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Competitive [4 + 2]-Cycloaddition versus [1,5]-Hydrogen Sigmatropy in a Cycloheptatriene. An Efficient Route to 3-Azatricyclo[5.3.1.$0^{4,10}$]undeca-5,8-diene

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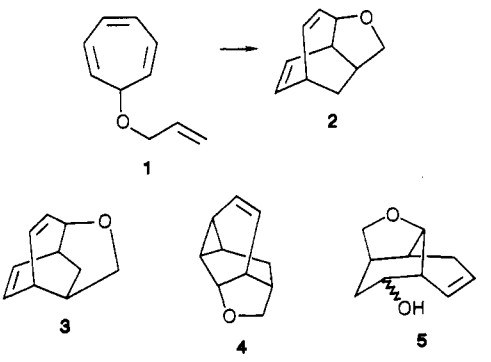
Thermal rearrangements of *N*-acyl-7-aminocyclohepta-1,3,5-trienes **7b–e** in octane or xylene provide [4 + 2]-cycloaddition products **8b–e** and [1,5]-hydrogen sigmatropic rearrangement products **9b–e**. The relative rate of formation for **8e**/**9e** is 1.5 in refluxing octane. At a higher reaction temperature in xylene and longer reaction times, **7b** afforded a second hydrogen-shift product **10b**. No thermal [3,3]-carbon shift products were observed from *N*-allyl cycloheptatrienes **9b–e** or **10b** in octane or xylene. The thermal behavior of **7b–e** can be contrasted with that of *O*-allyl cyclohepta-1,3,5-triene **1**.

Weth and Dreiding[1] in a study of the thermal (150 °C) behavior of 7-(allyloxy)cyclohepta-1,3,5-triene (**1**) isolated allyltropones derived from [1,5]-hydrogen sigmatropic rearrangements followed by Claisen rearrangements, but no intramolecular cycloaddition to **2** was reported. Subsequently, Majerski and Zuanic,[2] following an earlier communication without experimental details by Cupas and co-workers,[3] heated **1** to 200 °C for 24 h; although a pair of allyltropone cycloadducts were the main products, they did manage to isolate 4% of the tricyclic ether cycloadduct **2**. Recently, Clemans and Dobbins[4] have reported that tropylium ion and allyl alcohol in aqueous medium at 25 or 65 °C led to mixtures of bridged oxatricyclic and oxatetracyclic cycloaddition products **2–5**; however, allyl ether **1** did not afford these products under identical reaction conditions (Scheme I).

Pursuant to our interest in bridged nitrogen heterocycles,[5] the above reports suggested that substitution of allylamine or an *N*-acyl-*N*-allylamine for allyl alcohol might provide a preparative route to azapolycycles having relatively rigid skeletal frameworks. However, when *N*-(ethoxycarbonyl)-*N*-allylamine (**6b**) was stirred for 50–70 h with tropylium tetrafluoroborate in water or 80% aqueous tetrahydrofuran, either at 25 °C or at reflux, a small amount of the nucleophilic addition product **7b** was isolated, but none of the expected nitrogen-containing cycloaddition products analogous to **2–5** were formed. Adduct **7b** was also obtained when allylamine (**6a**) and tropylium tetrafluoroborate were stirred in 7% aqueous ether and the oily amine addition product **7a** was acylated by using ethyl chloroformate; repetition of the reaction leading to **7a** in water or 80% tetrahydrofuran at 25 °C or at reflux still failed to afford nitrogen-containing cycloaddition products (Scheme II).

Scheme I



To our surprise, when *N*-(ethoxycarbonyl)-*N*-allylamine **7b** was refluxed for 46 h under conditions of high dilution in xylene, the intramolecular cycloadduct **8b** was recovered in synthetically acceptable 67% yield[6] accompanied by two

(1) Weth, E.; Dreiding, A. S. *Proc. Chem. Soc., London* **1964**, 59–60.
(2) Majerski, Z.; Zuanic, M. *J. Org. Chem.* **1983**, *48*, 898–901.
(3) Cupas, C.; Schumann, W.; Heyd, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 3237–3239.
(4) Clemans, G. B.; Dobbins, M. A. *Tetrahedron Lett.* **1982**, *23*, 387–390.
(5) For leading references, see: (a) Krow, G. R.; Carey, J. T.; Zacharias, D. E.; Knaus, E. E. *J. Org. Chem.* **1982**, *47*, 1989–1993. (b) Krow, G. R. *Tetrahedron* **1981**, *37*, 1283–1307. (c) Krow, G. R.; Carey, J. T.; Cannon, K. C.; Henz, K. J. *Tetrahedron Lett.* **1982**, *23*, 2527–2528. (d) Krow, G. R.; Szczepanski, S. W. *J. Org. Chem.* **1982**, *47*, 1153–1156. (e) Krow, G. R.; Johnson, C.; Boyle, M. *Tetrahedron Lett.* **1978**, 1971–1974.

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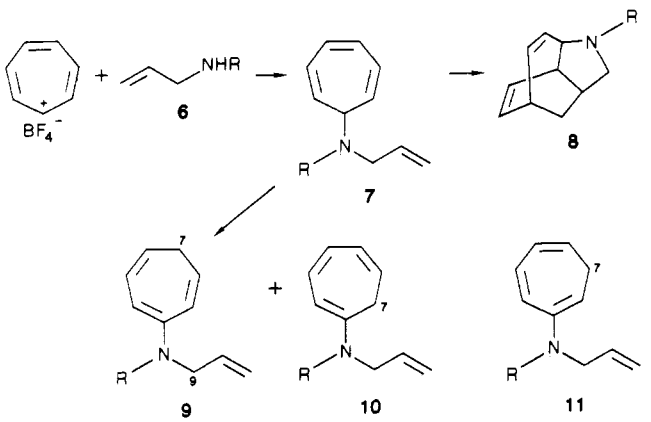
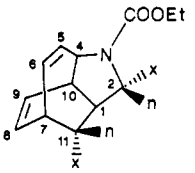
Scheme II[a]



[a] **a**, R = H; **b**, R = COOEt; **c**, R = COMe; **d**, R = COOBn; **e**, R = COPh.

Table I. Proton NMR Data for Structure 8b



proton	shift,[a] δ	multiplicity[b]
1	2.52	ddd, $J(1,10) = 7$, $J(1,2x) = J(1,11x) = 8$
2x	3.78	dd, $J(2x,2n) = 11$
2n	3.17	d
4	4.42	m
5	5.58	m, broadened by urethane conformers
6	6.25	dd, $J(6,7) = 6.5$, $J(5,6) = 10$
7	2.73	ddd, $J(7,8) = 8$, $J(7,11x) = 5.0$
8	6.65	dd, $J(8,9) = 8.5$
9	5.98	dd, $J(9,10) = 8$
10	2.90	ddd, $J(4,10) = 7$
11x	2.03	ddd, $J(11x,11n) = 12$
11n	1.72	d

[a] 360 MHz, 70 °C, $CDCl_3$. [b] J in hertz.

hydrogen-shift products **9b** and **10b**. The structural assignment for **8b** followed from the decoupled 360-MHz ^1H NMR spectrum shown in Table I.

Structure **9b** was partially ambiguous because of overlapping resonances for H-2, H-5, and H-10. However, the *N*-acetyl analogue **9c**, obtained along with cycloadduct **8c** following reflux of *N*-acetyl-*N*-allylamine **7c** for 4 h in refluxing xylene, proved helpful. The structure of **9c** was uniquely assigned with the aid of ^1H NMR decoupling experiments. Protons H-1 and H-6 of **9c** (δ 5.5 and 5.44, dt, J = 9, 7.5 Hz) were shown to be coupled to H-7 (δ 2.3, t, J = 7.5 Hz), and H-1 was coupled to H-2 (δ 6.0, d, J = 9 Hz). This finding rules out an isomeric *N*-acetyl-*N*-allyl-2-aminocyclohepta-1,3,5-triene structure (**11c**) in which the proton H-1 would be a triplet by virtue of its coupling to H-7. Structure **10b** was uniquely characterized by the appearance of H-7 (δ 2.57) as a doublet (J = 7 Hz).

In order to better understand the competition between [4 + 2]-cycloaddition and hydrogen sigmatropy, we followed the thermal reactivity of *N*-(benzyloxycarbonyl)-*N*-allyl-7-aminocyclohepta-1,3,5-triene (**7d**) in refluxing octane (124 °C) by HPLC using a UV detector. Under these conditions, after 90% reaction of **7d**, the only products observed were cycloadduct **8d** (56%) and [1,5]-hydrogen shift product **9d** (43%). Because of peak overlap between **7d** and its [1,5]-hydrogen shift product **9d**, it was not possible to follow the rate of the proton shift. This problem was overcome by using *N*-benzoyl-*N*-allyl-7-aminocyclohepta-1,3,5-triene (**7e**), which afforded **8e** (k = 0.20 h^{-1}) and **9e** (k = 0.13 h^{-1}). Both products were thermally stable under the reaction conditions. Although accurate relative rate data were not obtained for **7d** going to **9d**, the rates of formation of cycloadducts **8d** and **8e** were nearly identical, and the effect of changing the *N*-acyl substituent from alkoxycarbonyl to acyl was not significant.

The [4 + 2]-cycloaddition of the *N*-allyl side chain with two double bonds of the cycloheptatriene in **7d,e** competes favorably with [1,5]-hydrogen sigmatropy. The *N*-allyl and *O*-allyl side chains might have been expected to have similar dienophilicities. For example, using Taft σ_I values as an estimate of electron-withdrawing power, we estimate a value of σ_I = 0.26–0.28 for NRCOOEt, which is similar to σ_I = 0.26 for OMe.[7] Alternatively, if one makes an analogy to the catalytic effect of oxyanions on [1,5]-hydrogen sigmatropy,[8] it may be that one of the lone electron pairs of a 7-ether oxygen is better able to achieve proper orbital alignment to facilitate [1,5]-hydrogen sigmatropy than is a 7-nitrogen atom with a single lone pair of delocalized electrons. The *N*-acyl substituent may also interfere with attainment of the optimal orbital alignment for [1,5]-hydrogen sigmatropy.[9] As a consequence, intramolecular cycloaddition of **7** to give **8** becomes energetically competitive with [1,5]-hydrogen sigmatropy to **9**.[10]

For thermal reactions of **1**, [3,3]-carbon sigmatropy is an important process.[1,3] However, the absence of [3,3]-carbon shift products from **9** and **10** is not surprising.[11] This process would involve formation of a C=N—COR bond, and highly electrophilic *N*-acyl imines are relatively unstable species.[12] The driving force leading to formation of a carbonyl group from an *O*-allyl ether is greater than for creation of an *N*-acyl imine from an *N*-acyl-*N*-allylamine.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer 137, 710B or 727B spectrometer by using neat oils on sodium chloride plates. ^1H NMR spectra were recorded in $CDCl_3$ solutions with tetramethylsilane as reference standard by using a Perkin-Elmer R-32 90-MHz spectrometer. High field NMR spectra were recorded by using a Bruker 360-MHz spectrometer; ^{13}C NMR spectra were recorded by using a Varian XL-100 spectrometer at 25.16-MHz operating frequency. Analyses were performed by Micro-Tech Laboratories, Inc., Skokie, IL; high-resolution mass spectra were recorded at the Penn State University mass spectral facility. Ultraviolet spectra were recorded in methanol solutions by using an HP 8450A UV/visible spectrophotometer. Thin-layer chromatography was conducted by using Analtech-GF silica gel plates containing fluorescent indicator. Flash column chroma-

(6) Compare the photochemical formation of structurally similar cycloadducts. Gilbert, A.; Drestonosich, S.; Wilson, S. *Tetrahedron Lett.* **1982**, *23*, 4061–4064.

(7) Wells, P. R.; Ehrenson, S.; Taft, R. W. *Prog. Phys. Org. Chem.* **1968**, *6*, 147–322.

(8) Paquette, L. A.; Crouse, G. D.; Sharma, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 3972–3974.

(9) (a) Houk, K. N.; Rondan, N. G. *Tetrahedron Lett.* **1984**, *25*, 2519–2522. Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, 109, 3139–3140. (b) Note the difference between neighboring amide and amine upon the propensity for a [1,3]-shift. Krow, G. R.; Reilly, J. *J. Am. Chem. Soc.* **1975**, *97*, 3837–3838.

(10) Systematic investigation of competition between [4 + 2]-cycloaddition and [1,5]-hydrogen sigmatropy are few. (a) Shishido, K.; Ito, M.; Shimada, S.; Fukumoto, K.; Kametani, T. *Chem. Lett.* **1984**, 1943–1946. (b) Arnold, B. J.; Sammes, P. G.; Wallace, T. W. *J. Chem. Soc., Perkin Trans. 1* **1974**, 415–420.

(11) Jolidon, S.; Hansen, H.-J. *Helv. Chim. Acta* **1977**, *60*, 978–1032 and references cited. Aromatic amino-Claisen rearrangements are slower than the oxy-Claisen analogues.

(12) Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3087–3128.

tography[13] was performed by using Merck silica gel (230–400 mesh). Octane and xylene were distilled over calcium hydride and stored over sodium pellets. All reactions were performed under a positive pressure of dry argon or nitrogen.

***N*-(Ethoxycarbonyl)-*N*-allyl-7-aminocyclohepta-1,3,5-triene (7b).** Tropylium tetrafluoroborate (2.2 g, 12 mmol), allylamine (3.54 g, 62 mmol), and sodium bicarbonate (2.1 g, 25 mmol) in ether (30 mL) and 50% aqueous tetrahydrofuran (5 mL) were stirred for 24 h at 25 °C. Water was added to create two phases, the organic layer was separated, the aqueous layer was extracted with methylene chloride, and solvent was removed in vacuo. The resultant oily amine **7a** was dissolved in methylene chloride (30 mL), cooled to 0 °C, and aqueous potassium hydroxide (10 mL) and ethyl chloroformate (0.84 g, 17 mmol) were added. After 1 h at 25 °C, the organic layer was separated, washed successively with dilute hydrochloric acid and water, and dried over magnesium sulfate, and solvent was removed in vacuo. Elution through a silica gel column (1:1 hexane/ether) afforded 2.14 g (84%) of oil **7b** of greater than 90% purity. Further purification by preparative TLC afforded **7b**: R_f 0.77 (1:1 ether/hexane); 360-MHz ^{1}H NMR δ 6.60 (apparent t, J = 3.1 Hz, H-3,4), 6.12 (dm, J = 9.4, 3.1 Hz, H-2,5), 5.89 (m, vinylic CH), 5.45 (dd, J = 9.4, 4.9 Hz, H-1,6), 5.19 (dd, J = 11.8, 1.5 Hz, vinylic CH_2), 4.17 (q, J = 7.1 Hz, OCH_2), 4.0 (d, J = 5.3 Hz, NCH_2), 3.78 (t, J = 4.9 Hz, H-7), 1.25 (t, J = 7.1 Hz, CH_3); ^{13}C NMR δ 155.33 (s), 134.52 (d), 130.27 (d), 125.17 (d), 122.77 (d), 115.49 (t), 60.63 (t), 56.91 (d), 49.05 (t), 14.09 (q); IR 2950, 1700 cm^{-1}; UV λ_{max} 270 nm (ϵ 9000); high-resolution mass spectrum m/z calcd for $C_{13}H_{17}NO_2$ 219.1260, found 219.1252.

***N*-Acetyl-*N*-allyl-7-aminocyclohepta-1,3,5-triene (7c).** The amine **7a** (1.1 g, 7.5 mmol), prepared as described above, was added to a solution of triethylamine (2 mL) in dichloromethane (50 mL) at 0 °C, and acetyl chloride (1.2 g, 15 mmol) in dichloromethane (10 mL) was added dropwise. After 2 h, the reaction mixture was worked up as above to afford 1.34 g (94%) of oil **7c**: R_f 0.21 (1:1 ether/hexane); 90-MHz ^{1}H NMR δ 6.55 (br, H-3,4), 6.15 (br, H-2,5), 5.85 (br, vinylic CH), 5.60–5.05 (br, H-1,6 and vinylic CH_2), 4.30–3.95 and 3.70 (br, H-9's and H-7), 2.10, 2.00 (2 s, CH_3); ^{13}C NMR δ 169.62 (s, CO), 134.18 (d, C-9), 130.17, 124.14, 123.25 (all d, C-1 to C-6), 115.48 (t, C-10), 56.50 (d, C-7), 48.57 (t, C-8), 21.50 (q, Me); IR 3150, 1665, 1395 cm^{-1}; UV λ_{max} 273 nm (ϵ 5800); high-resolution mass spectrum m/z calcd for $C_{12}H_{15}NO$ 189.1154, found 189.1153.

***N*-(Benzyloxycarbonyl)-*N*-allyl-7-aminocyclohepta-1,3,5-triene (7d).** The amine **7a** (1.60 g, 10.9 mmol) was added to dichloromethane (40 mL) and 3 N sodium hydroxide (10 mL) cooled to 0 °C, and benzyl chloroformate (1.85 g, 10.9 mmol) in dichloromethane (10 mL) was added dropwise over 10 min. Reaction and workup as described above provided after chromatography (3:1 hexane/ether) 2.26 g (74%) of benzyl urethane **7d** as a clear oil: R_f 0.34 (2:1 hexane/ether); 90-MHz ^{1}H NMR δ 7.25 (s, 5 H), 6.50 (t, J = 4 Hz, H-3,4), 6.05 (m, H-2,5), 5.95–5.75 (m, vinylic CH), 5.46 (dd, J = 10, 5 Hz, H-1,6), 5.35–5.00 (m, 4 H), 4.00 (d, J = 5 Hz, H-9's), 3.71 (m, H-7); IR 3000, 1720 cm^{-1}; UV λ_{max} 268 nm (ϵ 4560); high-resolution mass spectrum m/z calcd for $C_{18}H_{19}NO_2$ 281.1416, found 281.1411.

***N*-Benzoyl-*N*-allyl-7-aminocyclohepta-1,3,5-triene (7e).** To a cold (0 °C) solution of the amine **7a** (1.76 g, 12 mmol) in dichloromethane (70 mL) and 3 N aqueous sodium hydroxide (10 mL) there was added dropwise benzoyl chloride (3.34 g, 24 mmol) in dichloromethane (10 mL). The reaction mixture was warmed to room temperature and stirred for 12 h. The usual workup and flash chromatography (2:1 ether/hexane) afforded 1.65 g (55%) of **7e** as an oil: R_f 0.33 (1:1 ether/hexane); 90-MHz ^{1}H NMR δ 7.26 (s, Ph), 6.45 (apparent t, J = 4 Hz, H-3,4), 6.15–5.90 (m, H-2,5), 5.85 (m, vinylic CH), 5.43 (dd, J = 9, 4 Hz, H-1,6), 5.35–5.05 (m, vinylic CH_2), 4.08 (d, J = 5 Hz, NCH_2), 3.65 (t, J = 4 Hz, H-7); ^{13}C NMR δ 171.25 (s), 136.19 (s), 134.31 (d), 130.48 (d), 129.11 (d), 127.75 (d), 126.27 (d), 124.36 (d), 123.39 (d), 116.19 (t), 58.31 (d), 49.13 (t); IR 2950, 1665 cm^{-1}; UV λ_{max} 311 nm (ϵ 2250); high-resolution mass spectrum m/z calcd for $C_{17}H_{17}NO$ 251.1311, found 251.1305.

***N*-(Ethoxycarbonyl)-3-azatricyclo[5.3.1.0^{4,10}]undeca-5,8-diene (8b), *N*-(Ethoxycarbonyl)-*N*-allyl-3-aminocyclohepta-1,3,5-triene (9b), and *N*-(Ethoxycarbonyl)-*N*-allyl-1-aminocyclohepta-1,3,5-triene (10b).** A 0.025 M solution of **7b** (612 mg, 2.95 mmol) in dry xylene (108 mL) was refluxed for 46 h under nitrogen. Removal of solvent in vacuo and elution through a silica gel 60 column (5:1 hexane/ether) afforded 411 mg (67%) of cycloadduct **8b** as an oil: R_f 0.36 (2:1 hexane/ether); 360-MHz ^{1}H NMR (70 °C) δ 4.17 (q, J = 7 Hz, OCH_2), 1.25 (t, J = 7 Hz, CH_3), and see Table I; ^{13}C NMR δ 154.48 (s), 141.45 (d), 137.94 (d), 126.70 (d), 125.84 (d), 60.48 (t), 56.56 (d), 52.93 (t), 42.21 (d), 39.69 (t), 35.11 (d), 33.41 (d), 14.49 (q); IR 2940, 1695, 1410 cm^{-1}; high-resolution mass spectrum m/z calcd for $C_{13}H_{17}NO_2$ 219.1260, found 219.1253. Anal. Calcd: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.87; H, 7.81; N, 6.10. The analytical sample of **8b** was prepared by VPC using a 2 m × 0.25 in., 5% SE 30 on Chromosorb G column at 175 °C, flow rate = 60 mL/min, t_R = 12.8 min. Additionally, there were obtained by column chromatography 93 mg (15%) of a 1,5-shift product **9b**, R_f 0.44 (2:1 hexane/ether), and 91 mg (15%) of **10b**, R_f 0.51 (2:1 hexane/ether), the product expected from two consecutive 1,5-hydrogen shifts. Structure **9b** was characterized by 90-MHz ^{1}H NMR δ 6.55 (d, J = 7 Hz, H-4), 6.2–5.9 (br, H-2, H-5, H-10), 5.40 (br, H-1, H-6), 5.20–5.05 (br, H-11), 4.15 (overlapping d, J = 6 Hz, H-9's and q, J = 7 Hz, OCH_2), 2.28 (t, J = 6 Hz, H-7), 1.20 (t, J = 7 Hz, CH_3); IR 1695 cm^{-1}; UV λ_{max} 271 nm (ϵ 5700); high-resolution mass spectrum m/z calcd for $C_{13}H_{17}NO_2$ 219.1260, found 219.1259.

Structure **10b** was characterized by 90-MHz ^{1}H NMR: δ 6.50 (apparent t, J = 3 Hz, H-3,4), 6.22 (m, H-5), 6.05 (m, H-2), 5.77 (m, H-10), 5.40 (dt, J = 9, 6 Hz, H-6, irradiation of H-7 removes the 6-Hz coupling to give a d), 5.17 (m, H-11), 5.02 (dd, J = 7, 2 Hz, H-11'), 4.20 (q, J = 7 Hz, OCH_2), 4.05 (d, J = 6 Hz, H-9's), 2.57 (d, J = 6 Hz, H-7), 1.25 (t, J = 7 Hz, CH_3); ^{13}C NMR δ 155.13 (s), 133.37 (d), 131.20 (s), 128.53 (d), 128.20 (d), 126.66 (d), 120.22 (d), 117.76 (d), 116.42 (t), 61.52 (t), 54.04 (t), 33.64 (t), 14.30 (q); IR (CH_2Cl_2) 2980, 1695, 1360 cm^{-1}; UV λ_{max} 271 nm (ϵ 5200); high-resolution mass spectrum m/z calcd for $C_{13}H_{17}NO_2$ 219.1260, found 219.1251.

Heating of cycloadduct **8b** (187 mg) in dry xylene (36 mL) for 16 h at reflux under argon and removal of solvent gave 180-mg (96%) recovery of **8b**.

***N*-Acetyl-3-azatricyclo[5.3.1.0^{4,10}]undeca-5,8-diene (8c) and *N*-Acetyl-*N*-allyl-3-aminocyclohepta-1,3,5-triene (9c).** To a degassed solution of dry xylene (220 mL) at reflux under argon there was added a solution of the amide **7c** (946 mg, 5.0 mmol) in dry xylene (30 mL). The solution was heated at reflux for 4 h and then worked up as previously described. Column chromatography (2:1 ether/hexane) provided 282 mg (30%) of a first fraction shown to be the [1,5]-shift product **9c**: R_f 0.20 (2:1 ether/hexane); 360-MHz ^{1}H NMR δ 6.55 (d, J = 6 Hz, H-4), 6.18 (dd, J = 9, 6 Hz, H-5), 6.0 (d, J = 9 Hz, H-2), 5.8 (ddt, J = 15, 9, 6 Hz, H-10), 5.50 and 5.44 (2 dt, J = 9, 7.5 Hz, H-1,6), 5.10 (d, J = 15 Hz, H-11), 4.20 (d, J = 6 Hz, H-9), 2.30 (t, J = 7.5 Hz, H-7), 2.0 (s, Me); ^{13}C NMR δ 169.25 (s, CO), 143.40 (s, C-3), 133.18 (d, C-9), 129.95, 127.15, 124.57, 122.39, 121.52 (all d, C-1, C-2, C-4, C-5, C-6), 116.97 (t, C-10), 51.05 (t, C-8), 27.44 (t, C-7), 21.70 (q, CH_3); IR 3020, 1665 cm^{-1}; UV λ_{max} 271 nm (ϵ 2000); high-resolution mass spectrum m/z calcd for $C_{12}H_{15}NO$ 189.1153, found 189.1151. The second fraction was 522 mg (55%) of the cycloadduct **8c**: R_f 0.73 (acetone); 90-MHz ^{1}H NMR δ 6.65 (overlapping dd, J = 8 Hz, H-8), 6.40–6.10 (m, H-6), 5.95 (overlapping dd, J = 8 Hz, H-9), 5.75–5.30 (m, H-5), 4.73 and 4.35 (2 t, J = 5 Hz, H-4), 4.05–3.70 (m, H-2x), 3.28 (d, J = 10 Hz, H-2n), 3.15–2.45 (m, H-1, H-7, H-10), 2.11 and 2.00 (2 s, COMe), 2.2–1.65 (m, H-11); IR 3000, 1720 cm^{-1}; high-resolution mass spectrum m/z calcd for $C_{12}H_{15}NO$ 189.1153, found 189.1145.

***N*-(Benzyloxycarbonyl)-3-azatricyclo[5.3.1.0^{4,10}]undeca-5,8-diene (8d) and *N*-(Benzyloxycarbonyl)-*N*-allyl-3-aminocyclohepta-1,3,5-triene (9d).** A solution of triene **7d** (274 mg, 0.98 mmol) in dry octane (80 mL) was refluxed under nitrogen for 16 h to provide after removal of solvent and chromatography (1:1 hexane/ether) 119 mg (43%) of **9d** and 154 mg (56%) of **8d**. **9d**: R_f 0.56 (3:1 hexane/ether); 90-MHz ^{1}H NMR δ 7.25 (Ph), 6.50 (br, H-4), 6.0 (m, H-2, H-5, H-10), 5.40 (m, H-1, H-6), 5.15 (br, H-11 and OCH_2Ph), 4.15 and 4.0 (2 d, J = 6 Hz, NCH_2), 2.27 (t, J = 6 Hz, H-7); IR 3000, 1710 cm^{-1}; IR 3000, 1710 cm^{-1}; UV λ_{max} 209 nm (ϵ 11 500); high-resolution mass spectrum m/z calcd for

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$C_{18}H_{19}NO_2$ 281.1416, found 281.1420. **8d**: R_f 0.28 (3:1 hexane/ether); 90-MHz ^{1}H NMR δ 6.63 (dd, J = 8, 8.5 Hz), 6.20 (dd, J = 10, 7 Hz), 5.90 (t, J = 8.5 Hz), 5.55 (br), 5.15 (s, $PhCH_2$), 4.45 (m), 3.80 (m), 3.15 (d, J = 11 Hz), 2.9–1.60 (br, 5 H); IR 2990, 1710 cm^{-1}; high-resolution mass spectrum m/z calcd for $C_{18}H_{19}NO_2$ 281.1416, found 281.1421.

***N*-Benzoyl-3-azatricyclo[5.3.1.0^{4,10}]undeca-5,8-diene (8e) and *N*-Benzoyl-*N*-allyl-3-aminocyclohepta-1,3,5-triene (9e).** A solution of triene **7e** (825 mg, 3.3 mmol) in dry xylene (218 mL) was refluxed under argon for 5 h to provide after workup and preparative TLC (1:1 hexane/ether) three fractions. The first was 45 mg (5%) of [1,5]-shift product **9e**: R_f 0.40; 360-MHz ^{1}H NMR δ 6.30 (d, H-4, collapses to a singlet upon irradiation at δ 5.9), 5.9 (m, H-2,5,10), 5.3–5.1 (br, H-1, H-6,11's), 4.42 (d, J = 7 Hz, H-9's), 2.05 (t, J = 7 Hz, H-7, collapses to a singlet upon irradiation at δ 5.15); IR 2890, 1665 cm^{-1}; high-resolution mass spectrum m/z calcd for $C_{17}H_{17}NO$ 251.1311, found 251.1306. A second fraction, R_f 0.30, was 279 mg (52%) of benzoylallylamine (**6e**) resulting from cleavage of the C-7–N bond of **7e**. The third fraction was 125 mg (15%) of cycloadduct **8e**: R_f 0.19; 90-MHz ^{1}H NMR δ 7.35 (br, Ph), 6.65 (br, H-8), 6.23 (br, H-6), 6.05–5.55 (br, H-5,9), 4.25 (br, H-4), 3.72 (br, H-2x), 3.25 (br, H-2n), 3.1–2.4 (br, H-1,7,10), 2.05–1.60 (br, H-11's); IR 2940, 1705, 1390 cm^{-1}; UV λ_{max} 219 nm (ϵ 12 000); high-resolution mass spectrum m/z calcd for $C_{17}H_{17}NO$ 251.1311, found 251.1312.

Kinetic Experiments. The starting cycloheptatriene **7d** or **7e** (0.975 mmol in 80 mL of octane, 12 mM solution) was added to refluxing octane (124 °C), aliquots were drawn at hourly intervals and injected into a Waters HPLC Model 440 fitted with a silica gel (Resolvex-Sil from Fischer Scientific) column using either the solvent system 2% 2-propanol in heptane for **7d** or 4% 2-propanol in heptane for **7e**, and the effluent was monitored by ultraviolet absorption at 254 nm with an integrating recorder for detection of the peaks. Peak integrals were adjusted for differences in absorption of **7–9** at 254 nm. Since cycloadduct **8b** was unchanged after 16 h in refluxing xylene, and [1,5]-shift product **9d** was stable for 16 h in refluxing octane, competitive parallel first-order rate constants were determined for effectively irreversible reactions.

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Oxymetalation. 21.[1] Regioselectivity, Rearrangement, and Direct 1,2-Dioxolane Formation in the Peroxymercuriation of *cis*- and *trans*-1,2-Diphenylcyclopropane

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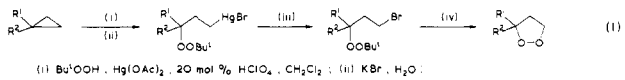
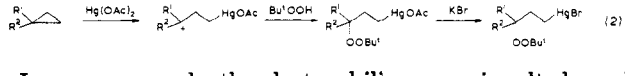
The regiochemistry and stereochemistry of the peroxymercuriation of *trans*- and *cis*-1,2-diphenylcyclopropane (**1a,b**) have been determined. The trans isomer reacted exclusively by 1,3-bond scission to give the threo and erythro γ-peroxymercurials (**3a,b**) along with an unexpected rearrangement product, β-peroxymercurial (**2**). The proportion of **2** varied from 29% for reaction 2 in neat *tert*-butyl hydroperoxide to 68% for reaction with 2 equiv of hydroperoxide in CH_2Cl_2. Methoxymercuriation of **1a** gave only threo and erythro γ-methoxymercurials (**11a,b**) in neat methanol but 60% of rearranged β-methoxymercurial (**10**) with 2 equiv of methanol in CH_2Cl_2. It is suggested that the reactions proceed via the benzylic cation (**12**), which undergoes unimolecular rearrangement by 1,2-phenyl migration competitively with bimolecular trapping by oxy reagent. Rearrangements have not been reported previously in the oxymercuriations of simple cyclopropanes. The cis isomer (**1b**), in contrast, reacted mainly by 1,2-bond scission and yielded the *trans*- and *cis*-1,2-dioxolanes (**15a,b**) and the meso and *d,l* diperoxides (**16a,b**) derived directly from the intermediate γ-peroxymercurials (**18a,b**) by oxidative demercuriation. Trialkylperoxonium intermediates (**19a,b**) are likely to be involved in the production of the dioxolanes. 1,2-Dioxolanes have not been prepared previously by oxidative demercuriation.

In a previous paper,[1] the results of the *tert*-butyl peroxymercuriation of cyclopropane and several mono- and 1,1-disubstituted cyclopropanes were described. A general method was given for the conversion of the resulting γ-peroxymercurials to 1,2-dioxolanes (eq 1).



(1)

(i) Bu^{t}OOH, Hg(OAc)$_2$, 20 mol % HClO$_4$, CH$_2$Cl$_2$; (ii) KBr, H$_2$O; (iii) Br$_2$, NaBr, MeOH; (iv) AgO$_2$CCF$_3$, CH$_2$Cl$_2$



(2)

In every example, the electrophilic mercuric salt cleaved the cyclopropane ring regiospecifically, becoming attached to the least substituted position to give the more stable carbocation. The nucleophile, *tert*-butyl hydroperoxide, added to this more substituted position to give the peroxymercurial (eq 2). This regiochemistry is consistent with the general behavior of mono- and 1,1-disubstituted cyclopropanes toward oxymercuriation.[2]

Oxymercuriations of stereoisomeric cyclopropanes tend to show the same regiochemistry as described above, while the stereochemical outcome may vary considerably.[2] The methoxymercuriation of various stereoisomers of cyclopropanes has been carefully studied by De Puy and McGirk.[3] They found that either retention or inversion can occur at the site of electrophilic substitution but that substantial or complete inversion is found at the site of nucleophilic attack.

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