

The relatively rapid buildup of a hydrazine-forming intermediate corresponds very closely with disappearance of **2B**. We are led to conclude that the loss of PPh_3 from **2B** leads to the early buildup in concentration of an intermediate in the ammonia-forming reaction that upon reaction with H_2O generates hydrazine.⁹ Significantly, hydrazine was not generated by HBr (or HCl^1) present in the reaction.¹⁰ Later, when all **2B** has reacted, the concentration of the intermediate is low because of the slower reaction of **2A** to produce ammonia.¹

The reaction of **2A** and **2B** to produce ammonia results in the formation of 0.5 mol of N_2 per mol of complex (eq 3). Interestingly, the formation of the hydrazine-forming intermediate does not result in any N_2 evolution. Thus, the amount of N_2 evolved, before quenching, corresponds to the amount of ammonia formed.

The behavior of **1** described in this communication is strikingly similar to that of nitrogenase.² No other "model" system has displayed this behavior: an analogy with the only recognized property of the substrate N_2 during turnover of the enzyme.¹¹ It is hoped that elucidation of the structure of the hydrazine-forming intermediate will provide a model for one of the intermediate stages in ammonia synthesis by nitrogenase. Further work in this direction is in progress.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE80-11423.

(9) A solid begins to precipitate from the reaction solution after ca. 0.5 h. This golden-yellow solid is soluble in CH_2Cl_2 but shows no signal in the $^{31}\text{P}\{\text{H}\}$ NMR spectrum. This compound is not $\text{MoBr}_3(\text{triphos})$: George, T. A.; Lester, R. K., unpublished results.

(10) $(\mu_3\text{-N}_2)[(\eta^5\text{-C}_{10}\text{H}_8)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2][(\eta^1\text{-}\eta^5\text{-C}_3\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_1][(\eta\text{-C}_5\text{H}_5)_2(\text{C}_6\text{H}_4\text{O}_3)\text{Ti}] \cdot \text{C}_6\text{H}_4\text{O}_3$ reacts with $\text{THF}/\text{H}_2\text{O}$ to give N_2H_4 and NH_3 but with HCl to give mainly N_2 . Pez, G. P.; Appgar, P.; Crissey, R. K. *J. Am. Chem. Soc.* **1982**, *104*, 482-490.

(11) HD formation by nitrogenase occurs in the presence of D_2 and N_2 . It has been proposed that dinitrogen-dependent HD formation arises from a bound reduced dinitrogen intermediate. Burgess, B. K.; Wherland, S.; Newton, W. E.; Stiefel, E. K. *Biochemistry* **1981**, *20*, 5140-5146 and references cited therein.

Preparation and Diels-Alder Reactions of 1,3-Dienes Containing both Sulfur and Nitrogen Substituents. Complete Orientational Control by the Acylamino Group

Larry E. Overman,* Charles B. Petty, Takashi Ban, and Glenn T. Huang

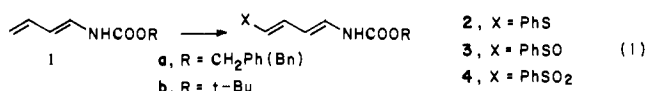
Department of Chemistry, University of California
Irvine, California 92717

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In recent years the Diels-Alder reaction of heterosubstituted 1,3-dienes has emerged as a powerful method for preparing highly functionalized ring systems.¹ As a result of the enhanced functionality imparted to their cycloadducts, dienes substituted with two different heteroatoms are of considerably interest, and those with oxygen and sulfur substitution have received significant attention.² In contrast, the Diels-Alder chemistry of 1,3-dienes containing both nitrogen and sulfur substituents is completely unexplored.¹ The successful use of heterosubstituted 1,3-dienes in synthesis typically demands knowledge of the substituent's effect on cycloaddition rate, regioselectivity, and endo stereoselectivity. Both acylamino³ and thiophenyl^{2a} substituents endow 1,3-dienes

with useful Diels-Alder reactivity and positional selectivity,¹⁻⁴ although only the former substituent^{3,4} exhibits good stereochemical-orienting characteristics.⁵ In this communication, we describe a convenient synthesis of 1-(acylamino)-1,3-dienes that have sulfenyl, sulfinyl, and sulfonyl substitution at carbon 4. We also detail initial observations concerning Diels-Alder reactions of these new heterosubstituted 1,3-dienes, which exhibit excellent Diels-Alder reactivity, regioselectivity, and endo stereoselectivity, with regiocontrol being completely dominated by the acylamino substituent.

Dropwise addition of phenylsulfonyl chloride (1.05 equiv) at -78°C to (*E*)-1,3-butadiene-1-carbamates **1⁶** (0.1 M in ether) and *N,N*-diisopropylethylamine (~ 3 equiv), followed by warming to room temperature and purification on silica gel, gave directly⁷ 4-(phenylsulfonyl)-1,3-butadiene-1-carbamates **2** (85-95% yields) as crystalline 1:1 mixtures⁸ of *1E,3E* and *1E,3Z* stereoisomers (eq 1). Oxidation¹⁰ to the sulfoxides, followed by base-catalyzed



equilibration (1 M Et_3N in refluxing benzene),⁹ afforded the crystalline (*1E,3E*)-4-(phenylsulfonyl)-1,3-butadiene-1-carbamates **3** in 50-65% overall yields from **1**. Further oxidation¹⁰ gave the corresponding (*1E,3E*)-4-(phenylsulfonyl)-1,3-butadiene-1-carbamates **4** (50-75% yields). These new dienes^{11,12} are stable, highly crystalline solids, which are well suited for Diels-Alder transformations.

Sulfide diene carbamate **2a**¹³ reacted with *N*-phenylmaleimide (110°C , 24 h, dioxane) and phenyl vinyl ketone (56°C , 26 h) to give endo cycloadducts^{11,14} **5** and **6**¹¹ in 70% and 89% yields, respectively. A 4:1 mixture^{13b} of cycloadducts **7** and **8** was formed from the reaction of **2a** with excess acrolein at 56°C for 24 h (eq 2). The major endo adduct **7**^{11,14} (mp $83-84^\circ\text{C}$) could be

(4) (a) Evans, D. A.; Bryan, C. A.; Sims, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2891-2892. (b) Cohen, T.; Mura, A. J., Jr.; Shull, D. W.; Fogel, E. R.; Ruffner, R. J.; Falck, J. R. *J. Org. Chem.* **1976**, *41*, 3217-3219. Cohen, T.; Kosarych, Z. *Ibid.* **1982**, *47*, 4006-4008.

(5) Good endo stereoselectivity is seen in cycloadditions of 2-methoxy-1-(phenylthio)-1,3-butadiene.^{2c,4b}

(6) Jessup, P. J.; Petty, C. B.; Roos, J.; Overman, L. E. *Org. Synth.* **1980**, *59*, 1-9.

(7) Chlorosulfonylation-dehydrochlorination has been employed to prepare 1-(phenylsulfonyl)-1,3-butadiene, see ref 4a and: Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208-1217.

(8) Changing the base, solvent, or reaction temperature had surprisingly little effect on the ratio of stereoisomers. These mixtures could not be cleanly equilibrated to the *1E,3E* isomers.⁹

(9) For related isomerizations, see: Overman, L. E.; Clizbe, L. A.; Freerks, R. L.; Marlowe, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 2807-2815.

(10) *m*-Chloroperbenzoic acid (1.05 equiv) in CH_2Cl_2 at -20°C .

(11) New compounds exhibited NMR, IR, and mass spectra and elemental compositions consistent with their assigned structures.

(12) *1E,3E* isomer of **2a**: mp $94-95^\circ\text{C}$; $J_{1,2} = 13$ Hz, $J_{3,4} = 15$ Hz. *1E,3Z* isomer of **2a**: mp $81-82^\circ\text{C}$; $J_{1,2} = 14$ Hz, $J_{3,4} = 9$ Hz. **3a**: mp $131-132^\circ\text{C}$; $J_{1,2} = 12$ Hz, $J_{3,4} = 15$ Hz. **3b**: mp $146-147^\circ\text{C}$; $J_{1,2} = 13$ Hz, $J_{3,4} = 15$ Hz. **4a**: mp $159-161^\circ\text{C}$; $J_{1,2} = 12$ Hz, $J_{3,4} = 14$ Hz. **4b**: mp $145-146^\circ\text{C}$; $J_{1,2} = 12$ Hz, $J_{3,4} = 14$ Hz.

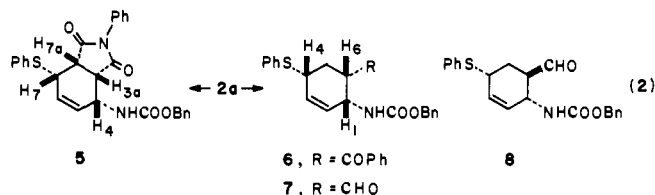
(13) (a) A 1:1 mixture of *1E,3E* and *1E,3Z* dienes was employed. Careful monitoring of the reaction by HPLC showed that only the *1E,3E* isomer reacted under these conditions. (b) Cycloadduct ratios were determined by HPLC and/or 250-MHz ^1H NMR analysis of crude cycloadduct mixtures.

(14) Stereochemical assignments were made from decoupled ^1H NMR spectra measured at 250 MHz. These assignments follow from arguments similar to those utilized in ref 3. Selected characterization data, diagnostic chemical shifts (δ) and coupling constants (in Hz), for representative cycloadducts: **5**: ^1H NMR $J_{3a,4} = 6$, $J_{4,5} = 3$, $J_{7,7a} = 7$, $J_{6,7} = 4$. **7**: ^1H NMR (H_1) 4.83, (H_6) 2.72, (H_4) 3.76, $J_{1,6} = 4$, $J_{5,6} = 3$, $J_{5a,6} = 10$, $J_{3,4} \sim 0$. **10**: ^1H NMR (H_1) 4.9, (H_6) 2.65, (H_4) 3.85, $J_{1,6} = J_{5,6} = 3.5$, $J_{5a,6} = 14$, $J_{3,4} = 1.4$. **11**: ^1H NMR (H_1) 4.6, $J_{1,2} = 3.6$, (H_6) 2.95, m, half-height width = 21 Hz, (H_4) 3.85, $J_{3,4} = 3.1$. **13**: ^1H NMR (H_1) 4.91, (H_3) 5.67, (H_2) 2.70, $J_{1,6} = 3.7$, $J_{5a,6} = 13$, $J_{4,5a} = 10$. **14**: ^1H NMR (H_1) 4.92, (H_3) 6.08, (H_6) 2.65, $J_{1,6} = 4$, $J_{5a,6} = 13$, $J_{4,5a} = 10$. **18**: mp $111-112^\circ\text{C}$; ^1H NMR (H_2) 4.14, br s, half-height width = 10 Hz, (H_1 and CHHOH) 3.6-3.9, m; $J_{5a,6} = 11$ Hz. **19**: mp $176-178^\circ\text{C}$; IR (CHCl_3) 3470, 1770, 1682 cm^{-1} ; ^1H NMR (H_2) 5.14, (H_1) 4.47, (H_6) 3.76, $J_{1,2} = 7.4$, $J_{1,6} = 1.8$; $J_{2,3} = 3.1$; $J_{5,6} = 6.6$; $J_{5a,6} = 10.2$. **20**: ^1H NMR (4 vinylic H), 5.9-6.1, m; (H_1 and $\text{OCH}_2\text{CH}_2\text{O}$) 3.6-4.1, m, (H_6) 3.15, br s, half-height width = 14 Hz.

(1) For a recent review, see: Petrzilka, M.; Grayson, J. I. *Synthesis* **1981**, 753-786.

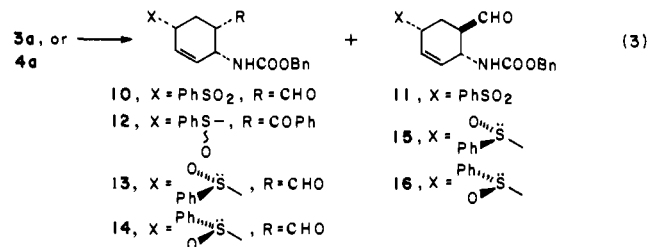
(2) Cf: (a) Trost, B. M.; Ippen, J.; Vladuchick, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 8116-8118. (b) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *Ibid.* **1980**, *102*, 3548-3554. (c) Cohen, T.; Kosarych, Z. *J. Org. Chem.* **1982**, *47*, 4005-4008 and references therein.

(3) Cf: Overman, L. E.; Freerks, R. L.; Petty, C. B.; Clizbe, L. A.; Ono, R. K.; Taylor, G. F.; Jessup, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2816-2822 and references therein.



directly crystallized from the crude cycloadduct mixture in 68% yield. Alternatively, this mixture could be treated with a catalytic amount of DBU¹⁵ in refluxing methanol to give the more stable exo adduct **8**¹¹ in 83% yield. Structural assignments for **6–8** followed from fully decoupled ¹H NMR spectra,¹⁴ which clearly showed that for all three cycloadducts the allylic hydrogen α to the NHCOOR substituent³ was coupled to the acyl methine hydrogen. The complete regiocontrol exercised by the NHCOOR substituent is striking in light of the excellent regiodirecting ability of the SPh substituent, which, in the thermal cycloadditions,² is greater than that of the OAc or OMe groups. That this regiocontrol derives from the powerful activating influence of the NHCOOR substituent is apparent from competition experiments between diene **1a** and (*E*)-1-(phenylsulfenyl)-1,3-butadiene (**9**),⁷ which demonstrate that the former diene is at least 10 times more reactive toward *N*-phenylmaleimide.¹⁶

Sulfone diene carbamate **4a** also reacted cleanly with excess acrolein at 56 °C to give a 7:1^{13b} mixture of stereoisomeric^{1c} adducts **10** and **11** in 78% yield (eq 3). This mixture was sep-



arated by high-performance liquid chromatography (HPLC) and the major endo cycloadduct **10** was isolated as a crystalline solid (mp 145–146 °C). Structural assignments again followed unambiguously from decoupled ¹H NMR spectra.¹⁴ In a similar fashion, sulfoxide diene carbamate **3a** reacted with phenyl vinyl ketone (25 °C, 3 days) to give cycloadduct **12**¹¹ (85% yield) as a crystalline 1:1^{13b} mixture of sulfoxide diastereomers and with acrolein at 56 °C to give a 10:10:1:1 mixture^{13b} of cycloadducts **13**, **14**, **15**, and **16**, respectively.¹¹ This latter mixture was separated by HPLC (30–45% combined yields) to give pure samples of the major endo adducts **13**^{14,17} (mp 126–127 °C) and **14**^{14,17} (mp 109–110 °C) and, as nearly pure oils, the minor exo adducts **15** and **16**. That the sulfoxide diastereomers **13** (**14**) and **15** (**16**) have the indicated regiochemistry and stereochemical relationship of NHCOOR and CHO groups was apparent from their preparation¹⁰ from sulfenyl cycloadducts **7** and **8**, respectively.

Clearly, the acylamino substituent has a stronger influence on both cycloaddition rate¹⁶ and regiodirection than the PhS, PhSO, and PhSO₂ groups. Of equal note in the reactions of **3a** and **4a** with acrolein was (a) the excellent reactivity of these dienes, even though they contain the strongly electron-withdrawing PhSO₂ and PhSO substituents and (b) the greater endo stereoselectivities observed with **3a** and **4a** than with sulfenyl diene carbamate **2a**.¹⁹

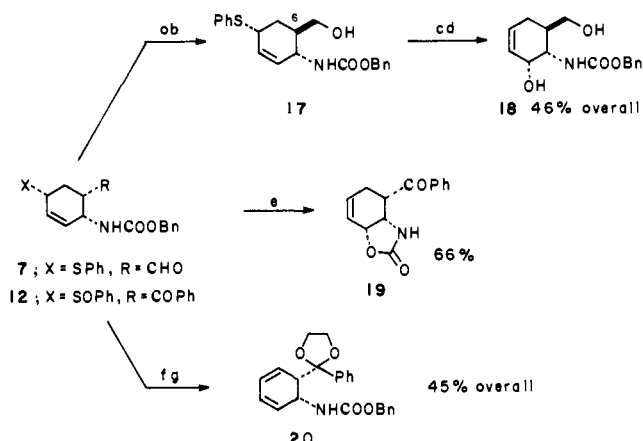
(15) 1,5-Diazabicyclo[5.4.0]undec-5-ene.

(16) (a) Competition experiments were conducted in benzene at 25 °C, with initial reactant concentrations: **1a** (1.0 M), **9** (1.1 M), *N*-phenylmaleimide (0.5 M). (b) Similar experiments conducted with **1a** and 1-(phenylsulfenyl)-1,3-butadiene^{4a} proved that **1a** was again much more (>10 times) reactive.

(17) The stereochemistry at sulfur was also determined by ¹H NMR data, using arguments similar to ones previously described.¹⁸ This point will be elaborated in a subsequent full account of this work.

(18) Nishoi, M. *J. Chem. Soc., Chem. Commun.* **1969**, 52–53. Confalone, P. N.; Kulesha, I. D.; Uskokovic, M. R. *J. Org. Chem.* **1981**, *46*, 1030–1032.

Scheme I



^a **7**, DBU, MeOH, 65 °C. ^b NaBH₄, MeOH, 0 → 25 °C. ^c *m*-Chloroperbenzoic acid, CH₂Cl₂, -20 °C. ^d P(MeO)₃, MeOH, 65 °C. ^e **12**, Me₃SiOSO₂CF₃, CH₂Cl₂, 25 °C. ^f **12**, (Me₃SiOCH₂)₂,^{23b} CF₃SO₃H, CH₂Cl₂, 25 °C. ^g Et₂NH, toluene, 110 °C.

To our knowledge, this marked effect of a remote diene substituent on endo stereoselectivity has no precedent.^{20,21}

The bisheterofunctionalized dienes reported here should find use in organic synthesis. Representative illustrations of transformations of these diene cycloadducts, which exploit their sulfur functionality,²² are shown in Scheme I. The direct conversion of carbamate sulfoxide **12** to bicyclic carbamate **19**^{11,14} upon treatment at room temperature with trimethylsilyl triflate (TMSOTf)^{23a} is particularly noteworthy. To our knowledge, this transformation is without precedent and likely involves intramolecular cyclization,²⁴ with allylic rearrangement, of the allyl-*O*-(trimethylsilyl)sulfoxonium cation formed from **12** and TMSOTf.²⁵ Although **12** was inert to conventional ketalization procedures, it was cleanly converted to the corresponding ethylene ketal, without formation of contaminating amounts of **19**, when treated with 1,2-bis((trimethylsilyloxy)ethane)^{23b} in the presence of CF₃SO₃H. Importantly, the transformations summarized in Scheme I demonstrate the ability to introduce functionality, in a controlled fashion, at all six carbons of a cyclohexane ring using these new cycloaddition components.

(19) Endo/exo ratios decreased somewhat with reaction time. In cycloadditions performed under identical conditions with acrolein at 80 °C with dioxane as the solvent, kinetic (early time) endo/exo selectivities were (diene **2a**) 6 ± 1:1, (diene **3a**) 18 ± 4:1, (diene **4a**) 12 ± 2:1.

(20) The complete orientational dominance of the NHCOOR substituent in cycloadditions of diene **2a** with acrolein as well as the remote effect of PhSO and PhSO₂ substituents on cycloaddition stereoselectivity are *not* rationalized by conventional frontier MO considerations.^{2a,21} Alternate theoretical treatments are being explored in collaboration with Professor W. Hehre and S. Kahn. Calculations (STO-3G level) of the relative energies of transition states for cycloadditions with different orientations are consistent with the greater regiodirecting ability observed for NHCOOR.

(21) For a recent critical survey, see: Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807.

(22) A variety of transformations of use in synthesis, which are based on the carbamate functionality of acylamino-1,3-diene cycloadducts, have been reported by us previously; cf: Overman, L. E.; Lesuisse, D.; Hashimoto, M. *J. Am. Chem. Soc.* **1983**, *105*, 5373–5379. Overman, L. E.; Petty, C. B.; Doedens, R. J. *J. Org. Chem.* **1979**, *44*, 4183–4185.

(23) (a) Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899–3910. (b) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, 1357–1360.

(24) Cyclic carbamates are readily produced by halocyclization of allylic carbamates, see, inter alia: Overman, L. E.; McCready, R. J. *Tetrahedron Lett.* **1982**, *23*, 4887–4890.

(25) An alternative mechanism involving an initial [2,3] shift of the allylic sulfoxide^{4a} is unlikely, since we were completely unsuccessful in affecting the related rearrangement of the sulfoxides derived from the C-6 epimer of **17**.²⁶ Sigmatropic reorganization is particularly disfavored in these cases, since cyclohexene conformers with the sulfoxide substituent axial are strongly disfavored as a result of 1,3-diaxial interactions with the cis substituent at C-6.

(26) Petty, C. B. Ph.D. Dissertation, University of California, Irvine, 1980.

Applications of these new dienes in the arena of alkaloid total synthesis are under current investigation in these laboratories.

Acknowledgment. Support of this research by National Science Foundation Grants CHE79-01833 and CHE82-03366 and the Camille and Henry Dreyfus Foundation (Teacher-Scholar Award to L.E.O.) is gratefully acknowledged. Mass and NMR spectra were determined with spectrometers purchased with the assistance of NSF Departmental instrumentation grants.

Registry No. 1a, 65899-49-2; 1b, 65899-50-5; (E,E)-2a, 86784-93-2; (E,Z)-2a, 86784-94-3; (E,E)-2b, 86802-62-2; (E,Z)-2b, 86821-99-0; (E,E)-3a, 86784-95-4; (E,E)-3b, 86802-63-3; (E,E)-4a, 86802-64-4; (E,E)-4b, 86784-96-5; 5, 86784-97-6; 6, 86784-98-7; 7, 86784-99-8; 8, 86785-00-4; 9, 36715-51-2; 10, 86785-01-5; 11, 86785-02-6; 12 (isomer 1), 86785-03-7; 12 (isomer 2), 86785-04-8; 13, 86785-05-9; 14, 86785-06-0; 15, 86785-07-1; 16, 86785-08-2; 17, 86785-09-3; 18, 86785-10-6; 19, 86785-11-7; 20, 86802-65-5; TMSOTf, 27607-77-8; phenylsulfenyl chloride, 931-59-9; N-phenylmaleimide, 941-69-5; phenyl vinyl ketone, 768-03-6; acrolein, 107-02-8; 1-(phenylsulfenyl)-1,3-butadiene, 36715-34-1.

Stereochemical Course of Thermal Cycloreversion of [3.2.1]Propellanes to 1,3-Dialkenylcyclohexanes

Michael A. Blaustein and Jerome A. Berson*

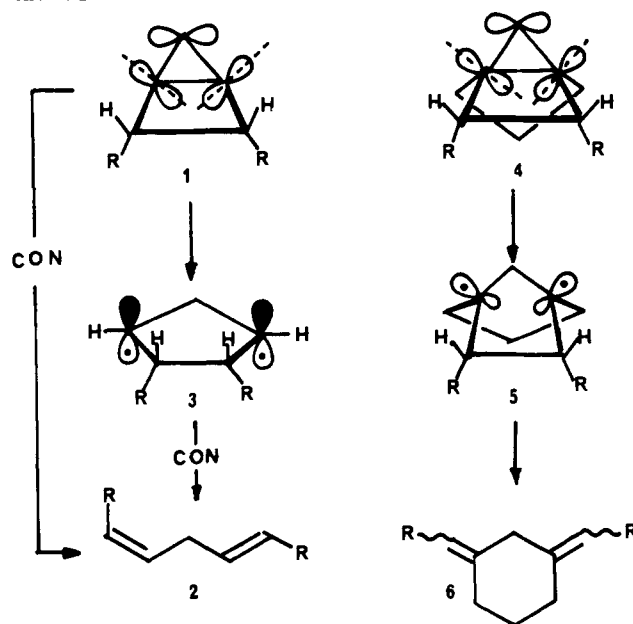
Department of Chemistry, Yale University
New Haven, Connecticut 06511

Received June 22, 1983

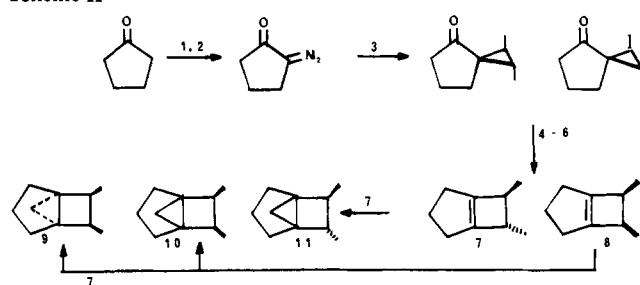
The observed conrotatory preference in the thermal cycloreversions of bicyclo[2.1.0]pentanes (**1**) to 1,4-pentadienes (**2**) has been discussed as an orbital symmetry effect operating in a concerted $[2\sigma_s + 2\sigma_a]$ reaction¹ (Scheme I). The transition state is formed either directly from the bicyclic hydrocarbon or from the biradical **3**, in which the lower energy component of the frontier orbital linear combination is imagined to be C_s symmetric. In an effort to block access to the latter pathway, we now have studied the pyrolysis of the three 6,7-dimethyltricyclo[3.2.1.0^{1,5}]octanes ([3.2.1]propellanes), e.g., **4** (R = CH₃). Achievement of a planar local configuration at the bridgeheads in the corresponding biradical **5** would be opposed by severe geometric constraints. This work provides stereochemical supplementation of the important contribution of Aue and Reynolds,² who demonstrated the thermal cycloreversion in the unsubstituted [3.2.1]propellane (**4** → **6**, R = H).

Synthesis of the three stereoisomers of propellane **4** (R = CH₃) was accomplished as shown in Scheme II.⁶ Cyclopropanation of trans olefin **7** gave the trans disubstituted propellane **11**, whereas the same procedure applied to cis olefin **8** gave a separable 4:1 mixture of cis disubstituted propellanes **9** and **10**, in which the CH₃ groups are, respectively, anti and syn to the cyclopropane CH₂ group. The anti vs. syn assignments are based upon the assumption that cyclopropanation occurs preferentially on the less hindered face of the double bond of **8** and the NMR chemical shifts of the methyl protons (δ 0.88 for **9** vs. 0.78 for **10**) and the 6- and 7-protons (δ 1.95 for **9** vs. 2.21 for **10**), which show the expected shielding effect of the cyclopropane ring.

Scheme I

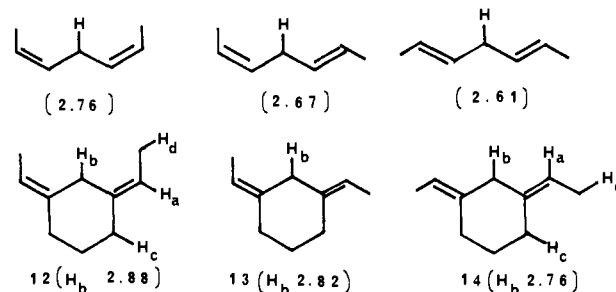


Scheme II^a



^a Methods: (1) Me₂NCH(OMe)₂, 95 °C; (2) TsN₃, CH₂Cl₂, 25 °C, 24 h; (3) Ph₂CO, *cis*- or *trans*-2-butene, -30 °C, *hν* (>280 nm)³; (4) separation; (5) TsNHNH₂; (6) NaOMe, DME, <0.5 torr 165 °C;⁴ (7) CH₂N₂, CuCl.⁵

Stereochemical assignments to the three observed pyrolysis products **12**–**14** are based on the absence of symmetry in the ¹H and ¹³C NMR spectra of **13** and on the following three criteria:



(1) chemical shifts (δ) of the doubly allylic methylene protons, which by analogy to those of the 2,5-heptadienes,⁷ would be expected to resonate furthest downfield in the *cis,cis* isomer **12**, furthest upfield in the *trans,trans* isomer **14**, and at an intermediate position in the *cis,trans* isomer **13**, because of the deshielding effect of a nearby methyl group; (2) magnitudes of the observed homoallylic proton–proton couplings, which in model systems⁸ are found to be larger in the *transoid* than in the *cisoid* configuration. (Double irradiation experiments at 500 MHz extracted the coupling constants $J_{cd} = 0.83$ and $J_{bd} < 0.35$ Hz for diene **12** and

(1) Berson, J. A.; Bauer, W.; Campbell, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 7515.

(2) (a) Aue, D. H.; Reynolds, R. N. *J. Org. Chem.* **1974**, *39*, 2315. (b) Reynolds, R. N. Ph.D. Thesis, University of California, Santa Barbara, CA, 1977, University Microfilms No. 78-587.

(3) Cf.: Jones, M.; Ando, W. *J. Am. Chem. Soc.* **1968**, *90*, 2200.

(4) Cf.: Kirmse, W.; Pook, K. H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 594.

(5) Cf.: Wiberg, K. B.; Burgmaier, G. J. *Tetrahedron Lett.* **1969**, 317.

(6) New substances were characterized by elemental composition and spectroscopic properties.

(7) Berson, J. A.; Olin, S. S. *J. Am. Chem. Soc.* **1969**, *91*, 777.

(8) Sternhell, S. *Rev. Pure Appl. Chem.* **1964**, *14*, 15.

(9) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779.