Forty-four percent (10 mmol) of the azide was decomposed (gas evolution) and 24% (1.7 mmol) of the aminimide (IR analysis) was decomposed; 1.0 mmol of azo compound **7** (UV analysis) was produced, which is 59% of the aminimide decomposed. The reaction mixture was concentrated (rotary evaporator), the aminimide **6** removed via ether trituration, and the resulting organic layer subjected to preparative TLC. The main product with R_f 0.5 was isolated and provided IR, NMR, and UV spectra identical with that of azo compound **7**.

Base Hydrolysis of *N*-(Dimethylcarbamoyl)-*N*,*N*',*N*'-trimethylazocarboxamide (7). To 0.2 g (0.9 mmol) of azo compound **7** in a 100-mL, helium-purged round-bottom flask connected by Tygon tubing to a 100-mL, three-necked flask filled and submerged in helium-purged $CHCl_3$ was added 20 mL of 10% NaOH via a syringe. The resulting yellow solution effervesced for 2 min. The solution was stirred 14 h and then extracted with 12 × 20 mL of $CHCl_3$. The chloroform layer was dried ($MgSO_4$) and concentrated under vacuum, producing a yellow oil that promptly crystallized. The yellow crystals were purified by preparative TLC (1:1:1 $CHCl_3$/hexanes/acetone). The major band at R_f 0.5 was isolated, producing a solid with spectral characteristics identical with that of 1,1,3-trimethylurea: IR ($CHCl_3$) 3500, 1650 cm^{-1}; NMR ($CDCl_3$) 2.83 (d, 6 H), 2.90 (s, 3 H).

Analysis by GC indicated the gas evolved during the reaction and collected in the 100 mL, three-necked flask was N_2. The presence of CO_2 (dissolved in the aqueous layer as Na_2CO_3) was indicated by a turquoise blue precipitate which resulted upon the addition of $CuCl_2$ (aq). The presence of carbonate ion was also indicated by the evolution of CO_2 when the aqueous layer was added dropwise to concentrated HCl. The aqueous layer was evacuated with a vacuum pump equipped with a helium-purged $CHCl_3$ trap cooled by dry ice/alcohol. After the pumping procedure, dry HCl gas was bubbled through the $CHCl_3$ in the trap, precipitating *N*,*N*-dimethylamine hydrochloride: mp 163-167 °C (lit. 171 °C); IR (Nujol) 3450, 1030, 890 cm^{-1}.

Photolysis of 1,1,4-Trimethyl-1,2,4-triazolidine-3,5-dione 1,2-Ylide (6) in the Presence of Methanol. A stirred solution of 0.526 g (3.67 mmol) of **6**, 5.00 mL of MeOH, and 55.0 mL of CH_2Cl_2 was photolyzed for 42.7 h, resulting in essentially quantitative decomposition of **6** (IR analysis). The photolysis yielded methyl methylcarbamate (**10**) [IR (CH_2Cl_2) 3450, 1730 cm^{-1}] and methyl dimethylcarbazate (**9**) [IR (CH_2Cl_2) 3450, 1738 cm^{-1}; NMR ($CDCl_3$) 3.68 (s, 3 H), 2.56 (s, 6 H)] determined by GC (QF-1, 175 °C) and the methanolysis product,[7] 1,1,4-trimethyl-4-(methoxycarbonyl)semicarbazide [NMR ($CDCl_3$) 3.78 (s, 3 H), 3.20 (s, 3 H), 2.63 (s, 6 H)], isolated by preparative GC (QF-1, 220 °C).

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Registry No. **6**, 54133-08-3; **7**, 103836-47-1; **8**, 33345-40-3; **9**, 55741-07-6; **10**, 6642-30-4; **16**, 103836-49-3; MeNCO, 624-83-9; $Me_2NC(O)N(Me)C(O)NHNHC(O)NMe_2$, 103836-48-2; $ClC(O)OCCl_3$, 503-38-8; Me_2NH·HCl, 506-59-2; dimethylcarbamoyl azide, 13750-17-9; 4,4-dimethylsemicarbazide, 40685-92-5; 2,4,4-trimethylsemicarbazide, 28163-21-5; 1,1,3-trimethylurea, 632-14-4; 1,1,4-trimethyl-4-(methoxycarbonyl)semicarbazide, 103836-50-6.

Cyclopentannulation with a 1,3-Dicarbonyl Dipole Equivalent. Synthesis of Bicyclo[3.3.0]oct-1(5)-ene-2,6-dione

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2-(2,2-Diethoxyethyl)-1,3-dithiane (**5**) in its anionic form undergoes Michael addition to 2-cyclopentenone. Acid hydrolysis of the adduct gives rise to the pair of epimeric diquinane aldols **9** and **10** as well as **11** in ratios that are sensitive to both acid concentration and reaction time. The dehydration of **9** and **10** can be controlled to deliver either the conjugated enone **12** or its β,γ isomer **13**. While **12** is the kinetic product, **13** is thermodynamically favored because of lesser steric strain. Removal of the dithioketal function in **12** and **13** with methyl iodide in hot aqueous acetone leads exclusively to enedione **14**, a molecule much more subject to air-oxidation and self-polymerization than its congeners **15** and **16**.

In the context of projected syntheses of the structurally interesting lycopodium alkaloids magellanine (**1**)[1] and paniculatine (**2**),[2] we have concerned ourselves with assembling the central B/C diquinane unit by an annulation scheme that would place both five-membered rings at oxidation levels suitable for subsequent controlled chemical modification. Since an attractive retrosynthetic analysis involved use of a 1,3-dicarbonyl dipole typified by **3** where the two carbonyl groups are suitably differentiated, efforts have presently been made to develop suitable methodology along these lines in a model system.

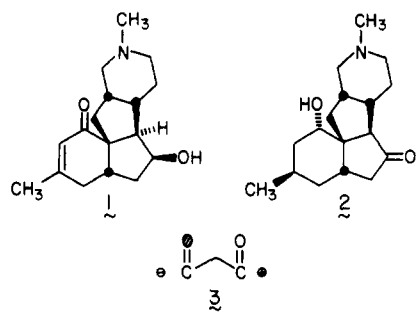

Table I. Product Distributions Arising from Acid-Catalyzed Hydrolysis-Aldolization of 7 (20 °C, Acetone Solution, N_2 Atmosphere)[a]

aqueous HCl, %	reactn time, h	product distribution, % 8	9	10	11
1	144	12.3	5.2	42.8	30.7
5	60	1.3	24.1	20.6	27.5
5	84	0.6	14.4	38.5	33.5
10	20			53.4	32.0

[a] Values represented isolated yields following MPLC on silica gel.

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0022-3263/86/1951-3861$01.50/0

When preliminary examination of the phenylsulfonyl acetal **4** showed this reagent to be an unsatisfactory Michael donor toward 2-cyclopentenone, attention was directed instead to the 1,3-dithiane derivative **5**.[3] A homologue of **5**, viz. **6**, had earlier been shown by Heathcock and co-workers to respond satisfactorily to the demands of conjugate addition to a 2-cyclohexenone derivative.[4] In line with this precedent, the anion of **5** in a solvent system composed of tetrahydrofuran and hexamethylphosphoramide (HMPA) added smoothly to 2-cyclopentenone to afford **7** (Scheme I). Subsequent hydrolysis of **7** with dilute hydrochloric acid in acetone gave rise to as many as four products depending upon reaction conditions. Product distributions realized with different acid strengths and reaction times are compiled in Table I.

Keto aldehyde **8** was, of course, readily identified on the basis of its characteristic spectral properties. A distinction between the diquinane keto alcohols **9** and **10** was arrived at on the basis of several criteria. The greater polarity of exo hydroxyl derivative **9** upon silica gel chromatography followed a pattern previously encountered with polycyclic aldols on several prior occasions.[5] Also, the ^{13}C NMR spectra of these epimers are characterized by a lower field carbinol signal for **9** (75.83 ppm) than for **10** (72.51 ppm). The influence of a variety of substituents on chemical shifts in a wide range of bicyclo[3.3.0]octances has been compiled, and the endo substituents are recognized to exert a greater shielding contribution than their exo counterparts.[6] Although **11** is a single epimer, the stereochemical disposition of its hydroxyl group has not been precisely defined. Neither have we examined the possibility of isomerizing **11** to **9** and/or **10** by previously developed methodology[5] for the purpose of enhancing the overall proportion of diquinane products formed in the annulation process.

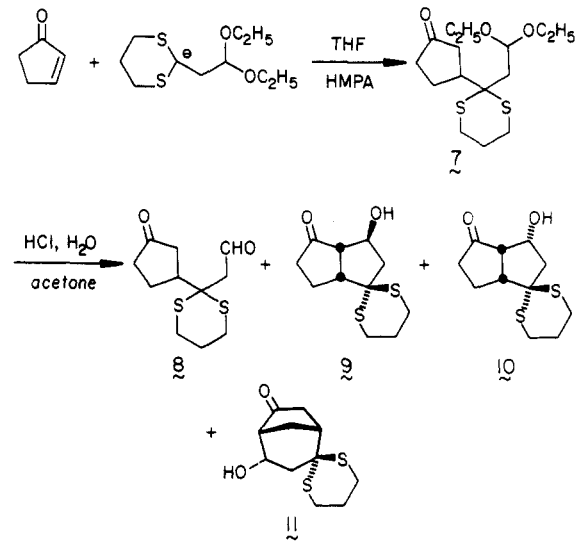
α,β-Unsaturated ketone **12** was obtained in good yield starting from either aldol (Scheme II). Thus, conversion of β isomer **9** to its mesylate and subsequent elimination with triethylamine in tetrahydrofuran solution at room temperature cleanly furnished **12** (82%). Under the conditions of the Mitsunobu reaction[7] involving benzoic acid as the coreagent, α isomer **10** underwent comparably smooth dehydration to **12**. In both circumstances, the formation of **12** is believed to come under kinetic control, loss of the α-carbonyl proton being preferred because of its latent enhanced acidity.

Agosta and Wolff have previously demonstrated that conjugated enones related to **12** are thermodynamically disfavored relative to their β,γ isomers because of ring strain.[8] The extent of destabilization was assessed as approximately 2.4 kcal/mol. To probe whether these thermodynamic factors could be utilized to advantage in the present circumstances, the mesylates of both **9** and **10** were prepared and subsequently exposed to the action of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in different solvent systems. These conditions gave rise efficiently to **13**. Since independent treatment of **12** in this manner also resulted in isomerization to **13**, this conjugated enone gives proper indication of being less thermodynamically stable than its β,γ-unsaturated isomer. The controlled manner in which either **12** or **13** can be generated from **9** or **10** is noteworthy.

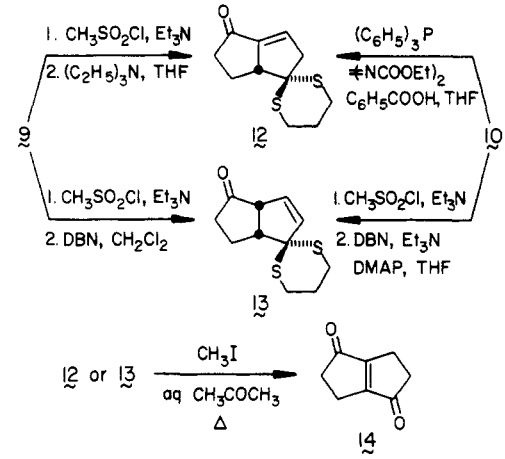
Removal of the dithioketal functionality in **12** and **13** was realized upon heating with excess methyl iodide in aqueous acetone for several hours.[9] In both instances, migration of the double bond to the most highly substituted central position took place to deliver **14**. This enedione proved to be rather sensitive to chromatographic absorbents and also decomposes rapidly on standing in air. These characteristics distinguish **14** from the other pair of known bicyclo[3.3.0]octenediones **15**[10] and **16**[11] and are a likely reflection of the untoward ring strain and electronic effects prevailing in this compact molecule.

Studies designed to explore the utility of the predes-

Scheme I



Scheme II



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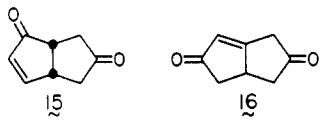

15 16

cribed annulation methodology to the synthesis of **1** and **2** are now underway in this laboratory.

Experimental Section

3-(Phenylsulfonyl)-1,1-(propylenedioxy)propane (4). 2-(2-Bromoethyl)-1,3-dioxane (72.2 g, 0.37 mol) was added to a solution of sodium benzenesulfinate (80.0 g, 0.49 mol) in 200 mL of dry dimethylformamide and the mixture was heated at 110 °C under a nitrogen atmosphere for 17 h. The cooled reaction mixture was poured into saturated brine (200 mL) and extracted with dichloromethane (3 × 200 mL). The combined organic extracts were washed with water, dried, and evaporated. The solid which crystallized after standing for several hours (59.8 g, 63%) was recrystallized from ethyl acetate–petroleum ether (9:1) to give pure **4** as colorless crystals, mp 86–87 °C: IR ($CHCl_3$, cm^{-1}) 3020, 2970, 2850, 1445, 1305, 1280, 1240, 1080, 1025, 875; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91–7.87 (m, 2 H), 7.66–7.52 (m, 3 H), 4.61 (t, J = 4.6 Hz, 1 H), 4.02 (dd, J = 10.7, 4.9 Hz, 2 H), 3.69 (td, J = 12.2, 2.1 Hz, 2 H), 3.26–3.21 (m, 2 H), 2.00–1.93 (m, 3 H), 1.33–1.27 (br d, J = 13.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 139.15, 133.58, 129.20, 128.00, 99.19, 66.71, 50.97, 28.44, 25.44; MS, m/z (M^+ − 1) calcd 255.0691, obsd 255.0695.

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.34; H, 6.37.

2-(2,2-Diethoxyethyl)-1,3-dithiane (5).[3] To a cold (−78 °C), nitrogen blanketed, magnetically stirred solution of 1,3-dithiane (2.0 g, 16.6 mmol) in 50 mL of dry tetrahydrofuran was added n-butyllithium (13.6 mL of 1.22 M, 16.6 mmol). The reaction mixture was strirred for 30 min at −78 °C and for 2 h at −20 °C before anhydrous HMPA (4.3 mL, 1.5 equiv) was introduced at −78 °C. After 15 min, bromoacetaldehyde diethyl acetal (3.4 g, 17.4 mmol) was added in one portion. Stirring was continued at this temperature for 2 h before warming to 0 °C and quenching with water. The product was extracted into ether (2 × 50 mL) and the combined ethereal solutions were washed with brine, dried, and concentrated. MPLC purification of the residue on silica gel (elution with 5% ethyl acetate in petroleum ether) gave **5** as a clear liquid (1.9 g, 74% based on recovered dithiane), bp 103–105 °C (0.1 torr): IR ($CDCl_3$, cm^{-1}) 2980, 2910, 1125, 1060; ^1H NMR (300 MHz, $CDCl_3$) δ 4.77 (t, J = 5.8 Hz, 1 H), 4.08 (t, J = 7.3 Hz, 1 H), 3.66 (dq, J = 7.1, 9.4 Hz, 2 H), 3.53 (dq, J = 7.0, 9.4 Hz, 2 H), 2.93–2.70 (m, 4 H), 2.14–2.02 (m, 3 H), 1.96–1.85 (m, 1 H), 1.21 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 99.79, 61.68, 43.04, 39.60, 29.97, 25.93, 15.32; MS, m/z (M^+) calcd 236.0905, obsd 236.0870.

Anal. Calcd for $C_{10}H_{20}O_2S_2$: C, 50.81; H, 8.53. Found: C, 50.91; H, 8.59.

2-(3-Oxocyclopentyl)-2-(2,2-diethoxyethyl)-1,3-dithiane (7). A cold (−78 °C), magnetically stirred solution of **5** (3.72 g, 15.7 mmol) in 38 mL of dry tetrahydrofuran was treated slowly via syringe with n-butyllithium (15.7 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min at −78 °C and for 2 h at −26 °C before anhydrous HMPA (6.0 mL, 34.5 mmol) was added at −78 °C. After 30 min, a reddish orange color developed. 2-Cyclopentenone (1.29 g, 15.7 mmol) was introduced dropwise during 30 min and the reaction mixture was stirred at −78 °C for 4 h prior to quenching with water at 0 °C. The product was extracted into ether (3×) and the combined ethereal extracts were washed with brine, dried, and evaporated. MPLC purification of the residue on silica gel (elution with 23% ethyl acetate in petroleum ether) furnished 2.21 g of **7** (70% based on recovered **5**) as a viscous, pale yellow oil; IR (neat, cm^{-1}) 2980, 2910, 1740, 1125, 1060; ^1H NMR (300 MHz, $CDCl_3$) δ 4.77 (t, J = 4.5 Hz, 1 H), 3.70–3.45 (m, 4 H), 3.01–2.90 (m, 2 H), 2.75–2.63 (m, 3 H), 2.62–2.27 (m, 5 H), 2.25–2.00 (m, 4 H), 1.86–1.78 (m, 1 H), 1.17 (t, J = 7.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 217.84, 101.51, 61.65, 54.63, 44.53, 41.02, 40.32, 38.97, 25.88, 25.18, 23.83, 15.40; MS, m/z (M^+) calcd 318.1323, obsd 318.1295.

Hydrolysis–Aldolization of 7. A solution of **7** (1.00 g, 3.14 mmol) in 160 mL of acetone was treated with 35 mL of 5% hydrochloric acid and stirred under a nitrogen atmosphere for 60 h at room temperature. The acetone was evaporated, and the residue was taken up in dichloromethane and washed with 10% potassium hydroxide solution and brine. Following drying and solvent evaporation, the residue was separated into its four components by MPLC on silica gel (elution with 70% ethyl acetate in petroleum ether).

For **8**: colorless oil, 10 mg (1.3%); ^1H NMR (300 MHz, $CDCl_3$) δ 9.35 (t, J = 2.7 Hz, 1 H), 3.03 (d, J = 2.9 Hz, 2 H), 3.02–2.74 (series of m, 5 H), 2.58–1.87 (series of m, 8 H).

For **9**: colorless solid, 185 mg (24%), mp 118.5–120 °C (from isopropyl alcohol); IR (KBr, cm^{-1}) 3450, 2905, 1720, 1420, 1215, 1155, 1080, 1050; ^1H NMR (300 MHz, $CDCl_3$) δ 4.33–4.27 (m, 1 H), 3.46 (d, J = 8.5 Hz, 1 H), 3.21 (q, J = 8.0 Hz, 1 H), 3.06–2.75 (m, 6 H), 2.45 (d, J = 5.3 Hz, 1 H), 2.34–2.16 (m, 2 H), 2.12–2.02 (m, 2 H), 1.99–1.82 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 217.39, 75.83, 62.23, 58.33, 52.01, 48.17, 39.17, 28.31, 27.86, 25.11, 23.00; MS, m/z (M^+) calcd 244.0592, obsd 244.0610.

For **10**: colorless crystals, 158 mg (21%), mp 145.5–146 °C (from ethanol); IR (KBr, cm^{-1}) 3530, 2945, 2890, 1730, 1265, 1155, 1100, 1050; ^1H NMR (300 MHz, $CDCl_3$) δ 4.79–4.70 (m, 1 H), 3.24 (q, J = 8.5 Hz, 1 H), 3.07 (t, J = 8.8 Hz, 1 H), 2.94–2.83 (m, 4 H), 2.77 (dd, J = 14.1, 7.0 Hz, 1 H), 2.58 (d, J = 3.7 Hz, 1 H), 2.42–2.26 (m, 2 H), 2.20–1.98 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 219.18, 72.51, 56.41, 55.84, 52.45, 47.47, 40.76, 27.92, 25.05; MS, m/z (M^+) calcd 244.0592, obsd 244.0568.

Anal. Calcd for $C_{11}H_{16}O_2S_2$: C, 54.07; H, 6.60. Found: C, 53.98; H, 6.55.

For **11**: colorless needles, 211 mg (28%), mp 121.5–122.5 °C (from ethanol); IR (KBr, cm^{-1}) 3540–3000, 2960, 2910, 1735, 1425, 1275, 1165, 1130, 1090–1065, 1000, 685; ^1H NMR (300 MHz, $CDCl_3$) δ 4.10–4.07 (m, 1 H), 3.05 (br s, 1 H), 2.90–2.68 (m, 5 H), 2.62–2.43 (m, 4 H), 2.24 (dd, J = 18.8, 7.1 Hz, 1 H), 1.97–1.88 (m, 3 H), 1.50 (dd, J = 14.4, 11.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 218.03, 68.36, 52.77, 52.45, 41.98, 41.34, 40.76, 30.28, 26.26, 26.13, 25.69, 24.86; MS, m/z (M^+) calcd 244.0590, obsd 244.0582.

Bicyclo[3.3.0]oct-1-ene-4,8-dione 4-(Propylene dithioketal) (12). A. Mesylation–Elimination of 9. A solution of **9** (28.8 mg, 0.21 mmol) in dry dichloromethane (10 mL) was cooled to 0 °C under nitrogen and treated with triethylamine (48.6 mg, 0.48 mmol) and methanesulfonyl chloride (28.1 mg, 0.25 mmol). The reaction mixture was stirrred at 0 °C for 30 min before being extracted with 10% hydrochloric acid and then with saturated sodium bicarbonate solution. The organic layer was dried and evaporated to give the mesylate, which was dissolved in dry tetrahydrofuran (5 mL) and treated with triethylamine (36.4 mg, 0.40 mmol). This mixture was stirred for 2 h at room temperature and for 3 h at 50 °C. After cooling, the solution was washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine prior to drying and solvent evaporation. Purification of the residue by MPLC on silica gel (elution with 40% ethyl acetate in petroleum ether) afforded 21.9 mg (82%) of **12** as a colorless crystalline solid, mp 108–109 °C (from ethanol): IR (KBr, cm^{-1}) 2930, 2905, 1700, 1630, 1425, 1405, 1210, 1190, 975, 810; ^1H NMR (300 MHz, $CDCl_3$) δ 6.42 (dd, J = 3.0, 5.8 Hz, 1 H), 3.76–3.68 (m, 1 H), 3.42–3.27 (m, 2 H), 3.00–2.81 (m, 4 H), 2.62–2.55 (m, 2 H), 2.32–2.16 (m, 2 H), 2.08–2.00 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 200.14, 146.10, 130.39, 62.18, 58.90, 55.36, 43.34, 28.95, 28.12, 25.13, 24.64; MS, m/z (M^+) calcd 226.0486, obsd 226.0524.

Anal. Calcd for $C_{11}H_{14}OS_2$: C, 58.37; H, 6.23. Found: C, 58.28; H, 6.30.

B. Mitsunobu Reaction on 10. A magnetically stirred solution of **10** (25.1 mg, 0.103 mmol), triphenylphosphine (108 mg, 0.41 mmol), and benzoic acid (50 mg, 0.41 mmol) in anhydrous tetrahydrofuran (10 mL) was blanketed with nitrogen and treated dropwise with diethyl azodicarboxylate (40.0 μL, 0.25 mmol). After 1.5 h, ether (10 mL) was added and the reaction mixture was extracted with sodium bicarbonate solution and brine prior to drying. Solvent evaporation gave a residue that was subjected to MPLC on silica gel (elution with 30% ethyl acetate in petroleum ether). There was isolated 16 mg (69%) of **12**, identical in all respects with the material described above, and 2 mg (8.5%) of a second substance identified as **13**.

Bicyclo[3.3.0]oct-2-ene-4,8-dione 4-(Propylene dithioketal) (13). A. Mesylation–Elimination of 9. A nitrogen-blanketed solution of **9** (24.5 mg, 0.10 mmol) in cold (0 °C), dry dichloro-

methane (4 mL) was treated with anhydrous triethylamine (9.07 mL, 50.9 mg, 0.50 mmol) and methanesulfonyl chloride (23.7 mg, 0.21 mmol). The reaction mixture was stirred at 0 °C for 30 min, diluted with more dichloromethane (6 mL), and extracted sequentially with 10% hydrochloric acid and saturated sodium bicarbonate solution. Following drying and evaporation of the organic layer, the unpurified mesylate was dissolved in dry dichloromethane (10 mL), treated with DBN (30.2 mg, 0.24 mmol) at room temperature, and stirred for 30 min. Following application of the predescribed workup, the residue was purified by MPLC on silica gel (elution with 40% ethyl acetate in petroleum ether) to give 13.2 mg (58%) of **13** as colorless prisms, mp 99-100 °C (from ethanol): IR (KBr, cm^{-1}) 2940, 2890, 1730, 1425, 1410, 1275, 1265, 1215, 1160, 870, 800; ^1H NMR (300 MHz, $CDCl_3$) δ 5.90 (dd, J = 5.4, 3.0 Hz, 1 H), 5.75 (dd, J = 5.4, 2.4 Hz, 1 H), 3.62-3.60 (m, 1 H), 3.38-3.30 (m, 1 H), 3.05-2.85 (m, 4 H), 2.42-2.23 (m, 2 H), 2.19-1.93 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 215.21, 135.10, 128.92, 62.99, 59.63, 50.78, 39.35, 28.86, 28.04, 24.68, 24.50; MS, m/z (M^+) calcd 226.0486, obsd 226.0493.

B. Mesylation-Elimination of 10. A 34.3-mg (0.14 mmol) sample of **10** was transformed into its mesylate in the fashion described earlier. The unpurified intermediate was dissolved in anhydrous tetrahydrofuran (10 mL) and treated with triethylamine (0.10 mL, 0.70 mmol), 4-(dimethylamino)pyridine (20 mg, 0.16 mmol), and DBN (0.05 mL, 0.40 mmol). The reaction mixture was stirred for 12 h before 3 mL of saturated brine was added to hydrolyze the DBN. Subsequently, the organic layer was washed with 10% hydrochloric acid and saturated sodium bicarbonate solution, dried, and evaporated. Purification of the residue by MPLC on silica gel (elution with 30% ethyl acetate in petroleum ether) afforded 27.8 mg (85%) of **13**.

Base-Promoted Isomerization of 12. A solution of **12** (16.5 mg, 0.073 mmol) in anhydrous tetrahydrofuran (2 mL) was added via canula to a rapidly stirred, nitrogen-blanketed suspension of dry triethylamine (21.8 mg, 0.22 mmol), DBN (50.3 mg, 0.40 mmol), 4-(dimethylamino)pyridine (2 mg, 0.02 mmol), and methanesulfonic acid (14.8 mg, 0.15 mmol) in anhydrous tetrahydrofuran (5 mL). After 24 h at ambient temperature, ether (10 mL) was added and the reaction mixture was extracted with 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine prior to drying. Solvent evaporation and purification by MPLC on silica gel (elution with 30% ethyl acetate in petroleum ether) afforded exclusively **13** (7.5 mg, 46%).

Bicyclo[3.3.0]oct-1(5)-ene-2,6-dione (14). A solution of **12** (45 mg, 0.198 mmol) and methyl iodide (0.1 mL, 1.6 mmol) in 8 mL in 5% aqueous acetone was heated at 55 °C for 11 h with more methyl iodide (0.1 mL) introduced every 2 h until no starting material remained as seen by TLC. After cooling, the acetone was evaporated in vacuo and the residue was taken up in dichloromethane (15 mL). This solution was extracted with sodium bicarbonate solution and brine, dried, and concentrated. MPLC purification (elution with 70% ethyl acetate in petroleum ether) of the concentrate gave 9.1 mg (34%) of **14** as a highly sensitive pale yellow oil: IR ($CDCl_3$, cm^{-1}) 2940, 1700, 1445, 1325, 1195, 1040; ^1H NMR (300 MHz, $CDCl_3$) δ 2.82-2.79 (m, 4 H), 2.58-2.55 (m, 4 H); MS, m/z (M^+) calcd 136.0525, obsd 136.0525.

Analogous treatment of **13** gave comparable results.

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π-Facial and Tautomeric Selectivities during Diels-Alder Capture of Isodicyclopentadienes by Highly Reactive Dienophiles[1]

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The reactions of isodicyclopentadiene (**1**) with hexafluoro-2-butyne, cyclooctyne, cyclobutadiene, and (methoxyvinylcarbene)tungsten pentacarbonyl have been investigated. Cycloaddition involving the two acetylenic dienophiles proceeds with exclusive below-plane stereoselectivity at room temperature and below. When the cyclooctyne reaction mixtures are warmed, increasing amounts of product arising from [4 + 2] addition to the [1,5] sigmatropic isomer of **1** make their appearance. Interestingly, cyclobutadiene was found to add only to **2**. In the case of the Fischer carbene complex, rapid reaction occurred to give the *syn*-sesquinorbornene adduct only. Oxidation of this product with dimethyl sulfoxide led to an ester identical with the adduct derived directly from methyl acrylate and **1**. Structural assignments were made where appropriate on the basis of spectral data, X-ray crystal structure determination, and chemical interconversions.

The three tautomers (**1-3**) of isodicyclopentadiene (**1**) have recently commanded considerable attention for different reasons. In contrast to norbornene which undergoes cycloaddition from its exo face, **1** reacts with dienophiles such as methyl acrylate,[3,4] benzoquinone,[4] dimethyl acetylenedicarboxylate,[5,6] methyl propiolate,[3,4] benzyne,[4] phenyl vinyl sulfone,[7] *N*-phenylmaleimide,[8] and (*Z*)-1,2-bis(phenylsulfonyl)ethylene[9] from below-plane. Inter-

1 **2** **3**

(1) Electronic Control of Stereoselectivity. 34. For Part 33, consult: Paquette, L. A.; Hathaway, S. J.; Schirch, P. F. T.; Gallucci, J. C. *Organometallics* **1986**, *5*, 500.

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