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.

Acknowledgment. This work was financially supported by Public Health Service Grant GM-28468.

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**

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pretation of this pronounced stereoselectivity has proven highly controversial.[10-12] In contrast, tetracyanoethylene[13] and (*E*)-1,2-bis-(phenylsulfonyl)ethylene[9] add to **1** with a decided kinetic preference for above-plane bonding because of the heightened steric bulk present on *both* flanks of their π bond. *N*-Phenyl-[13,14] and *N*-methyltriazolinedione[14] also undergo [4 + 2] addition to **1** with complete exo stereoselectivity. It has been suggested[14] that the stereochemical outcome observed in the last two examples is a direct result of the early timing of their transition states where a strong demand for secondary orbital overlap develops. This Alder-like behavior, which is assumed to be less impelling for the other dienophiles studied, similarly brings with it a unique sensitivity to steric effects that is better accommodated above-plane. Unfortunately, the directionality of stereoalignment is not revealed in the urazole products because of facile pyramidalization at nitrogen. Although tropone[15] and several oxyallyl cation.[15a,16] add exo to **1** for apparently related electronic reasons, certain mechanistic questions remain unanswered.

Despite the fact that **1** is thermodynamically favored, rapid equilibration with **2** can be effected by heating.[5,17] However, even at the highest reaction temperatures studied (180 °C), the concentration of **2** remains below the spectroscopically detectable limit.[18] Notwithstanding, an estimate that **2** is at least 10^4 times more reactive as a diene than **1** can be arrived at from knowledge of the rates of [1,5] hydrogen sigmatropy in these systems[19,20] and a steady-state assumption. As a consequence of this inequality in reactivity, dienophiles that add sluggishly to **1** can be selectively trapped by **2** above 100 °C. Examples of weakly reactive dienophiles that have been captured stereospecifically by **2** from the exo direction include vinylene carbonate,[5] 4-cyclopentene-1,2-dione,[5] (*E*)-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene,[17] (*E*)-1,2-dichloroethylene,[17] and phenyl vinyl sulfoxide.[17]

Maleic anhydride, dimethyl acetylenedicarboxylate, and tetracyanoethylene attack the exo face of **3**, the least thermodynamically stable member of the triad, to give Diels–Alder adducts in which the cyclopentene ring is trans-fused to the norbornane unit.[6,13] As a result of the imposed steric strain, these products are particularly prone to cycloreversion or thermal isomerization.

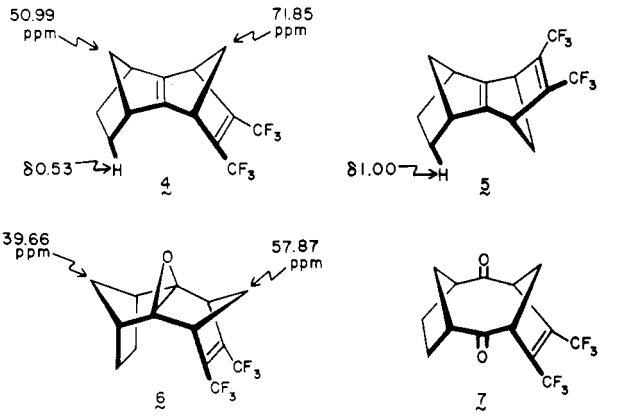
In this paper, we describe an investigation of the mode of reaction followed by isodicyclopentadiene when treated with hexafluoro-2-butyne, cyclooctyne, cyclobutadiene, and (methoxyvinylcarbene)tungsten pentacarbonyl. These reactive 2π reagents were selected for the purpose of providing additional insight into the factors controlling the π-facial and tautomeric selectivities of these unusual tricyclic dienes. The widely different structural features of these dienophiles bear little resemblance to the triazolinedione system. Consequently, the manner in which they might react was not at all clear and held out the possibility for providing new mechanistic information not uncovered with the earlier examples.

Table I. Crystallographic Data for 7

formula wt, amu	326.24
space group	$P2_{1/C}$
a, Å	13.328 (2)
b, Å	7.755 (2)
c, Å	13.657 (1)
β, deg	113.25 (9)
vol, Å^3	1296.77
Z	4
ρ_{calc}, g/cm^{-3}	1.671
$\mu_{(Mo\ K\alpha)}$ (λ = 0.7107)	1.597 cm^{-1}
reflections measd	$\pm h, +k, +l$
2θ limits	4–50°
scan type	ω–2θ
scan angle,	0.75 + 0.35* tan θ
scan speed, deg m^{-1}	0.65–5 (in ω)
data collected	2277
unique data with $I > 3.0\sigma(I)$	1530
R_f	0.053
R_{wf}	0.062

Results

Hexafluoro-2-butyne. Reaction of **1** with excess hexafluoro-2-butyne[21] in pentane solution under an inert atmosphere proceeded smoothly to completion within 4 h at −70 → 0 °C. Gas chromatographic and ^{1}H NMR analysis indicated that two cycloadducts had been produced quantitatively in a 9:1 ratio. The diminished efficiency with which major product **4** (45% isolated) could be obtained in a pure state following chromatographic separation from **5** (3% isolated) can be attributed to its volatility and to a marked propensity for air-oxidation, as witnessed by the isolation of epoxide **6** (6%) and diketone **7** (3%).



Assignment of stereochemistry to the pair of dienes was initially arrived at on the basis of a ^{1}H NMR chemical shift comparison. Especially diagnostic was the highly shielded nature of the endo ethano protons in **4** relative to those in **5** (see formulas). This phenomenon has been encountered previously.[22] In the *anti*-sesquinorbornadiene (**5**), the bis(trifluoromethyl)-substituted double bond is no longer proximal to these hydrogens and a downfield shift

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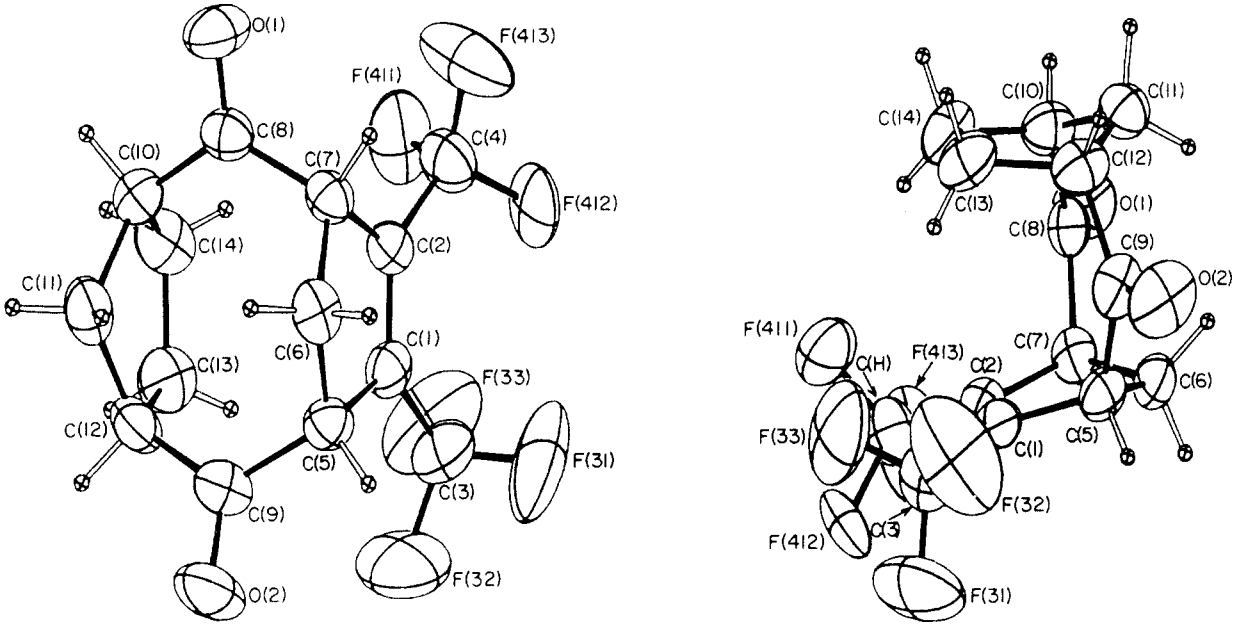


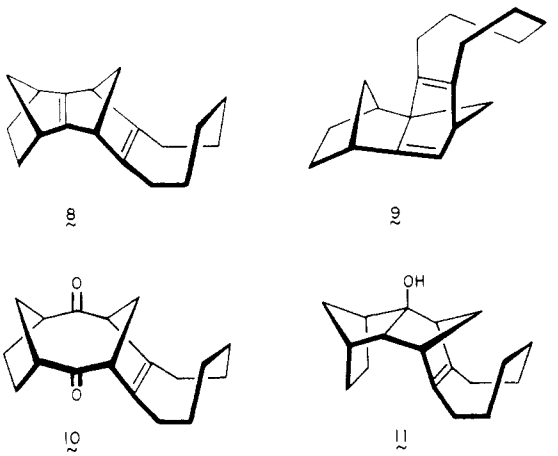
Figure 1. ORTEP drawings of **7** showing top (left) and side views (right) as well as the numbering used. Non-hydrogen atoms are drawn with 50% probability elipsoids, while hydrogen atoms are drawn with an artificial radius.

of 0.47 ppm becomes evident (in $CDCl_3$ solution).

That **4** had been correctly formulated was indicated by an independent assessment of its susceptibility to oxidation.[7] Exposure to air for 2 weeks resulted in complete conversion of a sample to a 57:43 mixture of **6** and **7** (^1H NMR integration of their respective bridgehead protons). As anticipated from precedent,[22c,23,24] **5** proved inert to the atmospheric environment. The syn architecture of **6** follows incontrovertibly from its ^{13}C NMR spectrum where the consequences of oxirane magnetic anisotropy[25] have combined to shield *both* of its apical methylene carbons relative to those in **4** (again see formulas).

Although diketone **7** proved to be of C_s symmetry, its three-dimensional features could not be ascertained with comparable confidence on the basis of NMR data alone. Consequently, recourse was made to X-ray crystallography (Table I). The ORTEP diagram of Figure 1 discloses that **7** is, as anticipated, stereochemically related to **4**. The conformation adopted by the diketone is of additional interest. Its two five-membered rings are almost parallel to each other, the dihedral angle separating them is only 5.1°. Of course, neither five-membered ring is fully planar, the dihedral angles between C(5)–C(6)–C(7) [plane I] and C(5)–C(1)–C(2)–C(7) [plane II] as well as between C(10)–C(11)–C(12) [plane III] and C(12)–C(13)–C(14)–C(10) [plane IV] being 23.8 and 28.4°, respectively. The angle between planes I and III is 32.7°, while that between planes (II) and (IV) is 19.6°.

Cyclooctyne. Cyclooctyne, a highly strained acetylene,[26] is recognized to undergo [4 + 2] cycloaddition with a variety of cyclic 1,3-dienes.[27,28] In order to best gauge its behavior toward the isodicyclopentadiene triad, condensation with **1** was effected at three different temperatures. In chloroform solution at 25 °C, cycloaddition proceeded very sluggishly. After 1 month, 70% conversion to cycloadduct **8** was noted by ^1H NMR analysis. The



unidirectionality of the process is to be noted and compared to the outcome of a like experiment performed in CD_2Cl_2 at 42 °C. Under the latter conditions, 80% conversion to **8** and the isomeric adduct **9** occurred during 10 days. Hydrocarbon **9** now constituted 4% of the product mixture. When the same pair of reactants was heated to 120 °C in toluene for 12 h, **8** continued to be formed as the major cycloadduct (71%), but the relative amount of **9** (28%) was substantially larger than heretofore. If the toluene solution of **1** was preequilibrated by heating at the reflux temperature for 30 min prior to the addition of cyclooctyne and the reaction time was extended for only an additional 3 h, a closely comparable product distribution (75:25) was realized.

A solution was prepared at room temperature in bromobenzene-d_5 in order to establish whether **8** is subject to facile retrograde Diels–Alder fragmentation. Subse-

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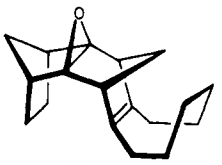
quent heating for relatively prolonged increments in the temperature range 42–120 °C (combined total of 63 h) gave rise to no observable NMR changes. Consequently, we consider the ratios determined for **8** and **9** to be the result of kinetic competition.

Whereas ^1H and ^{13}C NMR analyses of the original reaction mixtures showed only **8** and **9** to be present, medium-pressure chromatographic purification (MPLC) on silica gel afforded not insignificant quantities of diketone **10** and tertiary alcohol **11** as well. Evidently, the acidic nature of the adsorbent induces generation of a tertiary carbocation which is subsequently hydrated. Ions of a closely related structural type are known to return unrearranged products with nucleophilic capture occurring on the exo surface.[29]

Autoxidation of **8** by overnight exposure of $CDCl_3$ solutions to air gave rise to a 27:73 mixture of **10** and epoxide **12**. Although all attempts to purify these substances by chromatographic means resulted in the destruction of **12**, ^1H NMR assignments to this highly reactive substance could be made by suitable electronic subtraction of the signals due to **10**.

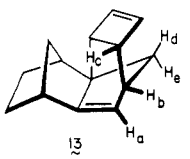


12

Cyclobutadiene. The release of cyclobutadiene from its $Fe(CO)_3$ complex with ceric ammonium nitrate[30] proved incompatible with **1**. Numerous attempts under a variety of conditions to effect this decomplexation resulted in the rapid consumption of isodicyclopentadiene. The majority of the cyclobutadieneiron complex could subsequently be recovered.

Success was achieved by making recourse instead to trimethylamine *N*-oxide as oxidant,[31] although the process occurred slowly despite an 8-fold excess of the *N*-oxide. The cleanest reactions resulted when the reactants were stirred in acetone at 25 °C for 2 days. Neither an increase in reaction time nor a higher temperature proved advantageous. Benzene proved to be a less desirable solvent than acetone.

Unexpectedly, the only cycloadduct formed from this reagent combination was **13** (42% isolated). The structural assignment to this polycyclic hydrocarbon was deduced primarily from its ^1H NMR spectrum. In common with all addducts of **2**, **13** exhibits at δ 5.21 a vinyl proton (H_a)

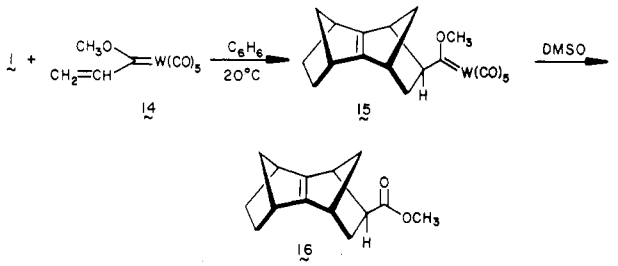


13

coupled uniquely to a neighboring allylic bridgehead proton. This methine hydrogen, which is positioned at δ 2.75 and identified as H_b, is the key to assignment of product stereochemistry. In view of its appearance as a well-resolved doublet whose multiplicity arises because of J_{AB}, a lack of spin–spin coupling between H_b and H_c is clearly apparent. Accordingly, the cyclobutene ring must possess an exo orientation.[32] Additional confirmation was derived from an NOE study at 500 MHz which showed the olefinic cyclobutene protons to be spatially proximal to H_d (4% enhancement).

Thus, the capture of cyclobutadiene by **2** follows an anti-Alder course.

(Methoxyvinylcarbene)tungsten Pentacarbonyl. The highly dienophilic Fischer carbene complex **14**[33] was found to react quickly and cleanly with **1** at room temperature to furnish cycloadduct **15** in 88% isolated yield.



Close monitoring of the progress of reaction by thin layer chromatography revealed that **1** was completely consumed within 15 min after its addition. **15** was oxidized to the corresponding methyl ester with dimethyl sulfoxide[33] to establish that complete below-plane stereoselectivity had been realized in anti-Alder fashion. Exposure of structurally related carbene complexes to these mild reaction conditions has been shown not to alter stereochemical composition. Comparison of the spectral data for **16** with those of an authentic sample[4] showed them to be identical.

Discussion

The preceding experiments reveal that hexafluoro-2-butyne, cyclooctyne, and (methoxyvinylcarbene)tungsten pentacarbonyl exhibit a similar overwhelming preference for [4 + 2] bonding to **1** from its bottom surface (as drawn). The reaction stereoselectivity adopted by the two acetylenic reagents is therefore identical with that previously demonstrated for dimethyl acetylenedicarboxylate (DMAD) and conforms to theoretical expectation.[10,12] From a qualitative viewpoint, hexafluoro-2-butyne reacts with **1** at a significantly slower rate than either of the N-substituted triazolinediones examined previously.[14] For this reason, the Diels–Alder transition-state options available to the hexafluorinated example can be thought of developing appreciably later in the reaction profile. One must inquire, however, if this issue bears directly on the stereoselection question.

Two facets of the behavior of cyclooctyne are noteworthy. The reduced dienophilicity of the somewhat distorted triple bond in this reagent is rather striking. After 1 month at room temperature, conversion to **8** proceeds only to the 70% level. This kinetic retardation may reflect the inability of cyclooctyne to bond in Alder fashion to either face of the diene for the obvious steric reasons. This hypothesis cannot, of course, be put to experimental test since cycloadduct **8** lacks the capacity for stereochemical marking about the newly installed double bond.

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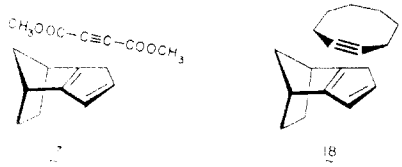
The ability of cyclooctyne to add to [1,5] hydrogen-shifted isodicyclopentadiene tautomer **2** at temperatures above 25 °C is unprecedented for triply unsaturated dienophiles when **1** serves as the precursor. Under conditions specifically designed to maximize the concentration of **2** available from **1**, DMAD reacts exclusively with **1** to deliver the *syn*-sesquinorbornadiene adduct.[5] The inertness of DMAD toward **2** had originally been traced to steric crowding involving one ester group of the linear dienophile and the methano bridge as in **17**.[5] Apparently, the



17 18

eight-membered ring in cyclooctyne pulls back the propargylic methylene groups to an extent adequate to deemphasize the steric feature (see **18**) and allow the greater inherent Diels–Alder reactivity of diene **2** to manifest itself. It remains important to recognize that DMAD does add smoothly to **2** which is free of **1** as pictured in **17** to give a single adduct in 82% yield.[6]

The heightened reactivities of carbene complexes such as **14** are believed to compare to those of $AlCl_3$-complexed methyl acrylate.[33] The tungsten reagent does indeed cycloadd completely to **1** in highly stereoselective anti-Alder fashion at 25 °C within 15 min. The reaction stereochemistry happens to be identical with that observed for methyl acrylate alone where the reaction time is significantly longer.[4] Therefore, a rate acceleration of this magnitude is not accompanied by a detectable level of stereochemical crossover, *suggesting that stereoselection is not uniquely linked to transition-state timing and must be dictated by more complex reasons.*

The reaction course followed by cyclobutadiene has proven informative. As already noted, oxidation of its $Fe(CO)_3$ complex with ceric ammonium nitrate led to selective oxidation of **1**. This untoward process did not occur with trimethylamine *N*-oxide which instead acted *slowly* on the complex to liberate the cyclobutadiene reagent. Although kinetic data are not available, monitoring of the progress of reaction clearly demonstrated that decomplexation of the reactive dienophile was complete only after 2 days at room temperature. The gradual liberation of cyclobutadiene in this fashion, coupled with its obvious reluctance to add to isodicyclopentadiene, proved particularly conducive to the capture of tautomer **2**. The anti-Alder course of this cycloaddition is attributed to steric congestion present in the other possible alignment of reactants. Particularly relevant is the fact that **2** competes effectively to capture cyclobutadiene despite its very low concentration. The isolated yield of **13** (42% based on cyclobutadiene) indicates that possible dimerization to *syn*-tricyclooctadiene is significantly curtailed.

The stereoselectivity patterns documented here serve to reemphasize the uniqueness of triazolinediones. Their proclivity for capturing **1** from above-plane causes us to continue to regard them as "maverick" dienophiles.[14]

Experimental Section

Diels-Alder Reaction of 1 with Hexafluoro-2-butyne. A cold (−70 °C), magnetically stirred solution of **1** (1.0 g, 8.0 mmol) and hexafluoro-2-butyne (3.0 g, 19 mmol) in pentane (10 mL) was blanketed with nitrogen and allowed to warm slowly to room temperature during 4 h. Careful evaporation of the solvent left a dark orange residue from which a dark solid precipitated. The oil was decanted from the solid and subjected to MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether) to give **5** (66 mg, 3%), **4** (1.02 g, 45%), and **6** (141 mg, 6%). The solid material was recrystallized from ethyl acetate to give pure **7** (70 mg, 3%).

For **4**: colorless solid, mp 34.5–35.5 °C; IR ($CHCl_3$, cm^{-1}) 2980, 2950, 1340, 1305, 1290, 1275, 1265, 1250, 1170, 1140, 1090, 995; ^1H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 2 H), 3.09 (s, 2 H), 2.51 (dt, J = 6.9, 1.9 Hz, 1 H), 2.17 (d, J = 6.9 Hz, 1 H), 1.57–1.48 (m, 3 h), 1.20 (dt, J = 8.4, 1.5 Hz, 1 H), 0.53 (dd, J = 8.4, 2.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.40, 122.36, (q, J_{CF} = 270.9 Hz), 71.85, 50.99, 49.27, 42.62, 21.91; MS, m/z calcd (M^+) 294.0843, obsd 294.0836.

Anal. Calcd for $C_{14}H_{12}F_6$: C, 57.15; H, 4.11. Found: C, 57.26; H, 4.23.

For **5**: colorless oil that solidifies below room temperature; IR ($CHCl_3$, cm^{-1}) 2980, 2940, 2880, 1350, 1290, 1180, 1165, 1140; ^1H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 2 H), 3.20 (s, 2 H), 2.60 (d, J = 6.4 Hz, 1 H), 2.10 (d, J = 6.0 Hz, 1 H), 1.74 (d, J = 7.3 Hz, 2 H), 1.38–1.35 (m, 1 H), 1.21 (d, J = 8.1 Hz, 1 H), 1.00 (dd, J = 7.4, 2.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 161.16, 122.15 (q, J_{CF} = 270.6 Hz), 78.93, 51.59, 50.51, 43.37, 25.90; MS, m/z calcd (M^+) 294.0843, obsd 294.0838.

For **6**: colorless oil that solidifies below room temperature; IR ($CHCl_3$, cm^{-1}) 3000, 2970, 2940, 2890, 1650, 1475, 1450, 1350, 1290, 1270, 1250, 1180, 1170, 1140, 1000, 640; ^1H NMR (300 MHz, $CDCl_3$) δ 3.36 (s, 2 H), 2.70 (s, 2 H), 2.25 (d, J = 8.4 Hz, 1 H), 2.00–1.95 (m, 1 H), 1.89 (dd, J = 8.2, 1.3 Hz, 1 H), 1.61–1.56 (m, 2 H), 1.08 (dd, J = 9.7, 3.0 Hz, 2 H), 0.95 (dd, J = 9.4, 1.0 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 121.43 (q, J_{CF} = 271.0 Hz), 64.48, 57.87, 47.19, 39.66, 39.29, 24.26; MS, m/z calcd (M^+) 310.0792, obsd 310.0788.

For **7**: colorless crystals, mp 230–231 °C; IR ($CHCl_3$, cm^{-1}) 2950, 1690, 1355, 1300, 1245, 1180, 1160, 1130, 940, 870; ^1H NMR (300 MHz, $CDCl_3$) δ 4.09 (d, J = 9.4 Hz, 2 H), 3.43 (t, J = 9.9 Hz, 2 H), 2.65–2.54 (m, 3 H), 2.32–2.23 (m, 3 H), 2.03–1.95 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 206.47, 120.29 (q, J_{CF} = 274.6 Hz), 60.39, 54.28, 35.68, 31.98, 27.41.

Anal. Calcd for $C_{14}H_{12}F_6O_2$: C, 51.54; H, 3.71. Found: C, 51.63; H, 3.72.

Air Oxidation of 4. A 100-mg sample of **4** was sealed into a 50-mL flask under air. After 2 weeks, ^1H NMR analysis of the material indicated that no **4** remained and that conversion to a mixture of **6** and **7** (ratio 57:43) had occurred completely. Separation of this mixture was effected by trituration with pentane in which **6** is soluble but **7** is not. Isolated were 55 mg (53%) of **6** and 45 mg (41%) of **7**, the ^1H NMR spectra of which were identical with those isolated from the original reaction mixture.

X-ray Structure Determination of 7. A prismatic colorless crystal of approximate dimensions 0.18 × 0.25 × 0.40 mm was mounted on the tip of a thin glass fiber. Both X-ray examination of the crystal and data collection were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K radiation. The cell parameters and standard deviations were determined at room temperature by least-squares fitting of those 24 reflections which were well distributed in reciprocal space and lying in the 2θ range between 25° and 30°. Intensity data were collected by the ω–2θ scan mode with the 2θ range lying between 4° and 50°. A total of 2277 independent reflections was measured with 1530 unique data having $I > 3.0\sigma(I)$. Details of the data collection are given in Table I. The data were corrected for Lorentz and polarization effects as well as absorption.

The analytical form of the scattering factors for neutral atoms was used throughout the analysis, both $\Delta f'$ and $i\Delta f''$ terms were included for all atoms. All of the crystallographic computations were carried out on a PDP11/44 computer using the SDP (Structure Determination Package).

The systematic absences unambiguously indicated the space group to be $P2_{1/c}$. From the calculated density, four molecules occupy the unit cell such that there is one molecule per asymmetric unit. The structure was solved via MULTAN82. All of the nonhydrogen atoms were located in the E-map. After several cycles of full-matrix least-squares refinements of the positional and isotropic thermal parameters for these atoms, the difference electron density maps indicated one of the trifluoromethyl groups and some of the hydrogen atoms to be disordered. After refining the multiplicities, the fluorine atoms labeled F(411), F(412), and

F(413) had 55%, and F(421), F(422), and F(423) and 45%.

The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$, where the assigned weights are given as $w = 4F_o^2/[\sigma^2(I) + (pI)^2]$, and $p = 0.025$ was chosen to make $\sum w\Delta F$ uniformly distributed in $|F_o|$, $\sin\theta/\lambda$, and parity class of the crystallographic indices. The final full-matrix least-squares refinement cycle, with anisotropic thermal parameters for all non-hydrogens and isotropic thermal parameters for the hydrogen atoms, gave $R_f = 0.053$, and $R_{wf} = 0.062$, for reflections with variable parameters, where $R_f = \sum||F_o| - |F_c||/\sum|F_o|$, and $R_{wf} = \sum w^{1/2}||E_o| - |F_c||/\sum^{1/2}|F_o|$. The largest parameter shift/error is 0.87. The final difference Fourier map showed no significant features (highest electron density = 0.185).

Diels–Alder Reaction of 1 with Cyclooctyne. A solution of **1** (2.12 g, 0.016 mol) and cyclooctyne (1.03 g, 0.010 mol) in dry dichloromethane (50 mL) was stirred at 42 °C for 1 week under a blanket of nitrogen. Removal of the solvent by distillation gave an oily residue that contained **8** and **9** in a ratio of 15:1 (^{1}H NMR analysis). MPLC purification on silica gel (elution with petroleum ether) afforded a mixture of **8** and **9** (215 mg, 9.4%) along with 205 mg of unreacted **1**. Further elution with 28% ethyl acetate in petroleum ether led to the isolation of 409 mg (17%) of **11** and 77 mg (3%) of **10**.

Preparative VPC (5% SE-30 on Chromosorb G, 180 °C) furnished **9** adequately free of **8** for spectral characterization: IR ($CHCl_3$, cm^{-1}) 3060, 2950, 2920, 2870, 2850, 1470, 1450, 910; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (d, J = 2.7 Hz, 1 H), 3.16 (d, J = 2.6 Hz, 1 H), 2.82 (d, J = 4.2 Hz, 1 H), 2.47 (d, J = 3.9 Hz, 1 H), 2.42–2.21 (m, 4 H), 1.85–1.74 (m, 4 H), 1.69–1.20 (series of m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 169.04, 148.80, 143.17, 121.70, 72.72, 56.66, 44.19, 37.60, 37.07, 31.43, 30.93, 29.11, 28.97, 26.95, 26.83, 25.51, 24.39, 24.27; MS, m/z (M^+) calcd 240.1878, obsd 240.1879.

Hydrocarbon **8** was not obtained sufficiently free from **9** for complete characterization. The ^{1}H and ^{13}C NMR assignments that follow were arrived at by computer subtraction of the signals due to admixed **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (s, 2 H), 2.95 (s, 2 H), 2.17–2.12 (m, 4 H), 1.87 (d, J = 6.1 Hz, 1 H), 1.70–1.30 (series of m, 12 H), 1.04 (dt, J = 1.6, 8.2 Hz, 1 H), 0.42–0.37 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 158.54, 142.67, 67.55, 54.33, 47.74, 43.08, 28.96, 27.18, 26.08, 22.49.

An analytical sample of **10** was obtained by recrystallization from ethyl acetate followed by sublimation (110 °C, 0.5 torr): mp 146.5–147.5 °C; IR ($CHCl_3$, cm^{-1}) 3000, 2930, 2850, 1675, 1460, 1260, 1160, 910, 875; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (d, J = 9.6 Hz, 2 H), 3.25 (t, J = 9.8 Hz, 2 H), 2.71 (dd, J = 3.8, 15.4 Hz, 2 H), 2.27–1.89 (series of m, 8 H), 1.79–1.69 (m, 4 H), 1.59–1.35 (series of m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 212.90, 139.61, 63.20, 54.82, 33.26, 30.70, 29.59, 28.18, 26.21, 25.76; MS, m/z (M^+) calcd 272.1776, obsd 272.1760.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 78.96; H, 8.86.

Alcohol **11** was obtained as colorless needles: mp 95–96 °C (from hexanes); IR ($CHCl_3$, cm^{-1}) 3620, 3000, 2940, 2880, 2860, 1470, 1460, 1440, 1260, 1060, 980; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36–1.99 (series of m, 12 H), 1.69–1.44 (m, 9 H), 1.31 (dd, J = 1.2, 9.4 Hz, 1 H), 1.22–1.06 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.39, 137.93, 89.67, 60.04, 57.59, 55.95, 47.71, 47.21, 45.13, 39.19, 28.99, 28.70, 28.65, 28.52, 26.31, 26.25, 23.61, 22.07; MS, m/z (M^+) calcd 258.1984, obsd 258.1971.

Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.67; H, 10.26.

The *p*-nitrobenzoate of **11**, prepared by conventional reaction with *p*-nitrobenzoyl chloride in pyridine solution, was obtained as pale yellow crystals, mp 210 °C (from ethanol–water); IR ($CHCl_3$, cm^{-1}) 3000, 2920, 2840, 1720, 1465, 1450, 1435, 1250, 1055, 975; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, 2 H), 8.17 (d, J = 8.8 Hz, 2 H), 3.15 (s, 1 H), 2.92 (d, 1 H), 2.64 (t, 1 H), 2.46 (br s, 1 H), 2.33–2.31 (m, 4 H), 1.70–1.10 (series of m, 13 H).

Autoxidation of 8. Approximately 10 mg of **8** was dissolved in $CDCl_3$ in an NMR tube and exposed to the atmosphere overnight. ^{1}H NMR analysis after this lapse of time showed that complete conversion to a 27:73 mixture of **10** and **12** had occurred. Since all attempts to separate this mixture chromatographically selectively destroyed the epoxide, the ^{1}H NMR assignments to **12** were arrived at by subtraction of the signals due to **10** which had been previously obtained pure.

For **12**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.71 (s, 2 H), 2.57 (s, 2 H), 2.39–2.14 (m, 5 H), 2.08 (d, J = 4.9 Hz, 2 H), 1.93 (d, J = 8.9 Hz, 2 H), 1.77–1.13 (series of m, 9 H), 0.78 (d, J = 8.7 Hz, 2 H).

Reaction of 1 with Cyclobutadiene. To a solution of **1** (503 mg, 3.8 mmol) and (cyclobutadiene)iron tricarbonyl (405 mg, 2.1 mmol) in dry acetone (25 mL) was added trimethylamine *N*-oxide (1.21 g, 0.016 mol) in a single portion. The reaction mixture was stirred a room temperature under nitrogen for 2 days, diluted with ether (25 mL), and filtered through Celite to remove insoluble iron compounds. The filtrate was washed with water (3 × 50 mL) and the aqueous phases were extracted with ether (2 × 25 mL). The combined organic layers were dried and concentrated to give a yellow oil, chromatography of which (MPLC) on silica gel (elution with petroleum ether) afforded 164 mg (42%) of **13** as a colorless liquid and 134 mg of recovered **1**. An analytical sample of **13** was obtained by preparative VPC (5% SE-30 on Chromosorb G, 120 °C): IR ($CHCl_3$, cm^{-1}) 3020, 3000, 2960, 2925, 2880, 2860, 1450, 1300, 1285, 1175, 910; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99 (d, J = 4.6 Hz, 1 H), 5.97 (d, J = 4.6 Hz, 1 H), 5.21 (d, J = 3.0 Hz, 1 H), 3.03 (t, J = 4.5 Hz, 1 H), 2.84 (d, J = 4.0 Hz, 1 H), 2.75 (d, J = 3.5 Hz, 1 H), 2.55–2.52 (m, 1 H), 2.24 (s, 1 H), 1.80 (dd, J = 1.7, 8.0 Hz, 1 H), 1.73–1.67 (m, 2 H), 1.55–1.45 (m, 3 H), 1.33 (d, J = 9.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 159.63, 140.88, 139.85, 111.61, 62.99, 57.07, 47.56, 47.09, 44.91, 42.27, 40.65, 38.54, 32.29, 24.86; MS, m/z (M^+) calcd 184.1252, obsd 184.1253.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.18, H, 8.73.

Cycloaddition of (Methoxyvinylcarbene)tungsten Pentacarbonyl to 1. Isodicyclopentadiene (**1**, 73 mg, 0.55 mmol) was added to a magnetically stirred solution of **14** (290 mg, 0.74 mmol) dissolved in dry benzene (3 mL) under a nitrogen atmosphere. After 30 min, the solvent was evaporated to leave a dark red oil. Purification of this oil by MPLC on silica gel (elution with hexane) afforded 254 mg (88%) of the yellow-orange crystalline adduct **15**: mp 73 °C dec; IR ($CHCl_3$, cm^{-1}) 2960, 2930, 2880, 2860, 2070, 1975, 1460, 1260; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.60 (s, 3 H), 3.78 (m, 1 H), 3.05 (s, 3 H), 3.00 (s, 1 H), 1.72–0.82 (series of m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 338.99, 203.31, 197.52, 156.16, 151.81, 73.28, 70.65, 50.41, 48.76, 47.46, 43.10, 42.98, 42.73, 32.44, 25.81, 24.98; MS, m/z (M^+) calcd 526.0613, obsd 526.0615.

Dimethyl Sulfoxide Oxidation of 15. A solution of **15** (80 mg, 0.15 mmol) was dissolved in dimethyl sulfoxide (1 mL) and stirred under nitrogen at room temperature for 58 h. The reaction mixture was diluted with ether (25 mL) and washed with brine (5 × 25 mL) prior to drying and solvent evaporation. MPLC of the residue on silica gel (elution with 10% ethyl acetate in hexane) gave 27.8 mg (85%) of ester **16**, whose spectra were identical with those recorded on an authentic sample; IR ($CHCl_3$, cm^{-1}) 2980, 2930, 2880, 1730, 1435, 1355, 1295, 1195, 1175, 1045; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.67 (s, 3 H), 3.14 (s, 1 H), 3.01 (s, 1 H), 2.06 (m, 1 H), 1.90 (dt, J = 4.0, 11.9 Hz, 1 H), 1.63–0.78 (series of m, 8 H).

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Registry No. **1**, 75725-33-6; **2**, 75725-33-6; **4**, 103794-76-9; **5**, 103881-89-6; **6**, 103794-77-0; **7**, 103794-78-1; **8**, 103794-79-2; **9**, 103794-80-5; **10**, 103794-81-6; **11**, 103794-82-7; **11** (4-nitrobenzoate), 103816-43-9; **12**, 103794-83-8; **13**, 103794-84-9; **14**, 83801-34-7; **15**, 103794-85-0; **16**, 58267-54-2; $F_3CC{\equiv}CCF_3$, 692-50-2; 4-$O_2NC_6H_4COCl$, 122-04-3; cyclooctyne, 1781-78-8; (cyclobutadiene)iron tricarbonyl, 12078-17-0.

Supplementary Material Available: Tables of positional parameters, refined temperature factor expressions, bond distances and angles, and least-squares planes, together with a unit cell diagram (9 pages). Ordering information is given on any current masthead page.