evaporated under reduced pressure. Chromatography on a Florisil column using pentane gave 62 mg of a mixture of unsaturated ketones 3 + 4[6] (GLC, ^{1}H NMR). 4: ^{1}H NMR δ 5.71 (d, 2 H, HC=CH), 2.10 (s, 3 H, $COCH_3$). Further elution with Et_2O leads to 6: 233 mg (yield 66%); ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 3 H, CH_3), 2.08 (s, 3 H, $COCH_3$); IR (CCl_4) 3400 (OH), 1705 cm^{-1} (C=O).

A solution of 6 (233 mg, 1.5 mmol) in 10 mL of Et_2O was added to a solution of CH_3MgI (5mmol) in 20 mL of Et_2O at room temperature. The mixture was stirred for 15 min and then hydrolyzed ($H_2O/NH_4Cl/Et_2O$). After extraction with ethyl acetate (3 times) the usual workup yielded 235 mg (92%) of *cis*-terpine (7), mp 108 °C, which was identified by comparison with an authentic sample.

α-Terpineol (9). A few drops of anhydrous MeOH was added to the mixture resulting from the dehalogenation of 600 mg of α-bromoketone 1. The solution was allowed to stir for 1 h at 40 °C and then was hydrolyzed (H_2O, $NaHCO_3$) and worked up. The crude product was a mixture (GLC and NMR) of the unsaturated ketones 3 and 4 (30%) and the γ,δ-unsaturated ketone 8 (70%) already described.[8]

8: ^{1}H NMR ($CDCl_3$) δ 1.65 (m, 3 H, CH_3C=C), 2.07 (s, 3 H, $COCH_3$), 5.32 (m, 1 H, HC=O); IR 1675 (C=C) 1720 cm^{-1} (C=O).

The separation of pure 8 from 3 and 4 was difficult. The following procedure was a better mode of preparation of 8.

A solution of hydroxy ketone 6 (359 mg, 2.3 mmol) in 15 mL of toluene was refluxed for 15 min in the presence of some crystals of I_2. After removal of the solvent in a rotatory evaporator, the residue was diluted in pentane, washed with an aqueous solution of $NaHSO_3$ and then twice with saturated $NaHCO_3$ aqueous solution, and dried (Na_2SO_4). Filtration on a Florisil column led to pure 8 (257 mg, 81%).

A solution of 8 (155 mg, 1.12 mmol) in 5 mL of Et_2O was added to an ethereal solution of CH_3MgI (4 mmol) and allowed to stir for 15 min at room temperature. The mixture was then hydrolyzed (H_2O, NH_4Cl), and the aqueous layer was extracted twice with CH_2Cl_2. The organic layers were gathered, washed with water, dried (Na_2SO_4), and concentrated. Filtration on a Florisil column (pentane–ether 3:1) gave 146 mg (85%) of α-terpineol (9). The spectra data of 9 are identical with literature data:[9] ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 6 H, Me_2C), 1.64 (m, 3 H, CH_3C=C), 5.35 (m, 1 H, HC=C); IR 3375 (OH), 1680 cm^{-1} (C=C).

Registry No. *cis*-1, 73839-18-6; *trans*-1, 73839-19-7; 2, 43103-57-7; 3, 22273-97-8; 4, 19876-42-7; 5, 470-82-6; 6, 61187-22-2; 7, 565-48-0; 8, 6090-09-1; 9, 98-55-5; 4-methylcyclohexanone, 589-92-4.

(8) J. H. Babler, D. O. Olsen, and W. H. Arnold, *J. Org. Chem.*, 39, 1656 (1974).
(9) J. G. Grasselli, "Atlas of Spectral Data and Physical Constants for Organic Compounds", CRC Press, Cleveland, OH, 1973.

A New 7-Ring Cycloaddition Reaction[1]

James B. Hendrickson* and James S. Farina

Edison Chemical Laboratories, Brandeis University, Waltham, Massachusetts 02254

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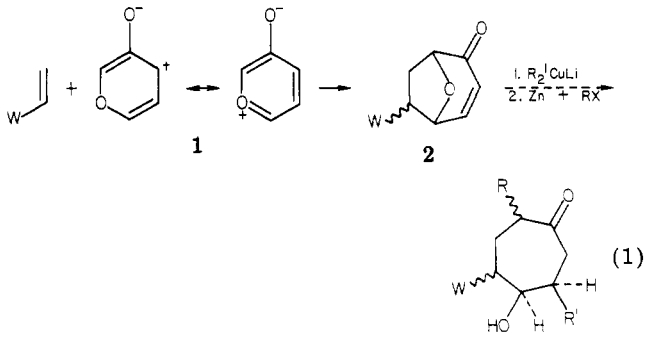
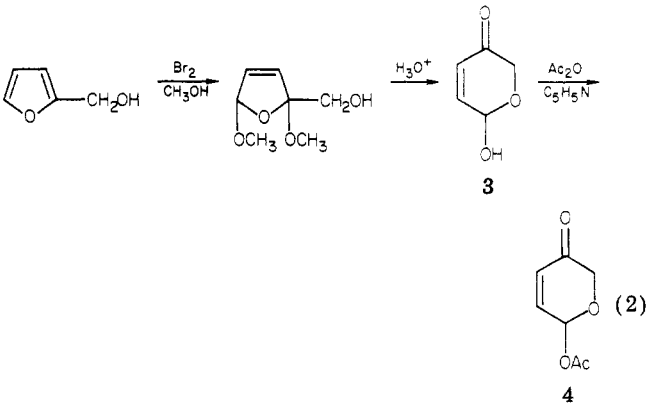
Whereas syntheses of three-, four- and six-membered carbocyclic rings are often efficiently constructed by cycloaddition reactions, there are no analogous general routes to five- and seven-membered rings. We focused on a ($_4\pi$ + $_2\pi$) cycloaddition for the latter and sought a $_4\pi$ component which would be rigid and cisoid in the reactant and rigid for later synthetic stereocontrol in the adduct. Such a model diene for six-membered rings is furan and this expands to 1 for seven-membered rings, with the oxygen anion substituent for regiospecificity and electron enrichment. The product 2 is a multiply functionalized rigid bicyclic system, presumably capable of subsequent synthetic elaboration by conjugate or direct addition from the upper (exo) face and zinc reduction to free the ether bridge as well as to create a specific enolate for α-alkylation by RX as projected in eq 1.



The preparation of a precursor (4) for the pyrylium zwitterion (1) was available from Achmatowicz[2] as summarized in eq 2.



A number of cycloadditions were then examined (summarized in Table I) with a view to examining the scope and the regio- and stereoselectivity of the cycloaddition. In general, the cycloaddition occurred on heating to 130-135 °C for 5–18 h and was monitored by NMR ($CDCl_3$) in sealed NMR tubes. When no adduct was formed (or 4 was heated alone), the precursor 4 was completely consumed and no product from 4 alone could be isolated; unreacted dienophile was generally recovered and acetic acid was always formed. The regiospecificity was secure as predicted for all adducts but the stereoselectivity varied, generally favoring the exo adduct, in contrast to Alder rule expectations based on furan adducts.[3,4] In general, the dienophiles which did not react were less active or more substituted, the latter especially evident in the methyl substitutions on acrolein. The stereochemistry of the adducts was determined by NMR; the exo adducts (e.g., entry 3) have a dihedral angle of ~90° between H-4 and H-5 so that the H-4 absorption at δ 5.46 is only a doublet and becomes a singlet on irradiation of H-3 at δ 7.41. The same reasoning assigns the major adduct stereochemistry

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) O. Achmatowicz, Jr., P. Bukowski, B. Szechner, Z. Zwierzchowska, and A. Zamojski, *Tetrahedron*, 27, 1973 (1971).
(3) J. Sauer, *Angew. Chem., Intl. Ed. Engl.*, 5, 211 (1966); 6, 16 (1967).
(4) We subsequently found that analogous cycloadditions were studied by Katritzky,[5] using oxypyridinium zwitterions with similar results and regiospecificity. The nitrogen bridges formed there, however, are not as easily cleaved or synthetically transformable to other functions.
(5) N. Dennis, A. Katritzky, and Y. Takeuchi, *Angew. Chem., Int. Ed. Engl.*, 15, 1 (1976).

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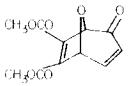
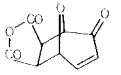
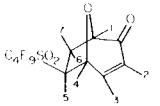
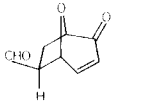
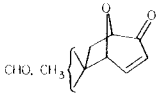
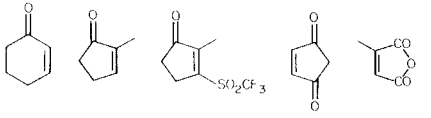
Table I. Cycloheptenones by Cycloaddition

entry	dienophile	product	isolated yield,[a] %	NMR chemical shifts (δ) of hydrogens[b] 1	2	3	4	5	6	7
1	$CH_3OCOC{=}CCOOCH_3$		42 (115–119 °C)	5.23 (2)	5.70 (10.8, 2)	7.43 (10.8, 4.5)	5.34 (4.5)			
2		 (exo:endo, ~3:1)	*c*	4.95 (5)	6.13 (10)	7.53 (10, 5)	5.30 (5)	3.70 (8)	3.94 (8)	
3	$CH_2{=}CHSO_2C_4F_9$		35 (175–180 °C)	4.79 (9, 2)	6.13 (10.8)	7.41 (10.8, 4.5)	5.46 (4.5)	4.29 (9, 5)	2.36 (14, 9, 2)	2.96 (14, 9, 5)
4	$CH_2{=}CHCHO$	 (exo:endo 4:1)	69	4.68 (9)	6.08 (10)	7.34 (10, 4.5)	5.12 (4.5)	3.02 (m)	2.5–2.9 (m)	
5	$CH_2{=}C(CH_3)CHO$	 (one isomer only)	50	4.60 (9, 1.5)	6.22 (10.8)	7.25 (10.8, 4.5)	4.86 (4.5)		1.57 (14, 1.5)	2.90 (14, 9)

Unreactive Dienophiles

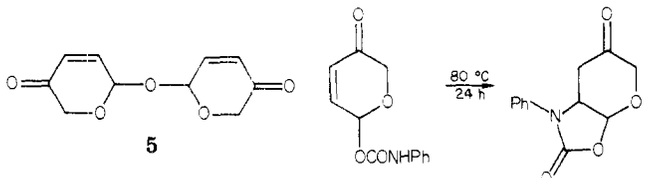
$HC{=}C{-}COOR$ (R = H, CH_3, traces of adducts), $CH_3CH{=}CHCHO$



[a] Isolated by preparative TLC; melting point in parentheses, otherwise noncrystalline. [b] Hydrogens are numbered in entry 3. Coupling constants (hertz) are given in parentheses. [c] Not isolated; exo/endo ratio from NMR of reaction.

in the adducts in entries 2 and 4 as well as their relative proportions in the isolated adduct mixtures. While only one isomer formed in entry 5, the stereochemistry is not available from this probe.

Attempts to vary the conditions of the reaction offered no useful alternatives. With catalysis by boron trifluoride etherate at room temperature, no adduct formed from **4** and dimethyl acetylenedicarboxylate and the precursor **4** was slowly destroyed. In sulfuric or trifluoroacetic acid **4** rapidly turned black. On initiation with bases, precursor **4** at room temperature with triethylamine formed a dimer, the subject of the following paper.[6] Other derivatives of **3** with more active leaving groups were studied. Triflation of **3** at −78 °C (pyridine/CH_2Cl_2) produced an ether dimer **5**, implying rapid loss of triflate to an oxonium interme-



5 6 7

diate which rapidly added a second mole of alcohol **3**. The trifluoroacetate derivative of **3** could be formed at low temperatures but decomposed rapidly at ambient temperature, alone or in the presence of dienophiles, and yielded no adducts or other isolable products. In an attempt to create an acyl derivative which might intramolecularly remove the hydrogen necessary for enolization, we allowed **3** to react with dimethylcarbamoyl chloride and with phenyl isocyanate. In the former reaction a product could not be isolated, but the latter **6**, mp 139–140 °C, formed in 80% yield at room temperature in 6 h. On heating at 80 °C, however, **6** cyclized quantitatively to **7** mp 142–143 °C, which gave no adducts on being heated further with dimethyl acetylenedicarboxylate.

In summary, the precursor **4** proves to be an equivalent of the pyrylium zwitterion **1** for thermal cycloadditions to form ether-bridged cycloheptenones suitable for further synthetic elaboration with regio- and stereocontrol. The cycloaddition, which requires strongly activated dienophiles, proceeds with complete regiospecificity and with stereoselectivity heavily favoring the exo adduct.

Experimental Section

General. Infrared spectra were determined with a Perkin-Elmer Model 137 or 567 infrared spectrophotometer and mass spectra on an AE1 MS-12 spectrometer. ^1H NMR and decoupling experiments were performed on a Perkin-Elmer R-32 90-MHz spectrometer. Chemical shifts are reported in δ values relative to tetramethylsilane as an internal standard. The solvent, $CDCl_3$ or CD_3CN, was filtered through a short column of activity grade I basic alumina immediately before use. Sealed-tube reactions were performed in sealed thick-wall NMR tubes which were also wrapped in aluminum foil during heating. Only dipolarophiles which had been purified by recrystallization or distillation were employed.

Pyrolysis of 2-Acetoxy-1-oxacyclohex-3-en-5-one (4) with Acrolein. The synthesis of 6-formyl-8-oxabicyclo[3.2.1]oct-3-en-2-one (entry 4, Table I) is representative. Pyranose acetate **4**[2] (59.7/mg, 0.38 mmol) was dissolved in 0.35 mL of $CDCl_3$ contained in a pyrolysis tube. To this solution was added 21.3 mg (0.38 mmol) of acrolein. The tube was sealed and placed in an oil bath maintained at ~134 °C for 13 h. Preparative TLC on silica gel with diethyl ether/ethyl acetate (6:5) as eluant (two elutions) afforded 39.9 mg (69% yield) of 6-*exo*-formyl-8-oxabicyclo[3.2.1]oct-3-en-2-one [NMR ($CDCl_3$), Table I; IR ($CHCl_3$) 1740, 1690 cm^{-1}] and the 6-endo isomer [NMR ($CDCl_3$) δ 9.82 (CHO, d, J = 2 Hz)] in a ratio of 4:1, respectively.

The other adducts were prepared in the same way, with yields and data shown in Table I. All showed the characteristic IR band of unsaturated ketone at 1690 ± 10 cm^{-1}.

Registry No. **3**, 35436-57-8; **4**, 62644-49-9; **5**, 65746-82-9; **6**, 74019-32-2; **7**, 74019-33-3; butynedioic acid dimethyl ester, 762-42-5; 2,5-furandione, 108-31-6; 1-(ethenylsulfonyl)-1,1,2,2,3,3,4,4,4-nonafluorobutane, 71561-58-5; 2-propenal, 107-02-8; 2-methyl-2-propenal, 78-85-3; 6,7-dicarbomethoxy-8-oxabicyclo[3.2.1]oct-3,6-dien-2-one, 74019-34-4; *endo*-4,8-epoxy-3a,4,8,8a-tetrahydrocyclohepta[*c*]furan-1,3,7-trione, 74019-35-5; *exo*-4,8-epoxy-3a,4,8,8a-tetrahydrocyclohepta[*c*]furan-1,3,7-trione, 74080-22-1; *exo*-6-nonafluorobutylsulfonyl-8-oxabicyclo[3.2.1]oct-3-en-2-one, 74019-36-6; *endo*-6-formyl-8-oxabicyclo[3.2.1]oct-3-en-2-one, 74019-37-7; *exo*-6-formyl-8-oxabicyclo[3.2.1]oct-3-en-2-one, 74019-38-8; 6-formyl-6-methyl-8-oxabicyclo[3.2.1]oct-3-en-2-one, 74019-39-9; dimethylcarbamoyl chloride, 79-44-7; phenyl isocyanate, 103-71-9.

(6) J. B. Hendrickson and J. S. Farina, *J. Org. Chem.*, following paper in this issue.

A Simple Synthesis of Eight- and Ten-Membered Carbocyclic Rings[1]

James B. Hendrickson* and James S. Farina

Edison Chemical Laboratories, Brandeis University, Waltham, Massachusetts 02254

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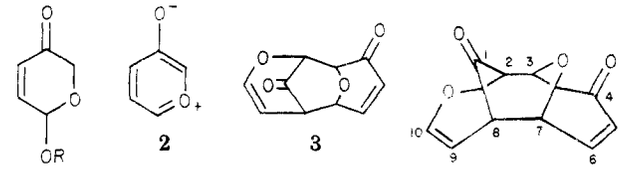
In the course of studies on the cycloadditions of **2** formed from **1** (R = Ac) by pyrolysis,[2] we could not isolate any products on heating in the absence of dienophile. However, when **1** (R = Ac) was treated at room temperature with triethylamine, it was transformed into the isomeric dimer **3**, mp 143–147 °C (mass spectrum, m/e 192 (M^+)) in 68% yield. The infrared spectrum showed carbonyl peaks at 1770 (5.65 μm) and 1690 cm^{-1} (5.92 μm), consistent with **3**. The stereostructure **4** for this doubly



1 2 3 4

bridged eight-membered ring was assigned by NMR decoupling experiments at 270 MHz.[3] The coupling constants for the two pairs of bridgehead protons are $J_{2,3}$ = 8.8 Hz and $J_{7,8}$ = 9.4 Hz. These are consistent with the dihedral angles of 0 °C expected[4] for the central boat ring (1–2–3–O–7–8) in **4**, whereas an analogous dimer of 3-oxypyridinium, formulated with a chair central ring,[5] showed the expected coupling constant of $J \simeq 2$ Hz. Furthermore, no possible dimer of **2** can exhibit more than

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) J. B. Hendrickson and J. S. Farina, *J. Org. Chem.*, preceding paper in this issue.

(3) Spectra were taken on Professor A. Redfield's 270-Hz NMR spectrometer, funded by the National Institutes of Health Grant GM 20168 and the Research Corporation. The assistance of David Harris for decoupling experiments is gratefully acknowledged.

(4) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); S. Sternhell, *Q. Rev., Chem. Soc.*, **23**, 236 (1969).

(5) N. Dennis, B. Ibrahim, and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 1*, 2296, 2307 (1976).

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