Preparation of 3-Cycloheptenyl and 3-Cyclooctenyl Derivatives by Solvolysis of Bicyclo[n.2.0]alkyl Esters

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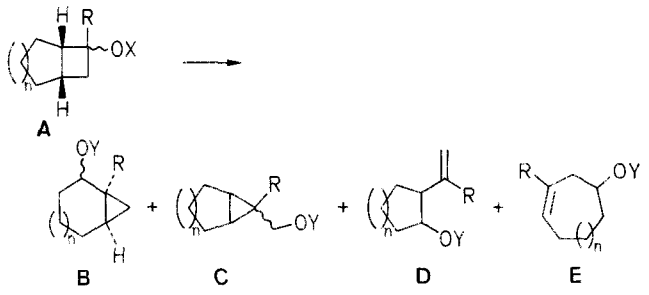
Ester derivatives of 6-substituted *cis*-bicyclo[3.2.0]heptan-6-ol, and of 7-substituted *cis*-bicyclo[4.2.0]octan-7-ol were solvolyzed to the corresponding cycloheptene and cyclooctene products. In general, acetolysis of the 3,5-dinitrobenzoates in glacial or aqueous acetic acid proved most effective for this transformation. The conjugated dienes obtained from *geminal* alkenylhydroxy starting materials were sensitive to polymerization and/or olefin isomerization, but were sufficiently stable to permit spectroscopic characterization and subsequent reaction with dienophiles.

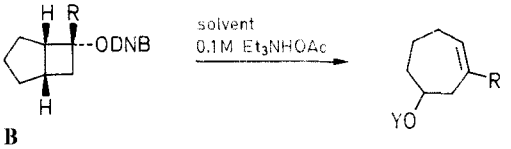
The use of bicyclo[3.2.0]heptane and bicyclo[4.2.0]octane derivatives as precursors to seven and eight-membered carbocyclic compounds is an attractive strategy, which has been put into practice chiefly by applications of the de Mayo reaction.[1,2] In the course of examining some *cis*-bicyclo[3.2.0]heptan-6-ol and *cis*-bicyclo[4.2.0]octan-7-ol derivatives for another purpose, we were prompted to reinvestigate their solvolysis reactions as a means of effecting equivalent ring expansions. Landmark studies by Wiberg et al.[3-6] were not encouraging, since few examples of the desired ring enlargement were reported among the manifold rearrangements of their substrates (Scheme A and Table 1). Because of the mechanistic focus of these early reports, we nevertheless concluded that the prospect for optimization of ring expansion product **E** was worth exploring. Indeed, a recent study on the reactions of 4-alkylidenebicyclo[3.2.0]hept-2-en-6-ol with triflic anhydride has demonstrated a substituent dependent conversion to cycloheptatriene and heptafulvene products.[7]



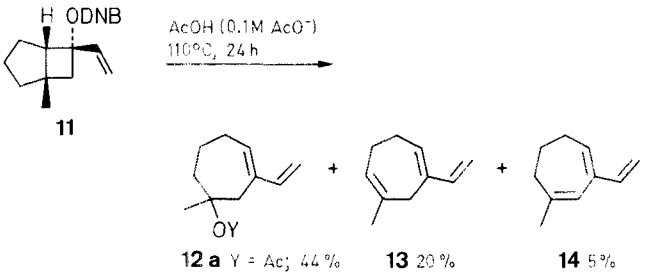
Scheme A

To facilitate comparison, the ensemble of cyclobutyl/cyclopropylcarbinyl/homoallyl products previously identified[3-6,8] are outlined in Scheme **A**, with specific data presented in Table 1. The secondary *endo*-tosylates were observed to solvolyze with assistance from disrotatory opening of the bridgehead bond, but for tertiary analogs such assistance was less pronounced.

The substrates for our study were derivatives of *endo*-3°-alcohols, prepared by Grignard reagent addition to bicyclo[3.2.0]heptan-6-one or bicyclo[4.2.0]octan-7-one. These bicyclic ketones were in turn made from appropriate cycloalkenes by cycloadditon of dichloroketene[9] followed by zinc dust dechlorination. After examining benzoate, *p*-nitrobenzoate, 3,5-dinitrobenzoate and a few tosylate derivatives in formic acid,



Scheme B



Scheme C

Table 1. Major Solvolysis Products from Bicyclo[n.2.0]heptyl and -octyl Derivatives[a]

Substrate (A)[b]	R	X[c]	Solvent[d]	Products[b]	Ref.
H OX, R, H	H	Ts	AcOH (0.05N NaOAc)	40% **D** + 35% **C** (n = 1, Y = Ac)	8
	CH_3	DNB	80% aq. acetone (EDA)	62% **B** + 23% **E** (n = 1, Y = H)	6
	4-$MeOC_6H_4$	DNB	80% aq. acetone (EDA)	>98% **A** (n = 1, X = H, mainly *exo*)	6
H R, OX, H	H	Ts	AcOH (0.05N NaOAc)	>98% **B** (n = 1, Y = Ac, mainly *endo*)	8
	CH_3	DNB	80% aq. acetone (EDA)	61% **B** + 26% **E** (n = 1, Y = H)	6
	4-$MeOC_6H_4$	DNB	80% aq. acetone (EDA)	>98% **A** (n = 1, X = H, mainly *exo*)	6
H OX, R, H	H	Ts	AcOH (0.05N NaOAc)	64% **E** + 32% **B** (n = 2, Y = Ac)	4
H R, OX, H	H	Ts	AcOH (0.05N NaOAc)	>90% **D** (n = 2, Y = Ac)	4

[a] Minor identified products are not listed.
[b] See Scheme **A** for structures.
[c] Ts = tosyl, DNB = 3,5-dinitrobenzoyl.
[d] EDA = ethyldiisopropylamine.

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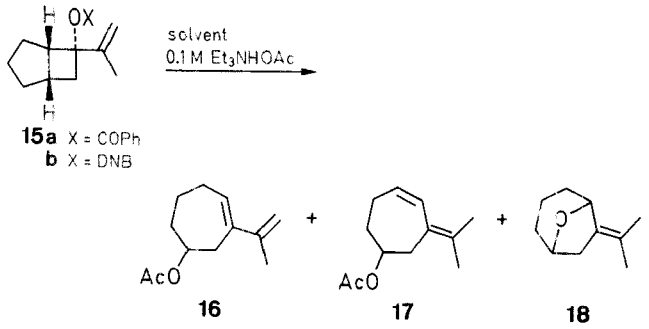


Scheme **D**

Table 2. Acetolysis of 3,5-Dinitrobenzoates **1–5**

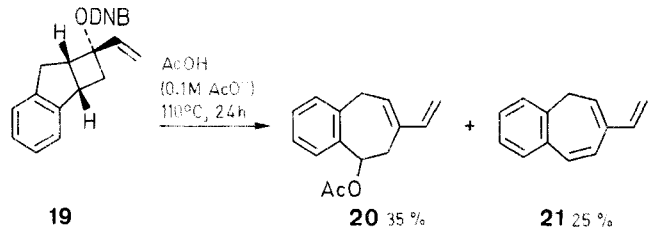
Substrate	R	Reaction Conditions		Products[a]	Yield[b] (%)
		Solvent	Temp (°C)/ Time (h)		
1	CH_3	AcOH	110/24	**6a**	72
				6b	9
2	Et	AcOH	110/24	**7a**	88
				7b	trace
3	Ph	AcOH	110/24	**8a**	80
				8b	6
4	CH_2=CH	AcOH	80/12	**9a**	66
				9b	8
		$AcOH/H_2O$ (3:1)	80/12	**9a**	54
				9c	28
5	CH_3CH=CH (E/Z = 2.5:1)	$AcOH/H_2O$ (3:1)	110/12	**10a**	51
				10c	14

[a] For the structure of substrates and products, see Scheme **B**. **a**, Y = Ac; **b**, Y = DNB; **c**, Y = H.
[b] Yield of isolated products.

Table 3. Solvolysis Products of **15**

Substrate	Reaction Conditions		Yield (%) of Products		
	Solvent	Temp (°C)	**16**	**17**	**18**
15a	AcOH	110	43	48	–
15b	AcOH	100	–	85	–
15a	$AcOH/H_2O$ (3:1)	110	–	35	53
15b	$AcOH/H_2O$ (3:1)	100	–	27	53
15a	$AcOH/H_2O$[a] (3:1)	110	–	–	80
15b	$AcOH/H_2O$[a] (3:1)	110	–	27	42
15a	H_2O	110	–	–	77
15b	H_2O	100	–	–	>90

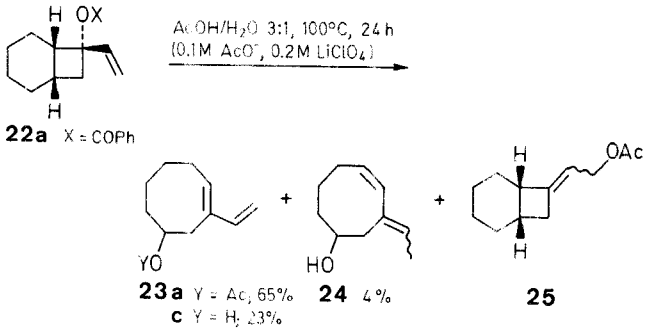
[a] In the presence of $LiClO_4$ (4 equiv).



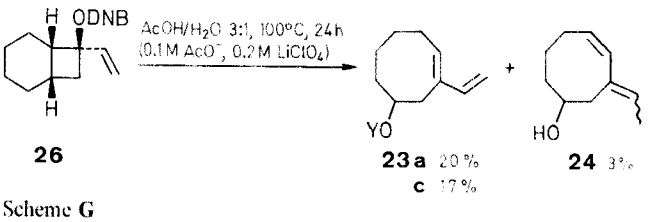
Scheme **E**

acetic acid, DMF, and DMSO solutions, we settled on the acetolysis of 3,5-dinitrobenzoates as the most effective system for our purpose. Finally, the results presented in Tables 2 and 3 together with Schemes **B–E** provide clear evidence that solvolytic conversion of 6-substituted *endo*-6-(3,5-dinitrobenzoyloxy)-bicyclo[3.2.0]heptane to cycloheptenol derivatives is an effective synthetic procedure.

The corresponding homologous transformation of the vinyl-substituted bicyclo[4.2.0]octane analog **(22)** proved capricious and appears to be less general in scope. Acetolysis of **22b**, under the anhydrous conditions that were used effectively with its lower homolog **4**, gave allylic isomer **25**[10] as the major product (70%) together with a small amount of the desired eight-membered ring acetate **23a**. In aqueous acetic acid (3:1) containing lithium perchlorate[11] carbocation formation is enhanced and vinylcyclooctenyl products (**23a** und **c**) dominate (Scheme **F**). Curiously, this was the only substrate, in which the benzoate derivative gave higher yields of ring expanded products than did the 3,5-dinitrobenzoate. The corresponding *exo* isomer **26** proved even less reactive (Scheme **G**).



Scheme **F**



Scheme **G**

Table 4. UV Absorption Data of Selected Compounds[a]

Compound	**8a**	**8b**	**9a**	**9b**	**10a**	**10c**	**12**	**17**	**20**	**21**	**23a**	**23c**
λ_{max} (nm)	247	238	232	234	235	237	234	238	233	236, 276	232	236
log ε	4.25	4.45	4.19	4.18	4.15	4.11	4.36	4.18	3.96	4.24, 3.61	4.12	4.15

[a] All samples were recorded in EtOH, with the exception of **9b**, which was run in CH_3CN.

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Table 5. Substrates and Products **1**–**25**, **27**, and **28** Prepared

Compound	mp (°C)[a]	Molecular[b] Formula or Lit. Data	IR (film/CH_2Cl_2)[c] ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[d] δ, J(Hz)	^{13}C-NMR[d] ($CDCl_3$/TMS) δ	MS (70 eV)[e] m/z (%)
1	129–131	126–127[6]	1727, 1275, 1170 (ester)	1.54–2.05 (m, 7H); 1.74 (s, 3H, CH_3); 2.44 (m, 1H); 2.58 (m, 1H); 2.9 (m, 1H); 9.1 (d, 2H, J = 2.2); 9.2 (t, 1H, J = 2.2)	–	–
2	103–105	$C_{16}H_{18}N_2O_6$ (334.3)	1728, 1275, 1170 (ester)	0.85 (t, 3H, J = 7.4); 1.4–2.9 (m, 6H); 2.1 (q, 2H, J = 7.4); 2.05 (m, 1H); 2.2–2.6 (m, 2H); 2.88 (m, 1H); 9.05 (d, 2H, J = 2.1); 9.14 (t, 1H, J = 2.1)	–	317 (0.44), 305 (2), 267 (6), 195 (80), 122 (18), 68 (100)
3	114–116	$C_{20}H_{18}N_2O_6$ (382.4)	1725, 1275, 1170 (ester)	1.4–2.0 (m, 6H); 2.4–2.7 (m, 3H); 2.9 (m, 1H); 7.1–7.6 (m, 5H); 9.1–9.2 (m, 3H)	–	–
4	84–85	$C_{16}H_{16}N_2O_6$ (332.3)	1730, 1275 (ester); 1630, 990, 900 (vinyl)	1.5–2.1 (m, 7H); 2.6–2.8 (m, 2H); 3.2 (m, 1H); 5.26 (d, 1H, J = 10.8); 5.35 (d, 1H, J = 17.4); 6.28 (dd, 1H, J = 10.8, 17.4); 9.17 (d, 2H, J = 2.0); 9.23 (t, 1H, J = 2.0)	27.2, 32.2, 32.4, 36.8, 49.0, 81.0, 113.8, 122.2, 129.2, 134.5, 139.7, 148.6, 160.7	332 (0.05), 315 (0.09), 247 (1.7), 195 (36), 120 (42), 92 (37), 68 (100)
5	160–165	$C_{17}H_{18}N_2O_6$ (346.3)	1730, 1275, 1170 (ester)	*trans:* 1.4–2.2 (m, 7H); 1.75 (dd, 3H, J = 1.2, 4.3); 2.3–2.8 (m, 2H); 3.2 (m, 1H); 5.6 (m, 1H); 5.8 (m, 1H); 9.1 (m, 2H); 9.3 (m, 1H) *cis:* 1.4–2.2 (m, 7H); 1.7 (dd, 3H, J = 1.7, 7.1); 2.3 (m, 2H); 3.1 (m, 1H); 5.6 (m, 1H); 6.1 (dq, 1H, J = 12.4, 1.7); 9.1 (m, 2H); 9.3 (m, 1H)	–	–
6a		$C_{10}H_{16}O_2$ (168.2)	1722, 1235 (ester); 1630, 1026, 860 (olefin)	1.5–2.2 (m, 6H); 1.78 (s, 3H); 2.0 (s, 3H); 2.5 (dd, 2H, J = 9.8, 10.8); 4.7 (ddd, 1H, J = 2.3, 3.6, 10.0); 5.66 (m, 1H)	21.3, 24.1, 26.1, 27.3, 37.4, 39.3, 71.2, 127.6, 134.1, 170.3	125 (1), 109 (100), 93 (58), 67 (8), 43 (53)
6b		$C_{15}H_{16}N_2O_6$ (320.3)	1725, 1235 (ester); 1640 (olefin)	1.8 (s, 3H); 1.4–2.4 (m, 7H); 2.74 (m, 1H); 5.1 (m, 1H); 5.8 (m, 1H); 9.1 (d, 2H, J = 2.1); 9.23 (t, 1H, J = 2.1)	24.0, 26.2, 27.2, 27.3, 39.1, 74.4, 122.2, 128.4, 129.4, 133.4, 134.6, 148.6, 161.7	195 (3), 108 (100), 93 (52), 80 (10)
7a		$C_{11}H_{18}O_2$ (182.3)	1725, 1235 (ester); 1630, 860 (olefin)	0.96 (t, 3H, J = 7.3); 1.5–2.2 (m, 8H); 2.0 (s, 3H); 2.5 (m, 2H); 4.64 (m, 1H); 5.62 (m, 1H)	12.5, 24.3, 27.3, 32.8, 37.7, 38.1, 71.7, 126.2, 139.8, 170.3	122 (39), 107 (27), 93 (75), 79 (26), 55 (11), 43 (100)
8a		$C_{15}H_{18}O_2$ (230.3)	1725, 1228 (ester); 1600, 860 (olefin)	1.4–2.4 (m, 6H); 2.0 (s, 3H); 2.86 (m, 2H); 4.84 (ddd, 1H, J = 2.6, 3.4, 9.7); 6.2 (dd, 1H, J = 7.2, 7.6); 7.1–7.4 (m, 5H)	21.3, 23.8, 27.8, 37.7, 38.2, 71.4, 125.7, 126.5, 128.1, 131.7, 138.5, 143.9, 170.3	230 (1), 170 (43), 155 (34), 142 (66), 129 (40), 91 (36), 77 (16)
8b	93–95	$C_{20}H_{18}N_2O_6$ (382.4)	1728, 1275 (ester); 1600, 865 (olefin)	1.4–2.36 (m, 6H); 2.8 (d, 1H, J = 14.3); 3.0 (dd, 1H, J = 10.0, 14.3); 5.1 (m, 1H); 6.15 (dd, 1H, J = 6.8, 7.0); 6.9–7.3 (m, 5H); 8.96 (d, 2H, J = 2.1); 9.0 (t, 1H, J = 2.1)	23.5, 27.7, 37.7, 74.3, 122.0, 125.5, 126.6, 128.1, 129.2, 132.1, 134.1, 137.7, 143.4, 148.4, 161.7	382 (4), 195 (17), 170 (100), 155 (61), 142 (93), 129 (44), 115 (29), 91 (56), 75 (31)
9a		$C_{11}H_{16}O_2$ (180.3)	1730, 1175 (ester); 1632, 1605, 995, 900, 860 (olefin)	1.3–2.3 (m, 6H); 2.0 (s, 3H); 2.54 (m, 2H); 4.66 (m, 1H); 4.9 (d, 1H, J = 10.8); 5.1 (d, 1H, J = 17.4); 5.95 (dd, 1H, J = 6.7, 7.1); 6.3 (dd, 1H, J = 10.8, 17.4)	21.2, 27.2, 29.2, 31.4, 73.7, 111.3, 133.6, 136.4, 139.4, 170.3	180 (0.5), 120 (21), 105 (33), 92 (31), 79 (33), 43 (100)
9b	96–99	$C_{16}H_{16}N_2O_6$ (332.3)	1730, 1265 (ester); 1630, 1608, 995, 900, 860 (olefin)	1.48–2.33 (m, 6H); 2.28 (m, 2H); 4.95 (d, 1H, J = 10.8); 5.07 (m, 1H); 5.13 (d, 1H, J = 17.3); 6.07 (dd, 1H, J = 6.9, 7.0); 6.35 (dd, 1H, J = 10.8, 17.4); 9.23 (d, 2H, J = 2.0); 9.28 (t, 1H, J = 2.0)	22.3, 26.4, 30.6, 35.9, 73.0, 110.0, 121.2, 128.4, 133.6, 134.6, 135.2, 138.9, 147.7, 160.8	212 (5), 195 (42), 149 (36), 120 (79), 105 (100), 92 (75), 79 (54)
9c		$C_9H_{14}O$ (138.2)	3250–3100 (OH); 1638, 1608, 998, 900, 860 (olefin)	1.3–2.3 (m, 7H); 2.48–2.57 (m, 2H); 3.65 (m, 1H); 4.88 (d, 1H, J = 10.7); 5.16 (d, 1H, J = 17.4); 5.97 (dd, 1H, J = 6.8, 7.0); 6.32 (dd, 1H, J = 10.7, 17.4)	23.4, 27.8, 35.0, 41.0, 68.4, 110.6, 135.6, 136.9, 140.2	138 (4), 120 (29), 105 (54), 91 (45), 79 (100), 67 (49)
10a		$C_{12}H_{18}O_2$ (194.3)	1725, 1235 (ester); 970, 860 (olefin)	1.3–2.2 (m, 6H); 1.8 (d, 3H, J = 6.5); 2.0 (s, 3H); 2.6 (m, 2H); 4.65 (m, 1H); 5.6 (m, 1H); 5.8 (dd, 1H, J = 6.7, 6.9); 6.0 (d, 1H, J = 15)	18.0, 21.2, 23.9, 27.4, 32.9, 37.2, 71.3, 122.2, 131.9, 134.4, 136.4, 170.2	194 (2), 152 (3), 134 (100), 119 (99), 106 (45), 91 (48), 43 (79)

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Table 5. (continued)

Compound	mp (°C)[a]	Molecular[b] Formula or Lit. Data	IR (film/CH_2Cl_2)[c] ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[d] δ, J(Hz)	^{13}C-NMR[d] ($CDCl_3$/TMS) δ	MS (70 eV)[e] m/z (%)
10c		$C_{10}H_{16}O$ (152.2)	3600–3300 (OH); 975, 860 (olefin)	1.3–2.25 (m, 7H); 1.76 (d, 3H, J = 6.3); 2.57 (m, 2H); 3.68 (m, 1H); 5.7 (m, 1H); 5.86 (t, 1H, J = 6.9); 6.05 (d, 1H, J = 15.6)	18.0, 23.6, 27.7, 36.0, 41.0, 68.4, 122.1, 132.3, 134.9, 136.4	152 (35), 134 (39), 119 (100), 106 (52), 91 (88), 79 (59), 65 (20)
11	112–114	$C_{17}H_{18}N_2O_6$ (346.3)	1723, 1270 (ester); 1630 (olefin)	1.5–2.0 (m, 6H); 1.3 (s, 3H); 2.2 (d, 1H, J = 13.8); 2.5 (dd, 1H, J = 13.8, 3.2); 2.65 (m, 1H); 5.3 (d, 1H, J = 17.4); 5.38 (d, 1H, J = 10.7); 6.3 (dd, 1H, J = 10.7, 17.4); 9.12 (d, 2H, J = 2.1); 9.22 (t, 1H, J = 2.1)	24.8, 26.5, 28.1, 39.8, 40.9, 42.3, 52.8, 79.8, 114.8, 122.1, 129.1, 135.5, 139.9, 148.6, 160.7	346 (0.03), 331 (0.3), 304 (1), 290 (0.5), 195 (12), 134 (13), 82 (100), 67 (25)
12a		$C_{12}H_{18}O_2$ (194.3)	1728, 1250 (ester)	1.4–2.0 (m, 6H); 1.44 (s, 3H); 1.93 (s, 3H); 2.7 (d, 1H, J = 14); 2.87 (d, 1H, J = 14); 4.88 (d, 1H, J = 10.8); 5.14 (d, 1H, J = 17.4); 5.85 (t, 1H, J = 6.8); 6.24 (dd, 1H, J = 10.8, 17.4)	22.3, 22.5, 23.7, 35.8, 42.6, 82.0, 111.0, 134.2, 137.3, 140.4, 170.4	–
12b		$C_{17}H_{18}N_2O_6$ (346.3)	–	1.45–2.1 (m, 6H); 1.66 (s, 3H); 2.8 (d, 1H, J = 14); 3.0 (d, 1H, J = 14); 5.0 (d, 1H, J = 10.8); 5.24 (d, 1H, J = 17.4); 5.96 (t, 1H, J = 6.8); 6.37 (dd, 1H, J = 10.8, 17.4); 9.0 (d, 2H, J = 2.1); 9.07 (t, 1H, J = 2.1)	–	–
13		$C_{10}H_{14}$ (134.2)	–	1.7 (d, 3H, J = 0.7); 2.1–2.3 (m, 4H); 2.9 (br s, 2H); 4.85 (d, 1H, J = 10.8); 5.04 (d, 1H, J = 10.8); 5.44 (m, 1H); 5.76 (t, 1H, J = 6.8); 6.25 (dd, 1H, J = 10.8, 17.4)	25.9, 26.7, 29.7, 30.1, 109.5, 110.1, 124.6, 133.0, 133.3, 140.9	–
14		$C_{10}H_{14}$ (134.2)	–	1.4 (s, 3H); 1.4–2.4 (m, 6H); 4.65 (m, 1H); 4.9 (d, 1H, J = 10.8); 5.1 (d, 1H, J = 17.4); 5.76 (m, 1H); 6.26 (dd, 1H, J = 10.8, 17.4)	–	–
15a		$C_{17}H_{20}O_2$ (256.4)	1725, 1275 (ester); 1640, 830 (olefin)	1.5–2.0 (m, 6H); 1.7 (m, 3H); 2.1 (m, 1H); 2.56 (m, 1H); 2.85 (m, 1H); 3.0 (m, 1H); 5.0 (m, 1H); 5.2 (m, 1H); 7.5 (m, 2H); 7.7 (m, 1H); 8.1 (m, 2H)	17.9, 25.5, 32.5, 36.0, 48.5, 80.7, 109.4, 128.2, 129.3, 130.8, 132.6, 142.2, 164.6	188 (9), 151 (2), 135 (4), 105 (100), 77 (34)
15b	116–118	$C_{17}H_{18}N_2O_6$ (346.3)	1730, 1275 (ester)	1.5–2.0 (m, 7H); 1.76 (m, 3H); 2.6 (m, 1H); 2.9 (m, 1H); 3.1 (m, 1H); 5.05 (m, 1H); 5.2 (m, 1H); 9.12 (d, 2H, J = 2.2); 9.23 (t, 1H, J = 2.2)	17.9, 25.7, 27.4, 32.4, 32.6, 36.0, 48.3, 83.4, 110.4, 122.2, 129.1, 134.5, 144.6, 148.4, 160.5	346 (0.2), 317 (0.2), 278 (2), 195 (44), 119 (36), 67 (100)
16		$C_{12}H_{18}O_2$ (194.3)	–	1.3–2.2 (m, 6H); 1.8 (s, 3H); 1.97 (s, 3H); 2.57 (m, 2H); 4.58 (m, 1H); 4.82 (s, 1H); 4.98 (s, 1H); 6.0 (t, 1H, J = 7)	–	–
17		$C_{12}H_{18}O_2$ (194.3)	1725, 1238 (ester)	1.55–2.8 (m, 6H); 1.67 (s, 3H); 1.69 (s, 3H); 1.96 (s, 3H); 5.0 (m, 1H); 5.6 (m, 1H); 6.28 (d, 1H, J = 11)	20.6, 21.4, 24.3, 32.0, 35.5, 73.3, 125.9, 129.1, 131.6, 132.0, 170.6	194 (3), 152 (5), 134 (31), 119 (69), 91 (87), 78 (22), 56 (26), 43 (100)
18		$C_{10}H_{16}O$ (152.2)	–	1.2–2.7 (m, 8H); 1.58 (s, 3H); 1.64 (s, 3H); 4.4 (m, 1H); 4.68 (m, 1H)	16.4, 20.4, 21.1, 30.2, 30.7, 34.8, 75.4, 76.4, 120.0, 134.7	152 (43), 135 (52), 109 (100), 95 (40), 81 (62), 67 (43), 55 (24)
19		$C_{20}H_{16}N_2O_6$ (380.4)	1723, 1270 (ester)	2.3 (dd, 1H, J = 4.8, 13.1); 3.0–3.2 (m, 2H); 3.3 (m, 1H); 3.5 (m, 2H); 5.2–5.4 (m, 1H, J = 10.8); 5.3 (d, 1H, J = 17.4); 6.2 (dd, 1H, J = 10.8, 17.4); 6.9–7.2 (m, 4H); 8.8 (d, 2H, J = 2.1); 9.0 (t, 1H, J = 2.1)	33.1, 39.1, 40.8, 48.4, 82.3, 114.7, 122.0, 123.8, 124.6, 126.7, 129.0, 134.1, 138.7, 144.2, 146.2, 148.4, 160.5	380 (0.1), 212 (2), 168 (27), 116 (100), 105 (7)
20		$C_{15}H_{16}O_2$ (228.3)	–	2.1 (s, 3H); 2.5 (m, 1H); 2.7 (d, 1H, J = 15); 3.36 (dd, 1H, J = 7, 17); 3.66 (d, 1H, J = 17); 4.8 (d, 1H, J = 10.8); 4.94 (d, 1H, J = 17.5); 5.86 (t, 1H, J = 7); 6.2 (dd, 1H, J = 10.8, 17.5); 6.28 (dd, 1H, J = 4, 11); 7.0–7.3 (m, 4H)	–	168 (26), 153 (5), 129 (10), 116 (100)

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Table 5. (continued)

Compound	mp (°C)[a]	Molecular[b] Formula or Lit. Data	IR (film/CH_2Cl_2)[c] ν(cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[d] δ, J(Hz)	^{13}C-NMR[d] ($CDCl_3$/TMS) δ	MS (70 eV)[e] m/z (%)
21		$C_{13}H_{12}$ (168.2)	–	3.0 (d, 2H, J = 7.0); 4.96 (d, 1H, J = 10.8); 5.16 (d, 1H, J = 17.5); 5.74 (t, 1H, J = 7.0); 6.3 (dd, 1H, J = 10.8, 17.5); 6.68 (d, 1H, J = 11.8); 7.0–7.32 (m, 5H)	34.2, 113.0, 125.7, 126.2, 126.7, 127.4, 128.5, 128.6, 130.0, 135.5, 137.4	168 (87), 167 (100), 152 (32), 141 (32), 115 (51), 98 (16), 63 (26)
22a		$C_{17}H_{20}O_2$ (256.3)	1715, 1275 (ester); 1640, 990, 895 (olefin)	1.0–1.9 (m, 8H); 2.25 (m, 1H); 2.4 (m, 2H); 2.64 (m, 1H); 5.16 (dd, 1H, J = 0.9, 10.7); 5.3 (dd, 1H, J = 0.9, 17.3); 6.25 (dd, 1H, J = 10.7, 17.3); 7.4 (m, 2H); 7.46 (m, 1H); 7.96 (m, 2H)	21.5, 22.0, 22.5, 25.2, 25.4, 35.2, 42.7, 79.6, 113.7, 128.2, 129.5, 130.9, 132.7, 139.0, 165.1	256 (0.1), 151 (0.8), 135 (2), 105 (100), 77 (51)
22b	103–104	$C_{17}H_{18}N_2O_6$ (346.3)	1725, 1275 (ester); 1630, 995, 900 (olefin)	1.0–1.9 (m, 8H); 2.27 (m, 1H); 1.38–2.5 (m, 2H); 2.7 (m, 1H); 5.3 (d, 1H, J = 10.8); 5.4 (d, 1H, J = 17.4); 6.3 (dd, 1H, J = 10.8, 17.4); 9.1 (d, 2H, J = 2.1); 9.2 (t, 1H, J = 2.1)	21.4, 22.0, 22.4, 25.0, 25.1, 34.9, 42.6, 81.9, 113.3, 122.1, 129.2, 134.6, 137.6, 148.4, 160.9	317 (0.1), 290 (0.1), 212 (0.2), 195 (27), 134 (10), 82 (77), 67 (94), 55 (100)
23a		$C_{12}H_{18}O_2$ (194.3)	1725, 1242 (ester); 1640, 1608, 1000, 903, 860 (olefin)	1.3–2.2 (m, 8H); 2.04 (s, 3H); 2.6 (m, 2H); 4.95 (m, 1H); 5.0 (d, 1H, J = 10.9); 5.3 (d, 1H, J = 17.5); 5.78 (t, 1H, J = 8.2); 6.33 (dd, 1H, J = 10.9, 17.5)	21.4, 21.7, 27.0, 29.1, 31.3, 73.9, 111.4, 133.8, 136.5, 139.5, 170.5	194 (3), 134 (37), 119 (39), 105 (41), 91 (35), 43 (100)
23c		$C_{10}H_{16}O$ (152.2)	3630–3320 (OH); 1638, 1607, 1000, 902, 860 (olefin)	1.15–1.86 (m, 7H); 2.26 (m, 2H); 2.58 (m, 2H); 3.8 (m, 1H); 4.96 (d, 1H, J = 10.8); 5.25 (d, 1H, J = 17.4); 5.76 (t, 1H, J = 8.3); 6.36 (dd, 1H, J = 10.8, 17.4)	21.2, 26.8, 28.8, 32.3, 34.9, 71.2, 110.7, 133.6, 136.8, 140.2	152 (37), 134 (40), 123 (60), 119 (100), 105 (49), 93 (95), 91 (89), 79 (78), 55 (37)
24-OAc		$C_{12}H_{18}O_2$ (194.3)	–	1.44–1.90 (m, 4H); 1.82 (d, 3H, J = 5.7); 2.06 (s, 3H); 2.4 (m, 2H); 2.8 (dd, 2H, J = 6.8, 16.4); 5.04 (m, 1H); 5.37 (ddd, 1H, J = 3.4, 8.5, 12.0); 5.67 (q, 1H, J = 5.7); 6.14 (d, 1H, J = 12.0)	–	–
26	121–123	$C_{17}H_{18}N_2O_6$ (346.3)	1725, 1335 (ester); 1660 (olefin)	1.1–1.9 (m, 9H); 1.45 (m, 2H); 2.8 (m, 1H); 5.23 (dd, 1H, J = 1.0, 10.7); 5.3 (m, 1H); 6.2 (dd, 1H, J = 10.7, 17.4); 9.05 (d, 2H, J = 2.1); 9.12 (t, 1H, J = 2.1)	22.0, 22.2, 22.8, 26.5, 27.0, 35.0, 42.3, 88.1, 117.8, 122.0, 129.3, 134.9, 136.0, 148.6, 161.2	346 (0.1), 303 (0.3), 290 (0.3), 212 (0.1), 195 (19), 134 (20), 82 (100), 67 (93), 55 (39)
27a	119–122	$C_{13}H_{16}O_4$ (236.3)	3600–3200 (OH); 1845, 1779 (anhyd.)	1.1–2.5 (m, 10H); 2.57 (ddd, 1H, J = 1.7, 7.0, 15.5); 3.4 (m, 1H); 3.5 (dd, 1H, J = 5.1, 9.3); 3.58 (ddd, 1H, J = 1.6, 7.0, 9.3); 3.72 (br s, 1H); 5.83 (m, 1H)	25.6, 26.2, 29.6, 40.8, 42.1, 42.6, 46.8, 47.7, 73.6, 123.8, 143.8, 173.7, 175.9	236 (5), 218 (4), 190 (39), 145 (100), 118 (52), 93 (58), 71 (58)
27b	103–107	$C_{13}H_{16}O_4$ (236.3)	3610–3290 (OH); 1846, 1778 (anhyd.)	1.4–2.5 (m, 10H); 2.35 (ddd, 1H, J = 1.7, 7.0, 15); 3.2 (br s, 1H); 3.5 (m, 1H); 3.58 (ddd, 1H, J = 1.8, 7.0, 9.0); 4.0 (m, 1H); 5.73 (m, 1H)	23.9, 25.5, 30.3, 38.1, 41.8, 42.6, 42.8, 68.2, 76.6, 124.9, 143.5, 173.8, 176.2	236 (1), 218 (6), 190 (56), 145 (100), 118 (30), 93 (29)
28	136–137	$C_{13}H_{14}O_4$ (234.3)	1849, 1781 (anhyd.); 1707 (ketone)	1.4–2.5 (m, 9H); 2.83 (d, 1H, J = 15); 3.18 (d, 1H, J = 15); 3.48 (m, 2H); 5.7 (m, 1H)	20.1, 24.6, 28.5, 40.3, 41.1, 43.6, 47.0, 50.9, 125.1, 138.5, 173.6, 175.8, 206.8	234 (50), 206 (32), 188 (34), 118 (51), 105 (61), 91 (100), 68 (72)

[a] Uncorrected, measured on either a Thomas-Hoover apparatus or a Reichert hot-stage microscope. Samples crystallized from *n*-hexane/ether.

[b] Satisfactory microanalyses obtained: C ± 0.2, H ± 0.10, or high resolution MS gave a mass value for the molecular ion within 0.0008 amu of the calculated value.

[c] Recorded on a Perkin-Elmer model 599 grating spectrophotometer.

[d] Recorded on a Bruker WM-250 spectrometer at 250 MHz for protons and 69.8 MHz for carbon.

[e] Obtained on a Finnigan 4000 mass spectrometer at 70 eV.

Vinyl alcohol substrates **4, 5, 11, 19**, and **22** yielded conjugated diene products in yields ranging from 60 to over 80%. Although these products **9, 10, 12, 20**, and **23** are prone to polymerization, when freshly prepared they may be used effectively in subsequent reactions, such as the Diels–Alder cycloaddition. The adducts from **9c** were assigned *endo* configurations on the strength of Alder's rule.[12] Poor facial selectivity led to a mixture of epimers, easily separated by chromatography. As expected, oxidation of the **27a** + **b** mixture gave a single ketone **28** (Scheme **H**).

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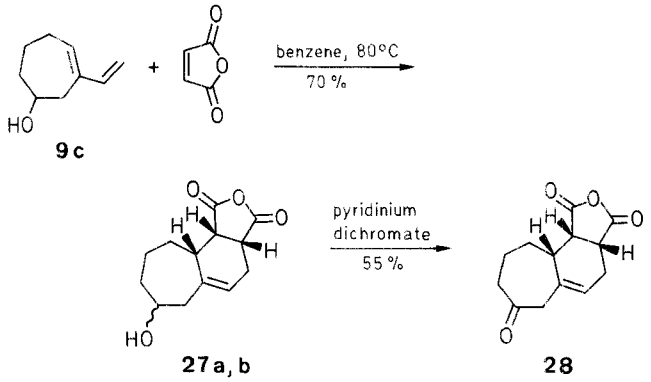
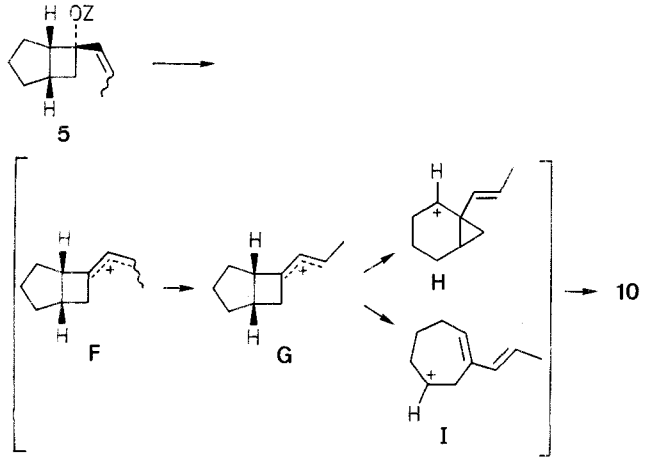


Scheme H

Interestingly, the products **10a** and **c** from the solvolysis of *cis/trans* mixture **5** display ^{13}C-NMR and ^{1}H-NMR spectra that indicate an exclusive *E* configuration. This suggests that an intermediate allylic cation **F** is formed and has sufficient lifetime to undergo isomerization to the more stable configuration **G** before rearranging to a cyclopropylcarbinyl **H** or homoallylic **I** precursor of **10** (Scheme I). The initial diene product **16** from substrate **15** is particularly sensitive to acid-catalyzed isomerization, and under anhydrous conditions the dinitrobenzoate gave acetate **17** as the chief product. The less acidic benzoate yielded **16** and **17** in roughly equal amounts; however, the sensitivity of **16** interfered with its purification, and our structure assignment in this case is tentative. With increasing amounts of water in the solvent, bicyclic ether **18** becomes the major product.



Scheme I

Characteristic properties of the compounds described in this report are presented in Tables 4 and 5.

Except where otherwise indicated, all reactions were conducted under a dry argon or nitrogen atmosphere using solvents distilled from appropriate drying agents. Chromatographic separations were accomplished by flash chromatography[13] (40-63-nm silica gel, Merck 9385). UV absorption spectra were recorded on a Perkin-Elmer/Hitachi model 200 spectrophotometer. Microanalyses were performed by Spang Microanalytical Labs, Eagle Harbor, MI. High resolution mass spectra were measured at the Michigan State University, Department of Biochemistry, Mass Spectroscopy Facility, East Lansing, MI.

Preparation of Starting Materials:
Fused cyclobutanones bicyclo[3.2.0]heptan-6-one,[5] 1-methylbicyclo [3.2.0]heptan-6-one,[15] 2,3-benzobicyclo[3.2.0]hept-2-en-6-one,[14,15] and bicyclo[4.2.0]octan-7-one[14,15] are known compounds. They are prepared by cycloaddition of dichloroketene to the appropriate cycloalkenes, followed by reductive dechlorination, and display properties corresponding to those in the literature.

Grignard reagents, prepared by treating the appropriate alkyl or alkenyl bromide (7.5 mmol) dissolved in THF (10 mL) with Mg (9 mmol), are reacted with solutions of the desired cyclobutanones (3 mmol) in THF (10 mL) at room temperature. These reactions are quenched by rapid addition to a mixture of ice and sat. NH_4Cl (25 mL), and extracted with ether (3 × 12 mL). The resulting 3°-alcohols are then converted to benzoate or 3,5-dinitrobenzoate esters for characterization. In the case of **1**,[5] **3**,[5] **4**,[16] and **22**[16] the alcohol precursors are known. The yields of these esterifications, using dimethylaminopyridine-catalyzed reactions of acid chlorides with the cyclobutanols, range from 55% to over 90%.

Acetolysis of Dinitrobenzoates or Benzoates in Glacial Acetic Acid (or Aqueous Acetic Acid) Containing Triethylammonium Acetate; Typical Procedures:

(i) *In AcOH at 80°C*: A solution of dinitrobenzoate **4** (166 mg, 0.5 mmol) in 0.1 M Et_3NHOAc in glacial AcOH (10 mL) is stirred at 80°C for 12 h. The mixture is cooled, quenched with water (25 mL), and extracted with ether (3 × 15 mL). The combined ether layer is washed with sat. $NaHCO_3$ (10 mL), and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (silica gel, ether/pentane, 1:3) gives dienyl acetate **9a**; yield: 59.4 g (66%) and dienyl dinitrobenzoate **9b**; yield: 13.3 mg (8%).

(ii) *In AcOH/H_2O (3:1) at 80°C*: To 0.1 M Et_3NHOAc in glacial AcOH (10 mL) is added benzoate **4** (166 mg, 0.5 mmol) and water (3.3 mL). This mixture is stirred at 80°C for 12 h, then cooled, and quenched with water (20 mL). Ether extraction and flash chromatography (silica gel, ether/pentane, 1:1) as in the previous example, yield acetate **9a**; yield: 48.7 mg (54%) and alcohol **9c**; yield: 19.4 mg (28%).

Cycloaddition of 3-Vinyl-3-cyclohepten-1-ol (9c) with Maleic Anhydride: A solution of dienyl alcohol **9c** (92.6 mg, 0.67 mmol) and maleic anhydride (131.5 mg, 1.34 mmol) in benzene (25 mL) is stirred at reflux for 16 h. The solvent is removed, and the residue purified by flash chromatography (silica gel, EtOAc/ether, 1:7) to afford cycloadduct products **27a** and **27b** as a 1:1 mixture; yield: 110 mg (70%).

Oxidation of 27a, b to *cis-cisoid*-4-Oxatricyclo[7.5.0^{2,6}]tetradec-8-ene-3,5,11-trione (28):
A mixture of epimeric alcohols **27a** and **27b** (45 mg, 0.19 mmol) is added to a stirred solution of pyridinium dichromate (144 mg, 0.4 mmol) in DMF (10 mL). Stirring is continued overnight at room temperature; the solution is diluted with water (10 mL) and then extracted with ether (3 × 5 mL). The extract, after washing with brine (10 mL), is dried ($MgSO_4$) and evaporated to give ketone **28** as a yellowish solid; yield: 24 mg (55%). An analytical sample is prepared by crystallization from EtOAc, colorless solid; mp 136–137°C.

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