhydride (92 mg, 0.50 mmol) was stirred at room temperature in 2 mL of dry methanol with 11 mg of (dimethylamino)pyridine. After 1 h the methanol was removed under reduced pressure and the residue was dissolved in 15 mL of dichloromethane. The dichloromethane solution was washed three times with 5% Na_2CO_3 solution. The carbonate washings were acidified

and extracted with ethyl ether. The ether layers were dried over magnesium sulfate and evaporated to dryness. To this mixture of acids was added 2 mL of freshly distilled thionyl chloride. The mixture was stirred at 45 °C for 2.5 h. Thionyl chloride was removed under reduced pressure and the residue was left under high vacuum for 12 h. To the mixture of acid chlorides in 2 mL of dry CH_2Cl_2 was added, dropwise, (2*S*,5*S*)-dimethylpyrrolidine in 5 mL of CH_2Cl_2 [135 mg of pyrrolidine hydrochloride (2.0 equiv) dissolved in 5 mL of CH_2Cl_2, washed with 2 mL of 5 N NaOH, and dried over KOH] with stirring at −10 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was washed with 5% Na_2CO_3 and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The major product by GC coeluted with the methyl ester derivative of the hexyl radical adduct **3a**, accounting for 72% of products identified by GC/MS as the desired methyl ester amide products.

Cyclohexylsuccinic Acid (9b). Cyclohexylsuccinic anhydride[46] (0.55 g, 3.0 mmol) and potassium hydroxide (1.48 g, 26.5 mmol) were dissolved in 20 mL of methanol and 8 mL of water and the resultant mixture was heated under reflux for 3 h. After the methanol had been removed in vacuo, the aqueous solution was acidified with concentrated hydrochloric acid. The precipitated product was collected by filtration and washed with water to yield the product (0.47 g, 78%) as a white solid: mp 143–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 12.11 (s, 2 H, COOH), 2.52–2.30 (m, 3 H, CH_2CH), 1.70–1.49, 1.21–0.98 (2 m, 11 H, c-C_6H_{11}); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.36, 173.66, 46.59, 32.98, 30.22, 29.60, 26.04, 26.03, 25.88; MS (CI) *m/z* (relative intensity) 218 (100, $M^+ + NH_4^+$), 201 (18), 200 (16), 183 (10), 182 (6), 137 (9), 123 (6), 95 (11), 81 (12), 54 (6), 39 (5). Anal. Calcd for $C_{10}H_{16}O_4$ (200.24): C, 59.99; H, 8.05. Found: C, 59.89; H, 8.27.

Cyclohexylsuccinyl Chloride. Cyclohexylsuccinic acid (0.4 g, 2.0 mmol) and two drops of pyridine were added to thionyl chloride (1.64 g, 14.0 mmol). The mixture was heated under reflux for 4 h and the excess thionyl chloride was removed in vacuo. Kugelrohr distillation (0.06 mbar, 110 °C) yielded 2-cyclohexylsuccinyl chloride (0.3 g, 51%) as a yellowish oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.35 (dd, *J* = 18.3, 10.1 Hz, 1 H, *H*′HC), 3.17 (ddd, *J* = 10.1, 5.3, 3.6 Hz, 1 H, *H*C, c-C_6H_{11}), 3.07 (dd, *J* = 18.3, 3.6 Hz, 1 H, H′*H*C) 2.0–1.55, 1.38–0.55 (2 m, 11 H, c-C_6H_{11}).

2-Cyclohexylsuccinic Bis[(2*R*,5*R*-dimethylpyrrolidinide] (*R*-11b and *R*-12b). (2*R*,5*R*)-Dimethylpyrrolidine (0.24 g, 2.4 mmol) and tetramethylguanidine (0.28 g, 2.4 mmol) were treated with cyclohexylsuccinyl chloride (0.3 g, 1.1 mmol) as described in the procedure for the formation of fumaric diamide **2**. Analysis of the reaction mixture by GC showed the presence of the two isomers *R*-**11b** (t_r = 20.78 min) and *R*-**12b** (t_r = 22.17 min). Flash chromatography (dichloromethane/methanol 50:1) yielded product *R*-**12b** (0.12 g, 30%), R_f = 0.29) and isomer *R*-**11b** (0.06 g, 15%; R_f = 0.20) as oils. The isomer *R*-**11b** showed the same spectroscopic data as listed above. *R*-**12b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37, 4.10 (2 m, 4 H, H_{pyr}-2, H_{pyr}-5), 2.89 (ddd, *J* = 10.5, 7.4, 3.1 Hz, 1 H, *H*C (c-C_6H_{11})), 2.68 (dd, *J* = 14.3, 10.5 Hz, 1 H, *H*′HC, 2.35 (dd, *J* = 14.3, 3.1 Hz, 1 H, H′*H*C), 2.35–2.15 (m, 4 H, H_{pyr}-3′, H_{pyr}-4′), 1.42–1.56 (m, 4 H, H_{pyr}-3, H_{pyr}-4), 1.79–1.58, 1.31–0.85 (2 m, 11 H, e-C_6H_{11}), 1.17, 1.12, 1.11, 1.09 (4 d, *J* = 6.4 Hz, 12 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.85, 170.52, 53.66, 53.37, 53.06, 52.97, 45.77, 40.49, 35.93, 32.03, 31.03, 30.59, 29.84, 29.05, 26.78, 26.56, 26.47, 22.76, 21.58, 19.44, 18.70; MS (EI) *m/z* (relative intensity) 362 (0.4, M^+) 264 (55), 222 (20), 182 (24), 180 (14), 154 (29), 126 (10), 98 (100), 84 (23), 83 (22), 70 (13), 67 (11), 55 (47), 42 (12), 42 (11), 41 (21).

(*S*)-(+)-Cyclohexylsuccinic Acid (*S*-9b). (*S*)-(+)-Phenylsuccinic acid (257 mg, 1.32 mmol, Chemical Dynamics Corp.) was dissolved in 14 mL of methanol. The solution was degassed with argon for 30 min, and 5% Rh on Al_2O_3 (564 mg, 20 mol %) was added. The solution was placed on a Parr apparatus at 48 psi H_2 and shaken for 6 h. An additional 5 mol % of catalyst was added and the mixture was shaken an additional 28 h at the same H_2 pressure. The solution was filtered through a plug of Celite and the Celite was washed with 20 mL of methanol. The methanol was removed in vacuo, leaving 260 mg of crude product as a yellow oil. The product was crystallized from benzene giving 242 mg (92%) of purified product as a waxy solid (lit[34b] mp 96 °C).

(*S*)-(+)-Cyclohexylsuccinic Anhydride (*S*-10b). (*S*)-(+)-Cyclohexylsuccinic acid (0.33 g, 1.7 mmol) was dissolved in 5 mL of freshly distilled acetyl chloride. The mixture was refluxed under argon for 45 min, and the acetyl chloride was removed under reduced pressure. The product was recrystallized from a 5:1 mixture of hexane/benzene affording 0.29 g (96%) of the product as a white solid: mp 41.5–43.0 °C (lit.[34b] mp 43.0 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10–2.88 (m, 2 H), 2.74 (dd, *J* = 17.9, 4.75 Hz, 1 H), 2.00–1.50 (m, 6 H), 1.38–0.94 (m, 5 H).

(46) Giese, B.; Kretzschmar, G. *Chem. Ber.* **1982**, *115*, 2012.

[2*S*-[1(*R*),2α,5β]]-β-Cyclohexyl-γ-oxo(2,5-dimethylpyrrolidin-1-yl)-butanoic Acid, Methyl Ester (*R*-7b) and 2*S*-[1(*R*),2α,5β]]-β-Cyclohexyl-γ-oxo(2,5-dimethylpyrrolidin-1-yl)butanoic Acid, Methyl Ester (*R*-8b). (*S*)-(+)-Cyclohexylsuccinic anhydride (74 mg, 0.41 mmol) was dissolved in 2 mL of dry methanol. To this was added 4-(dimethylamino)pyridine (11.1 mg, 0.2 equiv) and the solution was stirred under argon at room temperature for 1 h. The methanol was removed and the oily residue was taken up in 15 mL of CH_2Cl_2. The solution was washed with 3 × 25 mL of 5% Na_2CO_3, and the aqueous washings were acidified with concentrated HCl and extracted with 3 × 50 mL of Et_2O. The combined ether layers were dried over $MgSO_4$ and the ether was removed. The resulting residue was dissolved in 2 mL of freshly distilled thionyl chloride and stirred at 45 °C under argon for 2.5 h. The thionyl chloride was removed and the residue placed on a high vacuum overnight. The residue was dissolved in 2 mL of dry CH_2Cl_2 and (2*R*,5*R*)-dimethylpyrrolidine [(2*R*,5*R*)-dimethylpyrrolidine hydrochloride (111 mg, 0.82 mmol, 2 equiv) dissolved in 5 mL of dry CH_2Cl_2, washed with 2 mL of 5 N NaOH, dried over KOH, and filtered through a plug of K_2CO_3] was added dropwise at −10 °C. After addition was complete, the mixture was stirred an additional 30 min at −10 °C and then 2 h at room temperature. The solution was washed with 10 mL of 5% Na_2CO_3 and the organic layer was dried over $MgSO_4$. The solvent was removed, leaving 56.1 mg of brown oil. GC showed two peaks accounting for 92% of the products in a ratio of 1.6:1.0 (t_r = 9.44 and 9.86 min). These products were separated via preparative HPLC (25% EtOAc/hexane 10 mL/min, t_r = 41 and 52 min). The first eluting product was spectroscopically identical with and coeluted on the GC with *R*-**7** obtained by the iodoform sequence (Scheme II). Likewise, the later eluting product was identical with and coeluted on the GC with *R*-**8** obtained by the iodoform sequence (Scheme II).

2-*tert*-Butylsuccinic Anhydride (10c). Maleic anhydride (0.67 g, 6.8 mmol) was treated with *tert*-butylmercuric chloride (3.0 g, 10.2 mmol) and sodium borohydride (1.2 g, 31.7 mmol) according to the procedure described above. Kugelrohr distillation (0.02 mbar, 65 °C) yielded the crystalline product (0.80 g, 75%): mp 38–41 °C (lit.[47] mp 41.5–42.0 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.05–2.76 (m, 3 H, CH_2CH), 1.09 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.52, 169.94, 50.82, 33.19, 31.15, 26.63; MS (EI) *m/z* (relative intensity) 157 (1, M^+), 141 (31), 100 (54), 84 (39), 70 (100), 57 (93), 55 (29), 41 (93), 38 (52).

2-*tert*-Butylsuccinic Acid (9c). 2-*tert*-butylsuccinic anhydride (0.3 g, 1.8 mmol) and potassium hydroxide (0.81 g, 14.4 mmol) were dissolved in 20 mL of methanol and 8 mL of water and the resultant mixture was heated under reflux for 3 h. After acidification with concentrated hydrochloric acid, the solvent was removed in vacuo and the residue taken up in acetone. Filtration and concentration afforded the diacid (0.26 g, 83%) as a white solid, which was used without further purification: mp 102 °C (lit.[48] mp 132 °C); ^{1}H NMR (300 MHz, DMSO) δ 12.1 (s, 2 H, 2 COOH), 2.5 (m, 3 H, CH_2CH), 0.93 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz, DMSO) δ 175.57, 174.32, 50.91, 31.77, 27.74, 27.59; MS (Cl) *m/z* (relative intensity) 192 (100, M + NH_4^+), 174 (14), 157 (1), 100 (1).

2-*tert*-Butylsuccinyl Chloride. *tert*-Butylsuccinic acid (0.36 g, 2.4 mmol) and two drops of pyridine were dissolved in thionyl chloride (1.64 g, 14.0 mmol). The mixture was heated under reflux for 4 h and the excess thionyl chloride was removed in vacuo. Kugelrohr distillation (0.02 mbar, 100 °C) of the residue afforded the dichloride **12** (0.22 g, 51%) as a yellowish oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (dd, *J* = 19.1, 11.7 Hz, 1 H, *H*′HC), 3.18 (dd, *J* = 11.7, 3.2 Hz, 1 H, *H*C(CH_3)$_3$), 3.16 (dd, *J* = 19.2, 3.2 Hz, 1 H, H′*H*C), 1.08 (s, 9 H, $C(CH_3)_3$).

2-*tert*-Butylsuccinic Bis[(2*S*,5*S*-dimethylpyrrolidinide] (*S*-11c and *S*-12c. (2*S*,5*S*)-Dimethylpyrrolidine (0.05 g, 0.5 mmol) and tetramethylguanidine (0.06 g, 0.5 mmol) were treated with *tert*-butylsuccinyl chloride (0.04 g, 0.2 mmol) as described in the procedure for the formation of fumaric diamide **2**. Analysis of the reaction mixture by GC showed the presence of the two isomers, *S*-**11c** (t_r = 12.64 min) and *S*-**12c** (t_r = 12.78 min). The diastereomers were separated by HPLC (Waters Delta Prep. 3000 Polygosil 60-5 column, 25 cm, 30% ethyl acetate/hexane) to provide 8 mg (12%) of each isomer. One of the isomers showed the same spectroscopic data as *S*-**11c**.

S-**12c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.41–4.05 (m, 4 H, H_{pyr}-2, H_{pyr}-5), 3.00 (dd, *J* = 11.0, 2.2 Hz, 1 H, *H*C(CH_3)$_3$), 2.83 (dd, *J* = 13.8, 11.0 Hz, 1 H, *H*′HC), 2.29 (dd, *J* = 13.8, 2.2 Hz, 1 H, H′*H*C), 2.15–2.03 (m, 4 H, H_{pyr}-3′, H_{pyr}-4′), 1.60–1.46 (m, 4 H, H_{pyr}-3, H_{pyr}-4), 1.25, 1.17, 1.16, 1.14 (4 d, *J* = 6.4 Hz, 12 H, 4 CH_3), 1.06 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 174.00, 170.68, 54.00, 53.53, 52.20, 52.92,

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48.18, 35.44, 33.31, 31.44, 30.68, 29.33, 29.18, 28.23, 23.03, 21.67, 19.76, 19.62; MS (EI) m/z (relative intensity) 308 (1), 238 (21), 222 (6), 210 (2), 182 (9), 180 (2), 156 (16), 154 (15), 126 (6), 98 (100), 83 (14), 70 (9), 55 (20), 41 (14).

Acknowledgment. N.A.P. thanks NIH (HL17921) and NSF for generous financial support and Professors R. Polniaszek, D. Evans, and D. Curran for helpful discussions at an early stage of the project. B.G. thanks the Swiss National Science Foundation for financial support. D.M.S. and I.J.R. thank the Burroughs Wellcome Fund for receipt of fellowships.

Pentacoordinate 10-Electron Pnictogen–Manganese Adducts: Verification of the 10-Pn-3 Arrangement in ADPnO Molecules

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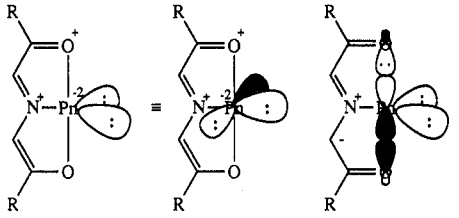
Contribution No. 5589 from the Central Research and Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19880-0328.
Received September 6, 1990

Abstract: The bis(cyclopentadienylmanganese dicarbonyl) complexes of 5-aza-2,8-dioxa-1-pnictabicyclo[3.3.0]octa-2,4,6-triene (ADPnO) molecules have been prepared and structurally characterized for arsenic and antimony. These complexes represent the first demonstration of chemical reactivity for both pnictogen lone pairs of electrons in ADPnO molecules. In the case of the phosphorus system (ADPO) only a monoadduct is obtained. The ADPO·$Mn(Cp)(CO)_2$ adduct exhibits a tetracoordinate 8-electron arrangement at phosphorus. These results support the 10-Pn-3 designations previously assigned to the ADPnO molecules and are in accord with recent theoretical models. Comparisons are made with pnictinidene bis(metal) complexes as well as 5-coordinated antimony derivatives of ADSbO.

Introduction

In previous reports we have described the synthesis,[1-5] structure,[1-4] chemistry,[1-4,6-11] and electronic structure[4,11] of unusual ring systems that contain 3-coordinate 10-electron pnictogen centers (10-Pn-3;[12] Pn ≡ pnictogen = P, As, Sb). Theoretical studies[4,11] on these ADPnO[13] ring systems have indicated that the arsenic and antimony compounds are adequately described by a simple valence bond model such as **1a**. This model places two



1a **1b**

lone pairs of electrons in equatorial sites of the idealized pseudo-trigonal-bipyramidal (Ψ-TBP) geometry at the pnictogen center. It is also possible to represent these lone pairs of electrons as a σ and π set rather than an equivalent set of approximate sp^2 hybridized orbitals.

The theoretical models of the phosphorus-derived ADPO system show characteristics similar to the heavier arsenic and antimony analogues.[4,11] However, because the size of the phosphorus is closer to those of the neighboring nitrogen and oxygen atoms, overlap between these centers is sufficient to allow delocalization of one phosphorus lone pair into the ligand backbone. This loss of electron density from phosphorus is not sufficient to cause a change in the ground-state structure to the more conventional folded 8-P-3 arrangement. Since the phosphorus center of ADPO remains in a planar T-shaped geometry, the designation of "10-P-3 ADPO" can still be applied semantically. Nonetheless, it is important to remember that the phosphorus π lone pair in 10-P-3 ADPO is delocalized and the 8-P-3 and 10-P-3 arrangements are close in energy: a fact that is reflected in ADPO's coordination chemistry.[4,6,10]

A description of the bonding in the ADPnO molecules in which the pnictogen center is viewed as an internally solvated pnictinidene (6-Pn-1) center has been discussed.[11] Structure **1b** depicts a pnictinidene center that is internally solvated by the carbonyl substituents of an azomethine ylide. As we have discussed previously, the pnictogen–oxygen interaction in the ADPnO molecules is too strong to be regarded as mere solvation. Although an exaggeration, the pnictinidene model of the ADPnO molecules does provide insight. With this view of these bonding systems in mind, it is useful to recall reports of pnictinidene bis(metal) complexes[14-28] (**2**), which can serve as reference points for

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