

59085-70-0; $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{SeC}_6\text{H}_5$, 69690-81-9; (*E*)-*n*- $\text{C}_3\text{H}_7\text{CH}=\text{CHCH}_2\text{SeC}_6\text{H}_5$, 90036-65-0; (*E*)- $\text{PhCH}=\text{CHCH}_2\text{SeC}_6\text{H}_5$, 69562-10-3; $\text{CH}_2=\text{CHCH}(\text{SeC}_6\text{H}_5)\text{-n-C}_3\text{H}_7$, 90036-67-2; $\text{BOC-NHCH}_2\text{CH}=\text{CH}_2$, 78888-18-3; $\text{CBZ-NHCH}_2\text{CH}=\text{CH}_2$, 5041-33-8; $\text{BOC-NHCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$, 91230-06-7; $\text{CBZ-NHCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$, 91230-07-8; $\text{BOC-NHC}(\text{CH}_3)_2\text{CH}=\text{CH}_2$, 91230-08-9; $\text{CBZ-NHC}(\text{CH}_3)_2\text{CH}=\text{CH}_2$, 91230-09-0; $\text{BOC-NHCH}(\text{n-C}_3\text{H}_7)\text{CH}=\text{CH}_2$, 91230-10-3; $\text{CBZ-NHCH}(\text{n-C}_3\text{H}_7)\text{CH}=\text{CH}_2$, 91230-11-4; $\text{BOC-NHCH}(\text{C}_6\text{H}_5)\text{CH}=\text{CH}_2$, 91230-12-5; $\text{CBZ-NHCH}(\text{C}_6\text{H}_5)\text{CH}=\text{CH}_2$, 91230-13-6; (*E*)- $\text{BOC-NHCH}_2\text{CH}=\text{CH-n-C}_3\text{H}_7$, 91230-14-7; (*E*)- $\text{CBZ-NHCH}_2\text{CH}=\text{CH-n-C}_3\text{H}_7$, 91230-15-8; (*E*)-*n*- $\text{C}_6\text{H}_{13}\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$, 43161-19-9; (*Z*)-*n*- $\text{C}_6\text{H}_{13}\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$, 3287-56-7; BOC-NH_2 , 4248-19-5; CBZ-NH_2 , 621-84-1; *i*- Pr_2NEt , 7087-68-5; NCS , 128-09-6; 3-(phenylseleno)cyclohexene, 83442-20-0; *trans*-2-(phenylseleno)-3-cyclohexen-1-ol, 91230-04-5; 10-(phenylseleno)carvone, 91230-05-6; *tert*-butyl *N*-(2-cyclohexen-1-yl)carbamate, 91230-16-9; benzyl *N*-(2-cyclohexen-1-yl)carbamate, 91230-17-0; *tert*-butyl *N*-(4-hydroxy-2-cyclohexen-1-yl)carbamate, 91230-18-1; benzyl *N*-(4-hydroxy-2-cyclohexen-1-yl)carbamate, 91230-19-2; *tert*-butyl *N*-(10-carbonyl)carbamate, 91230-20-5; benzyl *N*-(10-carbonyl)carbamate, 91230-21-6.

Crossover in π -Facial Stereoselection during [4 + 2] Cycloaddition of Triazolinediones to Isodicyclopentadiene and Its Dehydro Derivative¹

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The major thrust of our work involving cycloaddition reactions to norbornyl- and norbornenyl-fused cyclopentadiene systems such as 1 and 2 has been two-pronged.

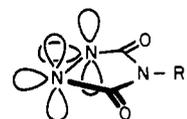


Elucidation of the extent and direction of π -facial stereoselectivity as a function of appendages grafted onto the diene or triene has been accorded considerable attention.^{3,4} The directionality of electrophilic capture⁵ and metal complexation⁶ within the derived cyclopentadienide anions

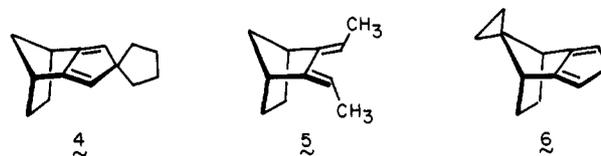
has comprised part of this effort. Companion activity directed at the development of synthetic applications based on this chemistry has resulted in the acquisition of *syn*-sesquiorbornene,^{3a,b,7} a diazabishomocubane,⁸ and [4]-peristylane.⁹

Detailed theoretical analysis of our findings has implicated strong σ/π coupling and resultant π lobe tilting as being chiefly responsible for the normally high stereoselectivity commonly observed.^{4,10} Of necessity, the prevailing long-range interactions have been diagnosed in a static, time-independent mode. Ideally, an extended dynamic approach involving coupling between diene and dienophile as a function of changing internuclear distance would be more satisfying. At present, however, computer simulations of such pathways are too costly.

Notwithstanding, common dienophiles have not given evidence of ambiguity along the reaction profile except in those cases where an additional π orbital oriented orthogonal to that involved in bonding is present. In this connection, triazolinediones 3 have been proved most



3a, R = CH₃
3b, R = C₆H₅



troublesome. For example, while 3a adds to 4 with high above-plane stereoselectivity, the corresponding dehydro congener is transformed under analogous conditions to a 61:39 *endo/exo* mixture.^{3e} Also, 3a adds to 5 to give only the *exo* adduct in contradistinction to the stereochemical response of other dienophiles.^{3e} Where 6 is concerned, [4 + 2] bonding to 3b occurs at equal rates from both diene faces.¹¹

For these reasons, we were prompted to examine the behavior of parent hydrocarbons 1 and 2 toward this pair of "maverick" dienophiles in some detail. *N*-Methyltriazolinedione addition to 2 in ether solution at -20 °C proceeded with rapid consumption of the dienophile as indicated by the almost instantaneous disappearance of its deep red color. Solvent evaporation provided in 84% isolated yield a single colorless solid having a melting point identical with that earlier reported.⁸ Its 300-MHz ¹H NMR spectrum (in CDCl₃) consists of a pair of doublet of doublets centered at δ 6.50 and 5.17 due to the olefinic protons and those at the bridgehead α to nitrogen, respectively. The second set of bridgehead hydrogens appear upfield (δ 3.59) as a broadened singlet, well separated from the multiplet arising from the methano moieties (δ 2.32-2.04). Since this adduct has been converted in five

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(2) Author to whom inquiries concerning the X-ray crystal structure analysis should be directed.

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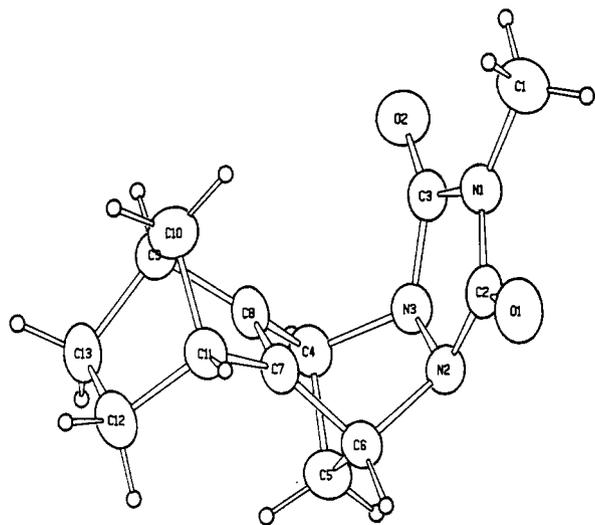
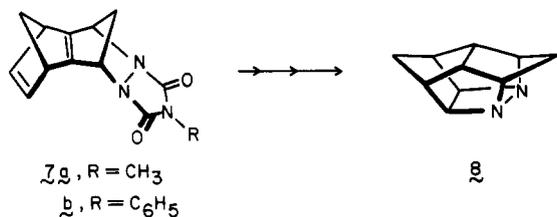


Figure 1. ORTEP drawing of **9a**. Non-hydrogen atoms are drawn with 50% probability ellipsoids. Hydrogen atoms have been drawn artificially small.

Table I. Crystallographic Details for **9a**

M_r	245.3
space group	$P2_1/n$
a , Å	6.603 (1)
b , Å	17.718 (2)
c , Å	10.766 (2)
V , Å ³	1181.74
Z	4.0
d_{calcd} , g/cm ³	1.379
μ , cm ⁻¹	0.894
radiation	Mo K α ($\lambda = 0.71073$ Å)
data collected	$+h, +k, \pm l$
2θ range	4–50°
scan type	ω -2 θ
scan angle (ω)	0.75 + 0.35 tan θ
scan speed, deg/min	0.65–5 (in ω)
reflections collected	total of 3036; 1955 data with $I > 3.0\sigma(I)$
standard reflection	4 measured after 3-h exposure; no decay indicated

steps to **8**,⁸ its formulation as **7** rests upon firm chemical evidence.



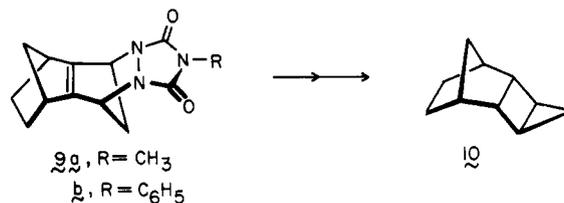
When **2** was similarly treated with **3b**, urazole **7b** was obtained (85%). The general features of its 300-MHz ¹H NMR spectrum very closely resemble those of **7a** (see Experimental Section). Additionally, both adducts share the propensity for relatively rapid decomposition when allowed to stand in solution. Although the colored substances which are produced have not been characterized, this lability does complicate purification procedures.

The reaction of *N*-methyltriazolinedione with **1** proceeded with equally high stereoselectivity to give a lone adduct (82% isolated) which when recrystallized from ethyl acetate was obtained as colorless prisms suitable for X-ray analysis (Table I). The molecule was found to possess an *anti*-sesquinorbornene backbone with a pseudo mirror plane bisecting its N(2)–N(3), C(7)–C(8), and C(12)–C(13) bonds (Figure 1). Interestingly, the central double bond in **9a** is pyramidalized to the extent of 12.9°,

with the distortion from planarity occurring in a downward direction as drawn. Since the intramolecular distances between the atoms of the urazole ring and the proximal *syn*-7-norbornenyl hydrogen vary from 3.84 to 5.04 Å, normal van der Waals distances are seen to be exceeded. Steric compression in this region of the adduct does not, therefore, appear to be a major contributor to the π -bond deformation.

X-ray crystal structure analyses for a number of *anti*-sesquinorbornenes have been recently reported.^{3e,f,g,8,12–14} Other than **9a**, only the *exo,anti*-Alder (*p*-nitrophenyl)-maleimide adduct of **1** features significant π tilting ($\theta = 13.2^\circ$).¹⁵ This property is particularly characteristic of *syn*-sesquinorbornenes. Possible causative factors for the presence of bent double bonds in the latter systems^{16–20} and the considerably higher π_{oc} ionization energy of *syn*-sesquinorbornene relative to the *anti*²¹ have been advanced. The pyramidalization in **9a** is supportive of the concept predicted by MM2 calculations that *anti*-sesquinorbornene double bonds are subject to facile deformation.¹⁹

Clearly, a crossover in stereoselection occurs when proceeding from triene **2** to diene **1**. An earlier report⁸ claimed that the urazoles from both sources were identical in their three-dimensional structure. Two forms of proof were advanced. The first involved transformation to the known hydrocarbon **10**. However, this reaction sequence confirms



only the gross structure and is not unequivocally diagnostic of stereochemistry. This issue was presumably addressed by partial catalytic hydrogenation of **7a**. Confusion arose at this point because spectral comparisons were made at 60 MHz, a field strength presently recognized to differentiate inadequately the two stereoisomers.

N-Phenyltriazolinedione also adds to **1** exclusively above-plane to give **9b**, in complete agreement with independent observations made by Bartlett and Wu.²² Crystallographic analysis of this adduct has substantiated that cycloaddition in this instance likewise proceeds entirely on the *exo* face of **1**.²³

The definitive experimental results described herein need to be contrasted with the knowledge that dienophiles

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other than **3a** and **3b** add to isodicyclopentadiene (**1**) with predominant or complete endo stereoselectivity.⁴ Its dehydro derivative **2** gives evidence of entirely similar response, the high preference for below-plane capture persisting with methyl propiolate,^{3a,b} benzyne,^{3a,b} and (*p*-tolylsulfonyl)acetylene.⁹

To what causative factor can the strikingly divergent behavior of **3a** to **3b** toward **1** be attributed? The point has been repeatedly made that the ethano and methano bridges in **1** appear too remote from the diene termini to introduce meaningfully different steric perturbations. However, both bridges are recognized to foster anti-Alder approach of the dienophile, at least in those cases where this feature can be recognized in the product(s). It is not unreasonable to presume that the high reactivity of the triazolinediones and the early timing of their cycloaddition states may cause these dienophiles to add preferentially in Alder fashion.^{24,25} A unique sensitivity to steric effects would now develop, which phenomenon is not particularly significant when less reactive reagents are involved. Although the directionality of alignment is not revealed in the urazole products because of facile pyramidalization at nitrogen, the above factors could be responsible for the observed crossover in π -facial stereoselectivity.

Experimental Section

N-Methyltriazolinedione Addition to 2. To a solution of *N*-methyltriazolinedione (192 mg, 1.7 mmol) in dry ether (45 mL) cooled to -20 °C was added **2** (250 mg, 1.92 mmol) dissolved in the same solvent (5 mL). After 20 min, the reaction mixture was allowed to warm to room temperature where solvent and excess **2** were removed under vacuum (30 and 0.03 torr). There was obtained 347 mg (84%) of **7a** as transparent prisms: mp 110 °C dec; ¹H NMR (CDCl₃, 300 MHz) δ 6.50 (dd, *J* = 1.81 and 1.81 Hz, 2 H), 5.17 (dd, *J* = 1.8 and 1.4 Hz, 2 H), 3.59 (br s, 2 H), 2.77 (s, 3 H), 2.32-2.04 (m, 4 H). This material was identical with that previously reported.⁸

N-Phenyltriazolinedione Addition to 2. Treatment of *N*-phenyltriazolinedione (297.5 mg, 1.7 mmol) with **2** (250 mg, 1.92 mmol) in ether (50 mL) as described above afforded 440 mg (85%) of **7b** as the only adduct. This substance, like **7a**, decomposed relatively rapidly when allowed to stand in solution at room temperature: ¹H NMR (CDCl₃, 300 MHz) δ 7.5-7.28 (m, 5 H), 6.60 (dd, *J* = 1.8 and 1.8 Hz, 2 H), 5.30 (dd, *J* = 1.8 and 1.4 Hz, 2 H), 3.66 (br s, 2 H), 2.42-2.15 (m, 4 H).

N-Methyltriazolinedione Addition to 1. Reaction of **3a** (50 mg, 0.44 mmol) with **1** (66 mg, 0.50 mmol) in dry ether (18 mL) at -20 °C for 30 min afforded 88.4 mg (82%) of **9a** as transparent prisms: mp 131 °C dec (lit.⁹ mp 129 °C dec) (from ethyl acetate); ¹H NMR (CDCl₃, 300 MHz) δ 5.06 (t, *J* = 1.5 Hz, 2 H), 3.01 (m, 2 H), 2.91 (s, 3 H), 2.36 (dt, *J* = 8.5 and 1.5 Hz, 1 H), 1.81 (m, 3 H), 1.33 (d, *J* = 7 Hz, 1 H), 1.17-1.07 (m, 3 H).

N-Phenyltriazolinedione Addition to 1. Reaction of **3b** (50 mg, 0.29 mmol) with **1** (42 mg, 0.32 mmol) in ether (18 mL) at -20 °C furnished 71.2 mg (80%) of **9b** as colorless crystals: mp 183 °C dec (lit.¹² mp 180 °C dec); ¹H NMR (CDCl₃, 300 MHz) δ 7.46-7.33 (m, 5 H), 5.18 (t, *J* = 1.43 Hz, 2 H), 3.10 (m, 2 H), 2.46 (dt, *J* = 8.0 and 1.4 Hz, 1 H), 1.90-1.83 (m, 3 H), 1.36 (br s, 2 H), 1.18 (d, *J* = 6.9 Hz, 2 H).

X-ray Analysis of 9a. A plate-like prismatic colorless crystal of approximate dimensions 0.125 × 0.30 × 0.375 mm was mounted on the tip of a thin glass fiber. Both X-ray examination of the crystal and data collection were at room temperature by using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation. At room temperature the cell parameters and standard deviations were determined by least-squares fitting from 24 reflections, well distributed in reciprocal

space and lying in the 2θ range between 25° and 30°. Intensity data were collected by the ω - 2θ mode with 2θ range between 4° and 55°. A total of 3036 reflections were measured with 1955 unique data having $I > 3.0\sigma(I)$. Details of data collection are given in Table I. The data were corrected for Lorentz and polarization effects but not absorption.

Solution and Refinement of the Structure. The analytical form of the scattering factors for neutral atoms were used throughout the analysis, and both $\Delta f'$ and $i\Delta f''$ terms were included for all atoms. All the crystallographic computations were carried out on a PDP 11/44 computer using the SDP (Structure Determination Package).

From systematic absences, the space group $P2_1/n$ was determined unambiguously. Statistic distributions of reflection intensities also pointed to the likelihood that the space group was centrosymmetric. There are four molecules per unit cell and, therefore, one molecule per crystallographic asymmetric unit. The structure was solved via a combination of MULTAN, difference Fourier, and least-squares refinements on these heavy atoms. All of the hydrogens appeared on the difference electron density map. The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$ where the assigned weights are given as $w = [\sigma(I)^2 + (\rho I)^2]^{-1/2}$; $\rho = 0.02$ was chosen to make $\sum w\Delta F$ uniformly distributed in $|F_o|$. The final full-matrix, least-squares refinement cycle with anisotropic thermal parameters for all non-hydrogen atoms (isotropic for the hydrogens) gave $R_f = 0.037$, and $R_{wt} = 0.045$; where $R_f = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_{wt} = \sum w^{1/2} ||F_o| - |F_c|| / \sum w^{1/2} |F_o|$ for the 1955 reflections having $I > 3.0\sigma(I)$ with 223 variables. The final difference Fourier map showed no significant features, with a maximum peak height of 0.177 e/Å³.

Acknowledgment. We thank the National Cancer Institute for their financial support of this research (Grant CA-12115).

Registry No. **1**, 6675-72-5; **2**, 6675-71-4; **3a**, 13274-43-6; **3b**, 4233-33-4; **7a**, 73321-36-5; **7b**, 91391-11-6; **9a**, 91463-92-2; **9b**, 89689-35-0.

Supplementary Material Available: Tables listing final positional and thermal parameters, bond distances, bond angles, dihedral angles between planes, and $|F_o|$ and $|F_c|$ (23 pages). Ordering information is given on any current masthead page.

(1S)-1 α ,4 α ,5 β ,5 α β ,6 β ,8 β ,9 β ,9 α β -Octahydro-5,8-dihydroxy-1,4-epoxy-6,9-methano-3-benzoxepin-7-(2H)-one (a Levoglucosone Derivative). The Product of a 1,4-Hydride Shift

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The potential for obtaining useful chemicals from cellulosic waste materials has been investigated through the pyrolysis of acid-treated newsprint.¹ Levoglucosone (**1**) is a major product of this pyrolysis¹ and its synthetic utility has been widely studied.² The [4 + 2] cycloaddition reaction between levoglucosone and 1,3-cyclopentadiene yields **2** as the major product³ (Scheme I). The reaction of **2** with an equimolar amount of osmium tetroxide produces an osmate ester which can be reductively cleaved

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